Degradation Process of Lead Chromate in Paintings by Vincent van Gogh Studied by Means of Synchrotron X-ray Spectromicroscopy and Related Methods. 1. Artificially Aged Model Samples

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ABSTRACT: On several paintings by artists of the end of the 19th century and the beginning of the 20th Century a darkening of the original yellow areas, painted with the chrome yellow pigment (PbCrO4, PbCrO4 · xPbSO4 or PbCrO4 · xPbO) is observed. The most famous of these are the various Sunflowers paintings Vincent van Gogh made during his career. In the first part of this work, we attempt to elucidate the degradation process of chrome yellow by studying artificially aged model samples. In view of the very thin (1–3 μm) alteration layers that are formed, high lateral resolution spectroscopic methods such as microscopic X-ray absorption near edge (μ-XANES), X-ray fluorescence spectrometry (μ-XRF), and electron energy loss spectrometry (EELS) were employed. Some of these use synchrotron radiation (SR). Additionally, microscopic SR X-ray diffraction (SR μ-XRD), μ-Raman, and mid-FTIR spectroscopy were employed to completely characterize the samples. The formation of Cr(III) compounds at the surface of the chrome yellow paint layers is particularly observed in one aged model sample taken from a historic paint tube (ca. 1914). About two-thirds of the chromium that is present at the surface has reduced from the hexavalent to the trivalent state. The EELS and μ-XANES spectra are consistent with the presence of Cr2O3 · 2H2O (viridian). Moreover, as demonstrated by μ-XANES, the presence of another Cr(III) compound, such as either Cr2(SO4)3 · H2O or (CH3CO2)2 Cr(OH)2 [chromium(III) acetate hydroxide], is likely.

Recent years have seen a growing interest in paintings of the end of the 19th Century and the beginning of the 20th Century from the field of analytical chemistry dedicated to the conservation of works of art. Since the beginning of 19th Century, the industrial expansion has stimulated the development of synthetic pathways for many new materials, including various pigments such as chrome yellow, cadmium yellow (CdS), emerald green [Cu(C2H3O2)2 · 3Cu(AsO2)2]3, viridian green (Cr2O3 · 2H2O), and lithopone white (BaSO4 · ZnS). These new pigments were either synthetic, purer equivalents of the traditional pigments employed by painters in earlier periods or entirely new compounds, yielding brighter colors and providing new stylistic possibilities. Among these, chrome yellow pigments took an important position, outclassing, because of their brightness and opacity, the already existing yellow pigments [such as Naples yellow (PbSb2O5), orpiment (As2S3), yellow ochre (a mixture of iron oxides and hydroxides), etc.]. Chrome yellow, often encountered in paintings of the end of 19th Century, such as by V. van Gogh (1853–1890), G. Seurat (1859–1891), J. M. W. Turner (1775–1851), J. Constable (1776–1837), P. Cézanne (1839–1906), C. Pissarro (1830–1903), and J. Ensor (1860–1949), is also employed on a wider scale for industrial purposes (painting of vehicles and air planes, road paint, and signs).

Chrome yellow belongs to a class of pigments based on either lead chromate (PbCrO4 yellow and found in nature as the rare mineral crocoite), lead chromate–oxide [PbCrO4 · xPbO · yellow-orange and found in nature as the mineral philocrococite with structure Pb2O2(Al2O3)2], in which the lead oxide conveys a reddish shade, or lead chromate sulfate (PbCrO4 · xPbSO4), in which the sulfate compounds are employed to obtain paler shades of yellow. At room temperature, PbCrO4 and PbSO4, respectively, have a monoclinic and orthorhombic structure as
their most stable crystalline forms. When the relative atomic percentage of sulfate exceeds 40% in PbCrO₄·xPbSO₄, a change from the monoclinic to the orthorhombic structure is observed. Given its high cost, PbCrO₄ was often extended with various white compounds, e.g., with sulfates [BaSO₄, CaSO₄·2H₂O, KAI(SO₄)₂·12H₂O, PbSO₄], with t alc, calcite, or kaolinite, or with other chromium-based yellow pigments such as CaCrO₄ and BaCrO₄.

The synthesis of chrome yellow has evolved over the years, since it was observed that its stability is related to the preparation procedure. To the presence of other species, such as organic compounds, or copper, phosphate, or chloride ions, or semiconductors particles, such as ZnO. In order to improve the light-fastness of PbCrO₄, the initial custom of using lead acetate as one of the starting reagents was replaced by the use of neutral solutions/suspensions of a soluble lead salt, (e.g., lead nitrate, lead chloride) as reaction partner for alkaline (di)chromate solutions [usually K- or Na-(di)chromate], according to the reaction:

\[
PbY_2 + M_2CrO_4 \rightarrow PbCrO_4 + 2MY
\]

where M = Na⁺, K⁺, and Y = CH₃COO⁻, NO₃⁻, Cl⁻, etc.

In the following years improvements in the stability of the pigment were obtained by treating it with a hydrous oxide of group IV or V metals. Alternatively, PbCrO₄ can be synthesized through the direct addition of PbO to chromates in paste form.

In some paintings by artists of the end of 19th Century such as Vincent van Gogh, more than one century after their creation, the areas painted with chrome yellow now appear darkened, likely because of degradation of the pigment itself. Because of its instability, the painters of the 1880s gradually abandoned the use of chrome yellow, replacing it by other pigments such as cadmium yellow, which was believed to be more stable.

Recently, it was established that cadmium yellow can also become unstable, being oxidized from the yellow and opaque CdS to the white/transparent CdSO₄·H₂O.

The darkening of chrome yellow is reported as early as 1829, when it was observed that the pigment is subject to alteration when it is combined with oil, with lead oxide, or with Prussian blue. Nevertheless, it was not until the 20th Century that the degradation phenomenon of chrome yellow was systematically studied. Several studies on PbCrO₄ alteration, induced by the single or composite use of UV—visible light, heat, contaminants, atmospheric gases, such as SO₂, and H₂S, are in agreement to attribute this degradation phenomenon to a reduction reaction of Cr(III) to Cr(II); however, this assumption was not based on experimental evidence, nor was insight provided into the degradation mechanism or detailed information given about the nature of the degradation products. In this regard, some authors have proposed that the PbCrO₄ could dissociate by a photochemical reduction, into lead metachromite [Pb(CrO₂)₂], oxygen, and element lead, or into chrome oxide whereby Pb²⁺ is oxidized to PbO²⁻. In the presence of SO₂, under similar conditions, the mixture of PbSO₄ and Cr(III) compounds can be formed.

After ca. 1950, the interest in the chrome yellow darkening problem diminished, probably because of the development of stabilized lead chromates and of more durable lead molybdates. However, in many scientific fields (e.g., in the environmental, industrial chemistry, biological, and geological areas) attempts have been made to better understand the reduction mechanism of Cr(VI). According to these recent literature data and consistent with the high oxidizing power of chromates, the reduction of Cr(VI) can be induced by many different agents, such as soil constituents (e.g., amino, humic, and fulvic acids) and Fe(II), sulfides and sulfates, and organic matter, by semiconductors particles in aqueous solutions, or even by H₂O₂ in acidic aqueous solutions.

In recent years, various authors reconsidered the problem of the darkening of chromium-based yellow pigments (Pb-, Ba-, Sr-, Ca-, Zn/K-chromate) in the context of the conservation of paintings, because the understanding of the pigments’ alteration process is of key importance both to adjust the conditions in which the works of art are stored and/or to allow the selection of an appropriate conservation treatment. Both studies that characterize several chromate samples taken from paints and paint tubes, or that investigate which factors can promote the deterioration of zinc—potassium chromate, are reported in literature, showing that the alteration problem is not limited to PbCrO₄ alone. More specifically, in the recently published work by Casadio et al., the discoloration of K₂O·4ZnCrO₄·3H₂O was attributed to the presence of Cr(III) dichromate and of Cr(III) oxide species in the outer layers of model samples aged in a moist (90% relative humidity) SO₂ atmosphere. Also in historic samples from a painting by G. Seraut the ochre-colored discoloration of K₂O·4ZnCrO₄·3H₂O was found to be associated with both Cr(III) and Cr(VI) dichromate ions.

During the past decade, the introduction of synchrotron radiation-based methods of analysis in conservation science has lead to increased insight into a number of alteration phenomena of different inorganic pigments. Especially, the ability of μ-XANES to visualize with micrometric resolution the distribution of specific species of a given chemical element is highly useful in this context. The capabilities of electron energy loss spectrometry (EELS) to render similar speciation information at the nanoscale level is equally valuable, and both methods are used in a complementary fashion here.

In what follows, we attempt to elucidate the chemical transformations leading to the darkening of chrome yellow and to formulate hypotheses as to their cause. For this purpose, in the first part of this work, on the one hand μ-XANES and μ-XRF spectroscopy were employed to study artificially aged model samples of lead chromate. The second part will focus on the study of two embedded paint cross-sections taken from paintings by Vincent van Gogh from the collection of the Van Gogh Museum (VGM), Amsterdam, where alteration of the chrome yellow is apparent.

**EXPERIMENTAL SECTION**

**Materials. Aged Model Samples.** Four model samples (A, B₁, B₂, C) were prepared for artificial aging by applying a thin layer of paint on glass microscopy slides (cf. Figure 2A). The paint layers were characterized before and after the aging process; some of their characteristics are summarized in Table 1. Model sample A was taken from a historic oil paint tube belonging to the Flemish Fauvist Rik Wouters (1882–1913); the tube was donated to the Royal Museum of Fine Arts of Antwerp after his death. Samples B₁ and B₂ similarly come from two different historic oil paint tubes of the end of 19th Century (Elsens, Bruxelles) provided by the Royal Academy of Fine Arts of Antwerp. As indicated by the labeling, the former is a light chrome yellow, while the latter is darker toned. Sample C was prepared in the laboratory by mixing pure PbCrO₄ with linseed oil (80:20 weight ratio). All the model samples were artificially...
Table 1. Overview of Results of the Preliminary Characterization of the Unaged Model Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin of Paint</th>
<th>XRF</th>
<th>SR-μ-XRD</th>
<th>μ-Raman</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>historic oil paint tube belonging to the Flemish Fauvist Rik Wouters (1882–1913)</td>
<td>Pb, Cr</td>
<td>PbSO₄ (anglesite)</td>
<td>lead chromate, lead sulfate</td>
<td>lead chromate, lead sulfate</td>
</tr>
<tr>
<td>B₁</td>
<td>historic end-19th century oil paint tube (Elsens, Bruxelles), light chrome yellow</td>
<td>Pb, Cr</td>
<td>PbCrO₄ (crocoite)</td>
<td>lead chromate</td>
<td>lead chromate, lead sulfate</td>
</tr>
<tr>
<td>B₂</td>
<td>historic end-19th Century oil paint tube (Elsens, Bruxelles), dark chrome yellow</td>
<td>Pb, Cr, Zn</td>
<td>PbCrO₄ (crocoite), PbO₂(CrO₄)₃ (phoenicochroite)</td>
<td>lead chromate, lead sulfate</td>
<td>lead chromate</td>
</tr>
<tr>
<td>C</td>
<td>80:20 mixture of PbCrO₄ powder with linseed oil</td>
<td>Pb, Cr</td>
<td>PbCrO₄ (crocoite)</td>
<td>lead chromate</td>
<td>lead chromate</td>
</tr>
</tbody>
</table>

Because in sample A the presence of a crystalline form of PbCrO₄ could not be observed (next to that of well-crystallized PbSO₄) while on the other hand, the Raman, FTIR and XRF spectra are consistent with the presence of a major amount of PbCrO₄, we conclude that (most of) the PbCrO₄ in this oil paint is present in amorphous form.
was used to fit the fluorescence spectra and separate the different elemental contributions. In the present context, it was in particular crucial to distinguish the partially overlapping Pb–M lines and S–K lines. This program was employed as a batch-fitting procedure on each pixel of two-dimensional (2D) maps.\textsuperscript{42} 

μ-XANES spectra were acquired by scanning the primary energy around the Cr K-edge (5.96–6.09 keV) with a step size of 0.2 eV. The energy calibration was performed using a metallic Cr foil. For all XANES spectra, the procedure of normalization was performed by means of ATHENA, a software program widely used for (E)XAFS(F)S data analysis. In particular, edge-step normalization of the data was performed by means of linear pre-edge subtraction and by regression of a quadratic polynomial by means of linear pre-edge subtraction and by regression of a quadratic polynomial.\textsuperscript{43} The same software was also used to carry out a linear combinatorial fitting of XANES spectra of unknown mixtures of Cr-species against a library of XANES spectra of pure Cr-reference compounds. During this procedure, ATHENA attempts to find the best fit between the XANES spectra of the unknown mixtures using a large number of different combinations of the available reference spectra. Prior to the analysis of the samples, reference XANES spectra were acquired from pure compound powders by using a 200 μm diameter X-ray beam, recorded in an air environment and in transmission mode.

Conventional transmission electron microscopy (TEM) imaging and EELS studies were conducted using a JEOL 3000F TEM/STEM, equipped with a postcolumn GIF2000 detector. The TEM specimens were prepared by site-specific focused ion beam milling (FIB) using in situ lift-out in a FEI FIB/SEM xT Nova Nanolab 200. The FIB sample preparation method allows an optimal sample thickness and is capable of producing micrometer sized, electron transparent samples from well-defined areas.

**RESULTS AND DISCUSSION**

Before discussion of the results obtained from (un)aged model samples, it is useful to describe the features of the XANES and EELS spectra derived from a series of Cr-reference compounds. Both XANES and EELS are techniques that are sensitive to the local chemical environment of the Cr atom and to its surrounding atoms. Because chromium can be present in compounds with various coordination geometries, oxidation states, and molecular structures, these properties are to some extent reflected in the XANES (Figure 1) and EELS spectra (Figure 4).

**XANES K-Edge Spectra of Cr-Reference Compounds.** Reference spectra of Cr(VI) and Cr(III) compounds were recorded and are shown in Figure 1A and 1B, respectively. Generally, the intensity of the pre-edge peak is correlated to the number of electron vacancies in the 3d orbitals of the Cr atom,\textsuperscript{44} so that the relative area of the pre-edge peak is proportional to the relative amount of Cr(VI) in a material.

For the Cr(VI) compounds (Figure 1A) having a tetrahedral coordination geometry, it is possible to observe a well-defined pre-edge peak around 5.993 keV for the Cr K-edge.\textsuperscript{45} This peak corresponds to a bound-state 1s to 3d dipole-forbidden transition. The presence of the pre-edge peak is related to the non-centrosymmetric nature of the tetrahedral structure that favors a strong hybridization of the Cr(3d) and O(2p) orbitals. In Cr(III) compounds, that commonly exist in a centrosymmetrical octahedral geometry, the pre-edge features have a low intensity. Two pre-edge peaks are present around 5.990 and 5.993 keV; these bands are assigned to 1s→3d(t_2g) and 1s→3d(e_g) electronic transitions, respectively. In addition, for Cr(VI) compounds, on the rising flank of the absorption edge it is possible to observe a shoulder that can be attributed to a simultaneous excitation of two electrons: next to the 1s core electron, also a t_2 valence electron is promoted to a t_2^* unoccupied orbital.\textsuperscript{46}

Another important parameter that provides information about the valence state of Cr from XANES spectra is the shift of the absorption edge position. In general, a shift toward higher energies is observed when there is an increase in the valency of the absorbing atom and/or of the electronegativity of the nearest neighbor atoms. A recent study on different chromium complexes\textsuperscript{47} has demonstrated the strong dependence of the shift of the absorption edge energy on the ligand geometry but also highlighted the impossibility to accurately determine oxidation states of unknown complexes by simply scaling their edge positions. As shown for Cr(VI) reference compounds (Figure 1A, spectra 03, 06, 08, 13), a shift of the absorption edge toward lower energy may be correlated to an increase of the degree of polymerization of the chromate moieties.\textsuperscript{48}
Artificially Aged Model Samples. In order to induce the darkening of chrome yellow under the influence of light and heat, several model paint samples were prepared and artificially aged in identical conditions. Prior to SR $\mu$-XANES and $\mu$-XRF analysis, a characterization of these model samples before and after aging was performed by means of different techniques, and the results are summarized in Table 1.

Optical and Microscopic Observations. Figure 2A shows the visual aspect of the oil paint model samples before and after aging. The formation of a thin brown layer on the outer surface of sample A is clearly visible, similar to that observed by Cole, who described the alteration process as superficial and attributed it to a defective lattice structure, indicating that other factors, such as dimension of the pigment particles and the method of preparation, can have a significant effect on the light-fastness of PbCrO$_4$.

Although in all model samples to some extent a darkening of the visual aspect can be observed, the other model samples do not show the same profound discoloration as does sample A.

SR $\mu$-XRD, $\mu$-Raman, and FTIR Analyses. In general, no significant difference in the XRD, $\mu$-Raman, or transmission FTIR spectra were observed between the unaged and the aged model samples. Hence, Figure 2C–E only show the results obtained prior to the aging process. This fact is attributed to the limited thickness of the alteration layer and to the fact that only $\mu$-XRD measurements in transmission mode were performed. Also, in a mixture of Cr(VI)- and Cr(III)-species, the high Raman scattering power of chromates makes it difficult to detect Cr(III) compounds. While linseed oil was present as organic binder in all model samples, XRD, $\mu$-Raman, and transmission FTIR analyses did show a marked difference between the inorganic composition of sample A and the other model samples. $\mu$-XRD measurements revealed crystalline lead chromate (crocoite, PbCrO$_4$) in all model samples except A, of which the diffraction pattern (Figure 2C) only reveals the presence of lead sulfate (anglesite, PbSO$_4$). A second, red-colored lead chromate pigment, called phoenicochroite [Pb$_2$O(CrO$_4$)$_2$], was mixed with crocoite in sample B$_2$ in order to obtain an orange paint. $\mu$-Raman analyses (Figure 2D) confirm the presence of crocoite in all paint samples, as characterized by a strong band at 841 cm$^{-1}$ (CrO$_4^{2-}$ symmetric stretching) and several bands of medium intensity at 407, 381, and 361 cm$^{-1}$ (CrO$_4^{2-}$ bending modes). In the Raman spectra of sample A, some differences in the shape of the bands located between 410 and 350 cm$^{-1}$ were observed, characterized by a signal of medium intensity at 349 cm$^{-1}$ that is not present in the spectra of the other model samples. In addition, the band at 974 cm$^{-1}$ (SO$_4^{2-}$ symmetric stretching) revealed the presence of lead sulfate. In agreement to $\mu$-XRD, Raman measurements on sample B$_2$ showed the presence of phoenicochoite, characterized by an additional band at 825 cm$^{-1}$ (CrO$_4^{2-}$ stretching). Two signals at 303 and 602 cm$^{-1}$ are attributed to cadmium yellow (CdS), likely present as an impurity of the pigment. FTIR measurements (Figure 2E) revealed the presence of lead sulfate on all samples except C, as demonstrated by the signals around 1100 and 1000 cm$^{-1}$ (SO$_4^{2-}$ asymmetric stretching) and the bands at 626 and 596 cm$^{-1}$ (SO$_4^{2-}$ asymmetric bending). This compound is less abundantly present in samples B$_1$ and B$_2$ than in A. In all samples, the presence of lead chromate is confirmed by the signals located between 900 and 800 cm$^{-1}$ (CrO$_4^{2-}$ asymmetric stretching).
perpendicular to the surface. In the case of sample A, this line is indicated in Figure 2B. Panels D and E: quantitative estimation of the related abundance of Cr(VI) and Cr(III) compounds vs depth in aged sample A. Panel D: Fitting of the experimental data (black) by combination of PbCrO4 (blue), Cr2O3 (red) and C. Panels B and C: series of Cr K-edge XANES spectra recorded from aged and cross-sectioned model samples of B2 (Panel B) and A (Panel C). The XANES spectra were recorded with an increment of 1 μm, moving from surface (exposed layer) toward the underlying bulk material along a line perpendicular to the surface. In the case of sample A, this line is indicated in Figure 2B. Panels D and E: quantitative estimation of the related abundance of Cr(III) and Cr(VI) compounds vs depth in aged sample A. Panel D: Fitting of the experimental data (black) by combination of PbCrO4 (blue), Cr2O3 (red), and Cr2(SO4)3·H2O (gray) and estimation of their relative abundances. Panel E: Percentage of the relative abundances of Cr(VI) (black) and Cr(III) (red) vs depth.

Local Cr-Speciation Measurements. Figure 3A demonstrates that the XANES spectra recorded on all unaged model samples are similar to that of the pure PbCrO4 reference. Several measurements performed on the aged B1, B2, and C samples, either at the outer layer or at unexposed material underneath the surface did not reveal any difference. As an example, Figure 3B shows a series of XANES spectra collected from a cross-section of aged sample B2 obtained along a line perpendicular to the exposed surface.

Similar measurements performed on aged sample A, however, show a significant difference between the discolored surface and the yellow material immediately below (Figure 3C). Since the XANES spectra from the surface show a clear decrease of the intensity of the Cr pre-edge peak at 5.993 keV and feature a shift of the absorption edge toward lower energies, a substantial reduction of the original Cr(VI) has taken place at the surface. However, also on the still-yellow areas of the material, the reduction of Cr is observed, albeit to a lesser degree than at the surface. In order to extract semiquantitative data on the abundance of Cr(III)- and Cr(VI)-species vs depth from the spectra in Figure 3C, each normalized spectrum was fitted as a linear combination of the XANES spectra of pure lead chromate (PbCrO4), viridian (Cr2O3·2H2O) (dashed), and Cr2(SO4)3·H2O (gray) and estimation of their relative abundances. Panel E: Percentage of the relative abundances of Cr(VI) (black) and Cr(III) (red) vs depth.

Both in the Raman and FTIR spectra, the differences in the shape of the bands assigned to sulfates and chromates are attributed to the different ratio between these two isostructural anions and their arrangement inside the pigment lattice. Additionally in samples B1 and B2, the presence of a hydrated carbonate compound (likely magnesium carbonate) is suggested by signals at 3650 (free -OH stretching, not shown) and 1485 and 1422 cm⁻¹ (CO3²⁻ asymmetric stretching). After aging, only the FTIR spectrum of aged sample A (blue line) features minor differences relative to the spectrum of unaged sample (black line), as illustrated in Figure 2E: a decrement of the signal at 1060 cm⁻¹ and an inversion in the intensity of the bands located at 626 and 596 cm⁻¹ are observed.

Considering that nevertheless a significant discoloration of sample A has taken place, regarding the model samples, most analytical efforts employing micro-X-ray techniques and EELS were focused on this material.
It is noteworthy that three fitting components [either Cr$_2$-(SO$_4$)$_3$·H$_2$O or (CH$_3$CO)$_2$Cr$_2$ (OH)$_2$, Cr$_2$O$_3$·2H$_2$O, and PbCrO$_4$] are required for a good description of the XANES spectra recorded along the first 3 μm below the brown layer, while only two components (Cr$_2$O$_3$·2H$_2$O and PbCrO$_4$) are required to fit the spectra recorded from 5 to 8 μm below the surface. As shown in Figure 3E, the Cr(VI) concentration, expressed as [Cr(VI)]/ΣCr, decreases progressively from the yellow bulk of the sample (where it is present at the level of 50–60%) toward the exposed, brown surface (where it reaches a value of around 30–40%). Clearly a positive correlation between the darkening and the Cr(III) abundance can be observed here (Figure 3E); a fairly thin alteration layer of ca. 2–3 μm thickness is observed, also confirmed by other measurements (see below). This thickness is similar to that observed by Casadio et al.$^{35}$ on altered K$_2$O·4ZnCrO$_4$·3H$_2$O samples. However, in contrast to their conclusions, the present XANES data do not reveal any indications about the presence of dichromate compounds. In case XANES reference spectra of dichromatic species (see Figure 1A, spectra 03, 06, and 08) are included in the fitting model, a fit of reduced quality is obtained. We also do not observe the slight broadening of the Cr−K pre-edge peak that is visible in the dichromate reference spectra of Figure 1A.

The formation of a hydrated version of the degradation species Cr$_2$O$_3$·2H$_2$O is understandable in view of the fact that (a) it was demonstrated by FTIR analyses, specifically by the presence of the stretching (around 3450 cm$^{-1}$, not shown) and bending mode (1620 cm$^{-1}$) bands of the OH group, that water is present in both the unaged and aged versions of sample A and (b) the aging process took place in an atmosphere having 50% RH while the aging temperature, kept between 50 and 60 °C, was not sufficiently high to drive off all the water present inside the sample.

EELS Measurements. In order to establish whether or not the brown alteration layer was a homogeneous mixture of compounds, a thin cross-section of the upper 2 μm of the brown alteration layer of sample A was prepared by FIB, and STEM/EELS measurements at the Cr L$_{2,3}$- and O K-edges were performed. Figure 4 summarizes some of the results obtained. In Figure 4A an overview picture of the cross-section is shown; the photograph depicts the upper 1 × 1.4 μm$^2$ of the alteration layer. In a C-rich matrix (light areas of the photograph) different types of grains with diameters between 10 and 150 nm are present. About half of the grains are rich in Pb and S and feature the crystalline structure of anglesite (PbSO$_4$). Some of these particles are coated with a Cr(III)-containing layer (Figure 4C).

In Figure 4B, EELS O-K and Cr-L$_{2,3}$ spectra of some reference compounds are shown. The spectrum of Cr$_2$O$_3$·2H$_2$O features a symmetric Cr-L$_3$ peak near 578 eV while for the PbCrO$_4$ compound this peak is close to 582 eV (see thick dashed line in Figure 4D). On the other hand, the O-K EELS spectrum of PbSO$_4$ distinguishes itself from that of Cr$_2$O$_3$·2H$_2$O and PbCrO$_4$ by the presence of a sharp feature at an energy-loss value of ca. 538 eV (thin dashed line in Figure 4D). These characteristic features are also visible in the EELS line scan shown in Figure 4D that was taken along the vertical axis of the area shown in Figure 4A by averaging horizontally the EELS signals obtained at different vertical coordinates. In this line scan, close to/just below the surface the averaged EELS spectra resemble closely that of PbSO$_4$ (thin dashed line) while deeper in the bulk, the average spectrum starts to looks more like that of PbCrO$_4$ (thick dashed line in Figure 4D). In between and at the very surface, spectra in which the Cr$_2$O$_3$·2H$_2$O character dominates are also apparent.

By exploiting the spectral features indicated with the dashed lines and more specifically by selecting energy windows in the regions of 532−534 eV and 538−540 eV in the EELS spectra, it is possible to visualize the distribution of Cr$_2$O$_3$·2H$_2$O and PbSO$_4$ on the nanoscale throughout the examined area. These maps, detailed in Figure 4C, reveal that the Cr$_2$O$_3$ phase is present as a (newly formed) precipitation coating on the anglesite particles.

Chemical State Mapping. In order to visualize the distribution of Cr(VI)- and Cr(III)-species vs depth in aged sample A and to compare to the results obtained from the linear combination fitting of the XANES spectra, μ-XRF maps of the same area were recorded at two different excitation energies: i.e., (a) at 5.993 keV, favoring the excitation of the Cr(VI)-species; (b) at 6.086 keV to obtain a Cr−K$_\alpha$ fluorescence intensity map that is proportional to the total Cr content at a given position (i.e., irrespective of its oxidation state). The resulting Pb and Cr μ-XRF maps (not shown) demonstrate that these elements appear as main constituents and that they are both homogeneously distributed.

The following simple semiquantitative image processing method was employed to convert the two Cr−K$_\alpha$ intensity maps into Cr(III) and Cr(VI) abundance distributions. In performing these calculations, we implicitly assume that the total amount of Cr present at any position in the map is either present as (a) one or more Cr(VI) compounds, all having XANES spectra very similar to that of PbCrO$_4$ or as (b) one or more Cr(III) compounds, all having XANES spectra very similar to that of Cr$_2$O$_3$·2H$_2$O, Cr$_2$ (SO$_4$)$_3$·H$_2$O, and/or (CH$_3$CO)$_2$Cr$_2$ (OH)$_2$. Under this assumption, and considering that at $E_0 = 5.993$ keV (the Cr pre-edge energy), there is a negligible fluorescence from Cr(VI) compounds (Figure 1B), the percentage concentration of Cr(VI) in every pixel $(x,y)$ of the images is equal to the scaled relative intensity of both images at this location:

$$c_{\text{Cr(VI)}}(x,y) = \frac{I_{\text{Cr}}(x,y)}{I_{\text{Cr},0}} \times \frac{I_{\text{Cr},0} - 5.993\text{keV}}{I_{\text{Cr},0} - 6.086\text{keV}} \times 100\%$$

while the local concentration of Cr(III) compounds is equal to:

$$c_{\text{Cr(III)}}(x,y) = \frac{100\% - c_{\text{Cr(VI)}}(x,y)}{1}$$

The scaling ratio $I_{\text{Cr},0} - 5.993\text{keV}/(I_{\text{Cr},0} - 6.086\text{keV})$ is derived from the intensity readings of the XANES spectrum of the PbCrO$_4$ standard (Figure 1A, spectrum 01) and is equal to a value of 1.2.

Figure 5A and 5B shows the $c_{\text{Cr(VI)}}$ and $c_{\text{Cr(III)}}$ maps derived in this manner from a polished cross-section of aged sample A. In good agreement with the data obtained from the linear combination fitting of XANES spectra (Figure 3E), Cr(III)-species are observed to be enriched in the superficial layer; this contains up to 60–70% of Cr(III). Because the Cr-speciation only gradually changes (see also Figure 3E), it is not possible to assign a very precise value to the layer thickness. In general, we observed alteration layer thicknesses between 1 and 3 μm.

Cr(III)-Species and the Dark-Brown Color of the Alteration Layer. On first sight, the green Cr(III) compound Cr$_2$O$_3$·2H$_2$O (the green pigment viridian) is not able to explain the dark-brown color of the superficial alteration layer. Nevertheless, it must be realized that the observation of reduced Cr-species implies that other components of the paint, organic and/or inorganic in nature, have played the role of electron-donors and...
therefore have become oxidized. In general, the following factors may contribute additionally to the observed color:

(a) The presence of (polynuclear) Cr(III) compounds such as Cr(III) acetates or sulfates, of which the color can vary from green, gray-green, violet, to blue-violet.\textsuperscript{55}

(b) The partial degradation of the organic binding medium of the paint.

(c) The possible formation of other inorganic degradation products, such as PbO\textsubscript{2} and PbS (both black).

To establish whether or not the formation of the brown alteration color is reproducible, a series of additional model samples were prepared by mixing linseed oil and several synthesized powders of coprecipitates of different PbCrO\textsubscript{4}:PbSO\textsubscript{4} ratios. The recently executed aging of these model samples (50% relative humidity, UV—visible irradiation) leads to a clear and reproducible darkening of the oil paint samples that is particularly significant for those containing larger amounts of sulfate (PbSO\textsubscript{4}:PbCrO\textsubscript{4} ≥ 1). The formation of a superficial brown-green layer is clearly visible, similar to that observed on aged model sample A. In contrast to the experiments conducted by Casadio et al.,\textsuperscript{35} the presence of SO\textsubscript{2} was not required to promote the alteration; possibly the sulfates present inside the PbCrO\textsubscript{4}:PbSO\textsubscript{4} mixtures play a role similar to that of SO\textsubscript{2}.

**Cr-Speciation in Original Paint Samples from Paintings of Vincent van Gogh and the Role of Sulfur Species on Cr(VI) Reduction.** To establish whether or not the above-described reduction phenomenon effectively takes place in real situations, \(\mu\)-XANES and \(\mu\)-XRF spectrometry were employed to study two
embedded paint cross-sections taken from paintings by Vincent van Gogh from the collection of the Van Gogh Museum (VGM), Amsterdam. In these paintings, alteration of the chrome yellow paint was apparent. As described in more detail in the Part 2 of this study, this is effectively the case.56 Consistent with the observations made on the model samples, the Cr-reduction appears to take place only in areas that are rich in sulfates. On the basis of this information, it was possible to formulate a hypothesis regarding the alternation mechanism taking place.

At this instance, however, considering the above-described results and those of Casadio et al.,35 in which SO2 was shown to be one of the agents promoting the alteration process of zinc potassium chromate pigments, we limit ourselves to concluding that sulfur species (i.e., sulfates or perhaps more reduced forms of S) appear to play a key role in the mechanism of chrome yellow degradation.

**CONCLUSIONS**

The darkening of chrome yellow is a complex alteration problem that affects specific paintings from the end of 19th Century. In the first part of the present work, a combination of synchrotron radiation-based X-ray techniques, such as μ-XRF, μ-XANES, and EELS, and more conventional spectroscopic methods was employed to investigate artificially aged model samples. This allowed us to elucidate part of the degradation mechanism of chrome yellow.

Our observations indicate that the alteration of yellow PbCrO4 is caused by reduction of the original Cr(VI) to Cr(III). Sulfates appear to play an essential role in promoting this reduction process. Only in model samples rich in lead sulfate and in which the lead chromate is present in a very fine-grained/amorphous form was the formation of a superficial brown colored layer (of 1–3 μm thickness) observed after an artificial aging process involving UV irradiation. The presence of SO2 was not required to promote the alteration.

By means of both μ-XANES and EELS, the alteration layer was shown to contain significant amounts (up to 60%) of Cr(III). Investigations at the nanoscopic level revealed that Cr2O3·2H2O has formed at the surface of the original yellow paint. This phase is formed as an external coating on submicroscopic anglesite grains present in the paint. Using a combination of PbCrO4, Cr2O3·2H2O, and either Cr2(SO4)3·H2O or (CH3COO)2Cr3-(OH)2, the Cr K-edge XANES spectra recorded from the altered model samples can be satisfactorily described, indicating that in the altered layer, Cr is roughly equally distributed over the three above-mentioned Cr-species. No indications of the presence of Cr(VI) dichromate ions were observed. The brown color of the alteration layer is attributed to either the oxidation of the binding medium, the presence of polynuclear Cr(III)-species, or a combination of both. To demonstrate that the chrome yellow alteration phenomena observed in the aged model samples also takes place in real paintings, the second part of this work focuses on the study of microsamples from paintings by Vincent van Gogh.

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