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- fill in a separate form for each project or series of measurements.
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- 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:** Systematic investigation of factors promoting darkening/reduction of chrome yellow (CY, PbCrO$_4$)	**Experiment number**: EC-799
Beamline: ID21	**Date of experiment**: from: 20/04/2011 to: 26/04/2011	**Date of report**: 08/09/2011
Shifts: 18	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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1. Introduction

Our previous investigations on both artificially aged model samples of commercial lead chromate [1] and two paint cross-sections taken from paintings by V. van Gogh [2] demonstrated for the first time that the alteration of chrome yellow is caused by the reduction of original $PbCrO_4$ to $Cr_2O_3 \cdot 2H_2O$ (viridian green).

Among the model samples analyzed, only the paint sample containing a high amount of $PbSO_4$ showed a clear darkening after the photochemical ageing treatment. A strong spatial correlation between the exposed brown altered layer and the Cr(III) abundance was found.
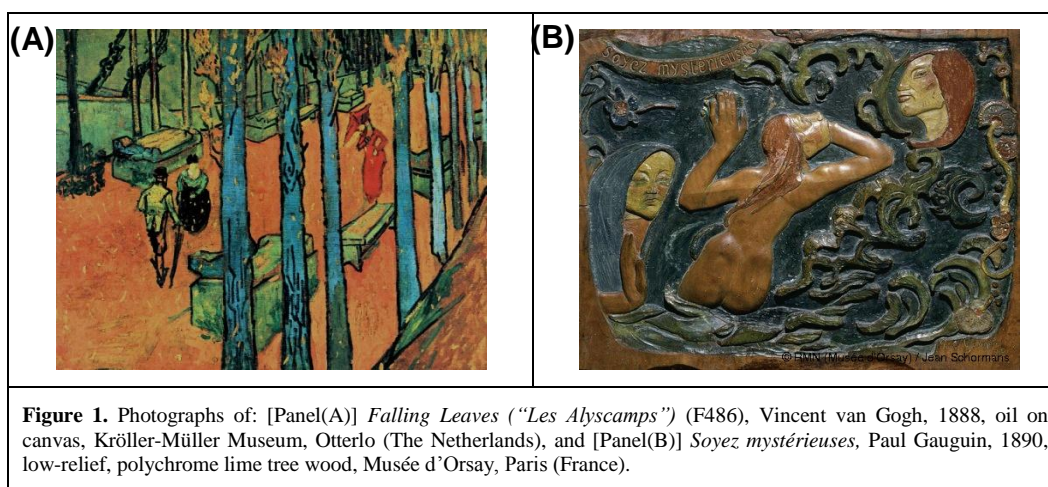
Cr K-edge μ-XANES analysis performed on both Van Gogh paint micro-samples, revealed the presence of Cr(III) species in areas rich in Ba and S and/or aluminum-silicate compounds.

Based on these previous investigations, we could arrive at the tentative conclusion that SO_4^{2-} anions are involved in some manner in the alteration mechanism of $PbCrO_4$, without however it being clear what exactly the role is they play. In this regard, a hypothesis was formulated that in the presence of abundant sulfate ions, also a minor amount of sulfide ions can be formed *in situ* that might act as reducing agent for the chromate ions. [3,4,5]
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2. Overview of samples investigated

In continuity with the first two parts of this work, [1,2] photochemical aged oil paint model samples, containing different $PbCrO_4$:$PbSO_4$ mixtures and co-precipitates (these latter sometimes added with a little amount of others sulfide/sulfate compounds) were examined at the beamline ID21 by means of μ-XRF and μ-XANES analyses around the Cr and S K-edge. All samples were prepared by applying a thin layer of paint on polycarbonate and glass microscopy slides.

Similar investigations were also performed on two embedded micro-paint samples, taken from the painting *Falling Leaves ("Les Alyscamps")* by Vincent van Gogh (sample F486) and the low-relief *Soyez mystérieuses* by Paul Gauguin (Figure 1).

Figure 1. Photographs of: [Panel(A)] *Falling Leaves ("Les Alyscamps")* (F486), Vincent van Gogh, 1888, oil on canvas, Kröller-Müller Museum, Otterlo (The Netherlands), and [Panel(B)] *Soyez mystérieuses,* Paul Gauguin, 1890, low-relief, polychrome lime tree wood, Musée d'Orsay, Paris (France).

2.1 Artificially aged model samples of co-precitates of lead chromate and sulfate

(a) Reproduction of the darkening process of the previous investigated historic aged model sample A

As Fig. 2A illustrates, after UVA-visible irradiation, the oil paint model samples prepared using a 25:75 $PbCrO_4:PbSO_4$ self-synthesized coprecipitate (sample S_{3D}) showed a similar tendency to darkening as previously was observed for the historic sample A ($\sim$ 60% SO_4^{2-}).[1]

Series of Cr-K edge XANES spectra were collected from embedded aged sample S_{3D} (Fig. 2B) revealing a relative concentration of Cr(III) [expressed as $Cr(III)/\sum Cr_{total}$] up to 60% in the exposed brown discoloured area (Fig. 2C, brown spectrum and Fig.2D). 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. 2C). However, the Cr(III) abundance decreased progressively when moving toward the yellow bulk of the sample, where it reaches a value of around 20% (Fig. 2C, orange spectrum, and Fig.2D).

Similar to the previously investigated sample A, [1] three fitting components, such as $PbCrO_4$, $Cr_2O_3 \cdot 2H_2O$, and either Cr(III) potassium sulfate dodecahydrate $[KCr(SO_4)_2 \cdot 12H_2O]$ or Cr(III) acetylacetonate $[Cr(C_5H_7O_2)_3]$ were required in order to obtain a good description of the XANES spectra recorded along the first 2-3 μm of the cross-section (see Fig.2D as an example); again only two components ($PbCrO_4$ and $Cr_2O_3 \cdot 2H_2O$) were necessary to fit the spectra recorded from greater depth (after several microns) below the surface.
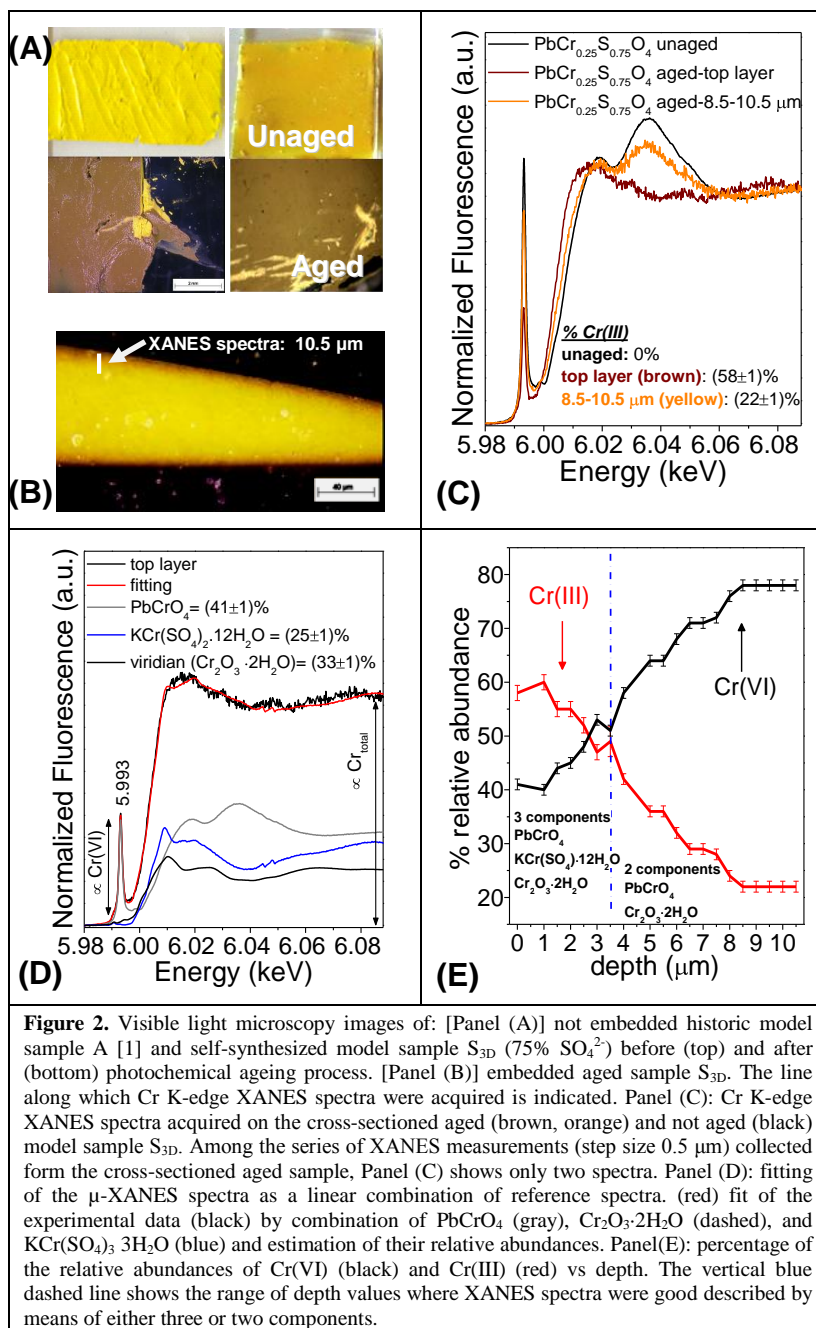

Figure 2. Visible light microscopy images of: [Panel (A)] not embedded historic model sample A [1] and self-synthesized model sample S_{3D} (75% SO_4^{2-}) before (top) and after (bottom) photochemical ageing process. [Panel (B)] embedded aged sample S_{3D}. The line along which Cr K-edge XANES spectra were acquired is indicated. Panel (C): Cr K-edge XANES spectra acquired on the cross-sectioned aged (brown, orange) and not aged (black) model sample S_{3D}. Among the series of XANES measurements (step size 0.5 μm) collected form the cross-sectioned aged sample, Panel (C) shows only two spectra. Panel (D): fitting of the μ-XANES spectra as a linear combination of reference spectra. (red) fit of the experimental data (black) by combination of $PbCrO_4$ (gray), $Cr_2O_3 \cdot 2H_2O$ (dashed), and $KCr(SO_4)_3 \cdot 3H_2O$ (blue) and estimation of their relative abundances. Panel(E): percentage of the relative abundances of Cr(VI) (black) and Cr(III) (red) vs depth. The vertical blue dashed line shows the range of depth values where XANES spectra were good described by means of either three or two components.

(b) Photochemical ageing treatments using narrow energy ranges of UV-visible radiation

In order to evaluate the extent to which the specific spectral range of the light had an influence on the (speed of the) degradation process, photochemical ageing treatments using various narrow energy ranges of UV-visible radiation were performed on several coupons prepared using a 25:75 $PbCrO_4$:$PbSO_4$ self-synthesized coprecipitate (Fig.3A).

According to the discoloration that was observed, semi-quanititatively linear fitting combination of a series of μ-XANES Cr-K edge spectra collected from the aged embedded samples revealed a correlation between the relative Cr(III) abundance and the darkening.

The highest amount of Cr(III) (up to 58%) was estimated after ageing by means of UVA-visible ($\lambda \geq 300$ nm) and UV light exposure (240 nm$\leq\lambda\leq$400 nm) (Fig. 3B, green and purple spectra). While still minor differences were observed in the XANES spectrum of paint sample aged by means of visible-blue light [~30% of Cr(III), Fig. 3B, blue spectrum], no changes were visible upon irradiation of the sample with visible-red light [only Cr(VI) presence, Fig. 3B, red spectrum]. Clearly light with a wavelength shorter than 570 nm is required to induce the reduction process of the Cr.

Once again, the most discolored samples revealed that the Cr(III) concentration decreased progressively from the superficial brown layer toward the yellow bulk of the sample (where it reaches a value of around 30-20%. See Fig. 3C as an example).
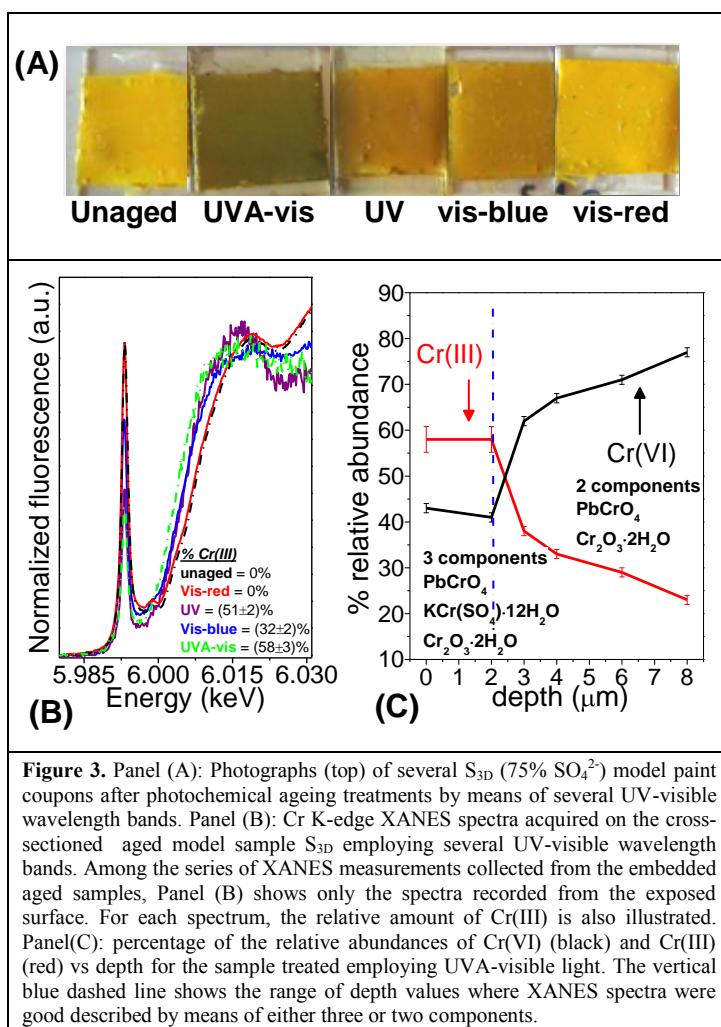

Figure 3. Panel (A): Photographs (top) of several S_{3D} (75% SO_4^{2-}) model paint coupons after photochemical ageing treatments by means of several UV-visible wavelength bands. Panel (B): Cr K-edge XANES spectra acquired on the cross-sectioned aged model sample S_{3D} employing several UV-visible wavelength bands. Among the series of XANES measurements collected from the embedded aged samples, Panel (B) shows only the spectra recorded from the exposed surface. For each spectrum, the relative amount of Cr(III) is also illustrated. Panel(C): percentage of the relative abundances of Cr(VI) (black) and Cr(III) (red) vs depth for the sample treated employing UVA-visible light. The vertical blue dashed line shows the range of depth values where XANES spectra were good described by means of either three or two components.

(c) artificially aged model paint samples containing different amount of sulfate
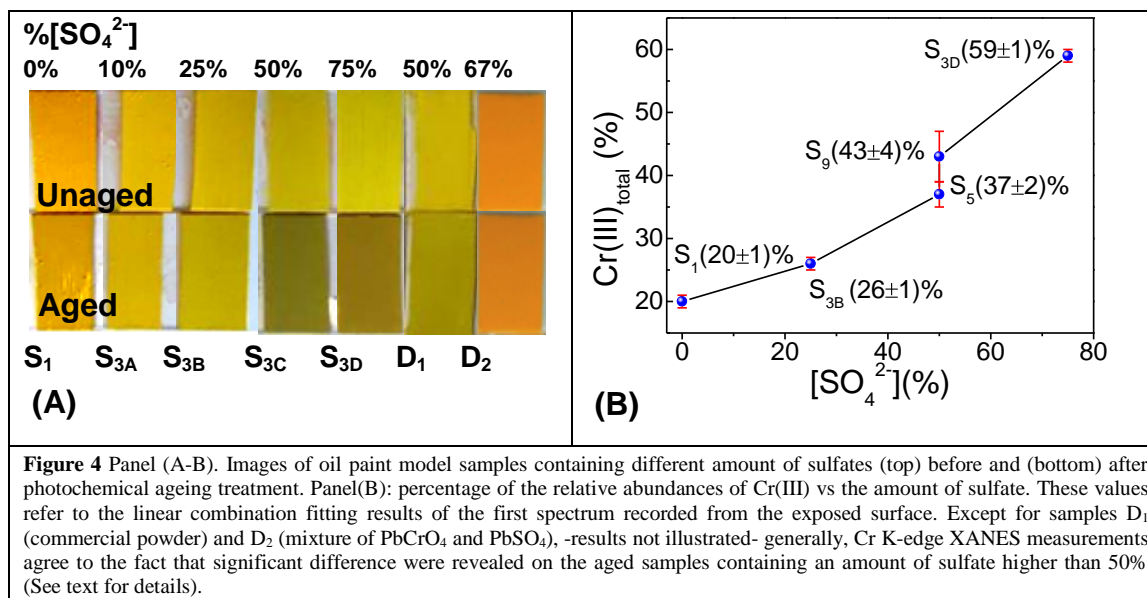
In order to explore the relation between the tendency towards darkening of the paint and its composition, photochemical ageing employing UVA-visible light were carried out on both self-synthesized (samples S_1, S_{3A}, S_{3B}, S_{3C}, S_{3D}) and commercial (sample D_1) powders of chrome yellow containing different amount of sulfate (from 10% to 75% see Fig. 4A). Investigations were also carried out on model paint samples has been prepared: (i) by simply mixing commercial $PbCrO_4$ and $PbSO_4$ in 1:2 molar ratio (sample D_2) instead of employing the above-mentioned co-precipitate; (ii) by mixing the synthesized powder of sample S_{3C} (50% SO_4^{2-}) with a little amount of $BaSO_4$ or ZnS (samples S_5 and S_9, not shown on Figure 4A).

After a preliminary XANES characterization of all above-mentioned not embedded paint samples (unfocused mode), because of the relatively high depth penetration value of the X-ray beam at the Cr K-edge energy, also measurements in focused mode were carried out in order to obtain a reliable estimation of the amount of reduced Cr(VI) present in the thin and superficial alteration layer.

For this purpose, series of Cr-K edge XANES spectra were collected from embedded cross-sections of aged sample S_1 (pure $PbCrO_4$), S_{3B} (25% SO_4^{2-}), S_{3D} (75% SO_4^{2-}), S_5 (50% SO_4^{2-}+$BaSO_4$), S_9 (50% SO_4^{2-}+ZnS) and D_1(50% SO_4^{2-}, commercial powder).

As shown in Fig.4B, the linear combination fitting of XANES spectra reveal that the amount of Cr(III) at the exposed surface progressively increased when going from aged samples S_1 (0% sulfate) to S_{3D} (75% sulfates) Particularly, for the aged samples S_1, S_{3B} and D_1 the relative Cr(III) concentration, was estimated to be around 30-20% along the first 3 μm of the cross-section, while for S_{3D}, S_5 and S_9 this value decreased progressively from the superficial brown layer [Cr(III) present at around 60-40% relative] toward the yellow bulk of the sample (where it reaches a value of around 40-20%).

Although the sulfate amount of the commercial co-precipitate (D_1) was estimated by means of SEM-EDX and XRD analysis to be similar to that of S_{3C} (~50%), its greater stability toward light exposure [Cr(III) present at around 20% relative] can be explained when its crystalline structure is taken into account. According to the literature [6] methods to favor the co-precipitation of the more stable monoclinic mixed crystal of lead-chromate and sulfate were introduced during the industrial manufacture of the modern chrome yellow pigments. Furthermore the fact that (i) only a negligible color change has been observed after ageing of a simple mixture of pure $PbCrO_4$:$PbSO_4$ (sample D_2, results not illustrated) and (ii) a similar relative Cr(III) amount was estimated for aged samples S_5 and S_9, indicates the necessity for the sulfate anions to be present in the crystalline structure of the yellow pigment to be able to play a key role on the darkening process.

Figure 4 Panel (A-B). Images of oil paint model samples containing different amount of sulfates (top) before and (bottom) after photochemical ageing treatment. Panel(B): percentage of the relative abundances of Cr(III) vs the amount of sulfate. These values refer to the linear combination fitting results of the first spectrum recorded from the exposed surface. Except for samples D_1 (commercial powder) and D_2 (mixture of $PbCrO_4$ and $PbSO_4$), -results not illustrated- generally, Cr K-edge XANES measurements agree to the fact that significant difference were revealed on the aged samples containing an amount of sulfate higher than 50% (See text for details).

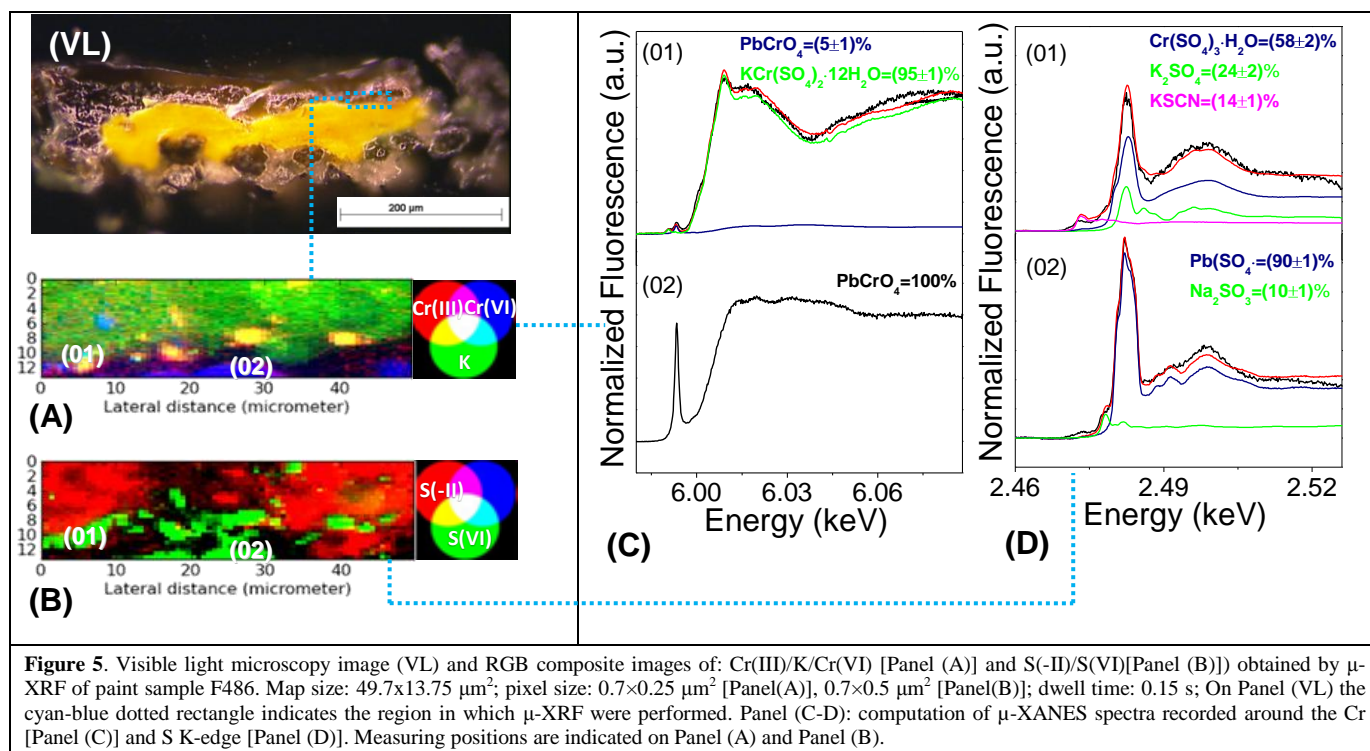## 2.2 Embedded micro-paint samples

Analogous with the aged model sample, both XANES and XRF measurements revealed the presence of reduced chromium. Particularly, this alteration species were present in those areas where the $PbCrO_4$:$PbSO_4$ paint is in contact with (degraded) varnish layers (applied as conservation treatment in the past).

As Figure 5 illustrates, (as an example are shown some of results collected from the micro-paint sample F486, taken from the painting by V. van Gogh).

Cr and S chemical state maps of a small region of the sample (Figs. 5A-5B) showed a correlation between the presence of Cr(III), K and S(VI) in the brown layer, while the surrounding unaltered yellow paint contained exclusively Cr(VI) and S(VI). **S species in their reduced oxidation states were present only in the superficial degraded layer and around Cr(III) grains.**

In the same area, both Cr and S K-edge μ-XANES point measurements (Figs. 5C-5D) confirmed the presence of Cr(III), that a procedure of linear combination fitting of the spectra revealed to be mainly composed of a KCr(III) sulfate compound (~95%), [Figs. 5C-5D, spectra (01)]. Differently, $PbCrO_4$ and $PbSO_4$ were confirmed to be the main components of the unaltered yellow layer [Figs. 5C-5D, spectra (02)].

Where no correlation between sulfate and Cr(III) grains were detected, the compound was identified as viridian ($Cr_2O_3 \cdot 2H_2O$) [results not shown].

Figure 5. Visible light microscopy image (VL) and RGB composite images of: Cr(III)/K/Cr(VI) [Panel (A)] and S(-II)/S(VI)[Panel (B)]) obtained by µ-XRF of paint sample F486. Map size: 49.7x13.75 µm²; pixel size: 0.7×0.25 µm² [Panel(A)], 0.7×0.5 µm² [Panel(B)]; dwell time: 0.15 s; On Panel (VL) the cyan-blue dotted rectangle indicates the region in which µ-XRF were performed. Panel (C-D): computation of µ-XANES spectra recorded around the Cr [Panel (C)] and S K-edge [Panel (D)]. Measuring positions are indicated on Panel (A) and Panel (B).

3. Hypotheses about the role of sulfate anions during the darkening of chrome yellow pigments

Investigations of model samples of self-synthesized mixed crystals of lead chromate sulfate indirectly has confirmed our previous hypothesis that locally a chemical mechanism must be in place that first causes some of the sulfates (SO_4^{2-}, S^{6+}) to reduce to sulfides (S^{2-}) [equilibrium (a)] which can then in their turn cause the reduction of the chromates via the regeneration of sulfates in an acidic medium (b):

(a) $SO_4^= + 8e^- + 8H^+ \leftrightarrow S^= + 4\,H_2O$
(b) $8\,CrO_4^= + 3\,S^= + 16\,H^+ \rightarrow 4\,Cr_2O_3 \cdot 2H_2O + 3\,SO_4^=$
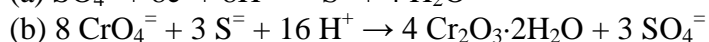
While the µ-XANES investigations at the S-K edge of artificially aged model samples did not show in any case the presence of S(-II) species, it is remarkable to see that in the original paint micro samples, S(-II) species are effectively present in those varnish areas trapping small grains of $PbCrO_4$ that had partially or completely been reduced. This strongly suggests (a) that the above described reactions indeed may describing the reduction process of Cr(VI) while (b) that is becomes highly relevant to study the influence of the organic components of the paint and their cover layers, as the latter may play a key role on the darkening of chrome yellow pigments.

References

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