doi:10.1017/S1431927613009112
Microsc. Microanal. 19 (Suppl 2), 2013

Degradation Process of Lead Chromate Yellows in Paintings by Vincent van Gogh

Letizia Monico[1,2], Koen Janssens[2], Costanza Miliani[1], Frederik Vanmeert[2], Brunetto G. Brunetti[1,3], Marine Cotte[4], Ella Hendriks[5], Muriel Geldof[6]

[1] CNR-ISTM, c/o Department of Chemistry, University of Perugia, 06123 Perugia, Italy
[2] University of Antwerp, Department of Chemistry, B-2020 Antwerp, Belgium
[3] Centre SMAArt and Department of Chemistry, University of Perugia, 06123 Perugia, Italy
[4] European Synchrotron Radiation Facility (ESRF), F-38000 Grenoble, France
[5] Van Gogh Museum, Paulus Potterstraat 7, 1070 AJ Amsterdam, The Netherlands
[6] The Netherlands Cultural Heritage Agency (RCE), 1071 ZC Amsterdam, The Netherlands

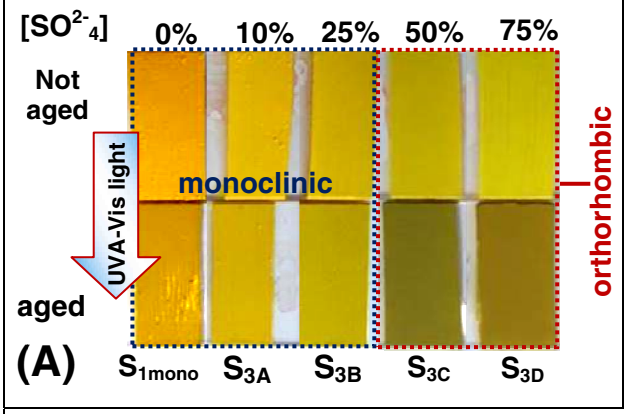
Chrome yellows represent a class of pigments commonly employed by painters of the late 19th-early 20th century, such as Vincent van Gogh [1]. These materials are characterized by a different chemical composition [$PbCrO_4$, $PbCr_{1-x}S_xO_4$, $0.1 \leq x \leq 0.75$] and crystalline structure (monoclinic and/or orthorhombic). Their shades range from the yellow-orange to the paler yellow hues with increasing sulfate amount. The understanding of the photochemistry of the lead chromate-based compounds is relevant, since in several paintings by Van Gogh and his contemporaries, the areas containing today chrome yellow appear darkened as consequence of an alteration of the original pigment.

Synchrotron radiation-based microscopic X-ray fluorescence analysis (SR μ-XRF), X-ray absorption near edge structure spectroscopy (μ-XANES) and Electron Energy Loss Spectrometry (EELS) investigations were performed on a series of accelerated photochemical aged oil paint models made up of different chrome yellow varieties [2]. Two paint micro-samples taken from darkened-yellow areas of two paintings by Van Gogh were also examined [3]. This allowed us to infer that the presence of Cr(III) species at the exposed altered layer is ascribable to a photo-reduction of the original Cr(VI). We also found that the darkening behavior of this class of compounds is critically influenced by their chemical composition and crystalline structure [4]. A profound discoloration was observed only for the aged paint models composed of a sulfate-rich orthorhombic $PbCr_{1-x}S_xO_4$ co-precipitate ($x \geq 0.5$) (Figure 1A). Cr K-edge μ-XANES analysis demonstrated the formation of up to ca. 60% of Cr(III)-species in the outer layer of the most altered samples (Figure 1B) [2,4]. To investigate how the speed of degradation of chrome yellow might be influenced by the nature of the organic binder in the paint, additional model samples prepared by mixing the unstable chrome yellow form and different binders (e.g., animal glue, acrylic, dammar resin and arabic gum) were studied before and after photochemical aging. Regardless of the nature of the organic binder, a profound darkening was observed; XANES analysis demonstrated that the relative Cr(III) amount ranges from ca. 40-50% in case glue, acrylic or dammar resin to about 70% in case of the arabic gum (Figure 2).

By employing SR-based microscopic X-ray diffraction (μ-XRD), Fourier-transform Infrared (FTIR) and Raman spectroscopy (using both benchtop and portable instrumentation) we were able to identify different chrome yellow varieties and demonstrate that Van Gogh employed the unstable form of chrome yellow in several of his well-known paintings [5], such as *Sunflowers*, *Portrait of Gauguin* (both in the Van Gogh Museum, Amsterdam) and *Falling leaves/Les Alyscamps* (Kröller-Müller Museum, Otterlo). Recent μ-XANES and μ-XRF investigations on a larger number of embedded paint micro-samples coming from several paintings by Van Gogh indicated that our hypothesis concerning the correlation between the properties of chrome yellows (chemical composition and crystalline structure) and the state of conservation of the pigment is a reasonable one. Cr(III)-based alteration products were especially found on samples containing $PbCr_{1-x}S_xO_4$ chrome yellow, located at the surface of the yellow paint and/or inside the S-rich areas of superficial varnish layer. (See Figure 3, for an example).

REFERENCES

[1] Hendriks, E. Van Gogh's Working Practice: A Technical Study. *In Vincent Van Gogh Paintings 2: Antwerp & Paris, 1885-1888,* Hendriks, E.; Van Tilborgh, L.; Waanders Publishers, **2011**, 90-143.
[2] Monico, L. et al., *Anal. Chem.* **2011**, *83*, 1214-1223.
[3] Monico, L. et al., *Anal. Chem,* **2011**, *83*, 1224-1231.
[4] Monico, L. et al., *Anal. Chem.,* **2013**, *85 (2)*, 860-867.
[5] Monico, L. et al., *Anal. Chem.,* **2013**, *85 (2)*, 851-859.



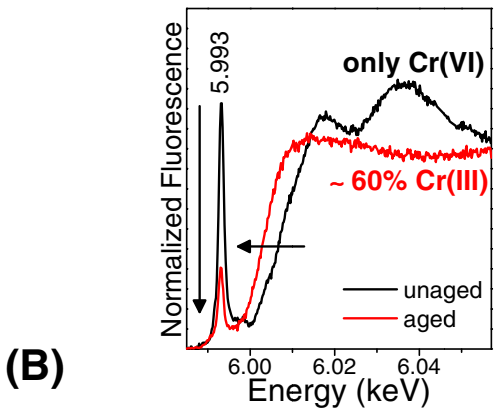


Figure 1. (A) Images recorded before and after 800 hours of UVA-visible light exposure for oil paint model samples made up of in-house synthesized lead chromate-based compounds containing different sulfate amount and crystalline structure. (B) Cr K-edge XANES spectra recorded from paint S_{3D} (orthorhombic $PbCr_{0.25}S_{0.75}O_4$) (black) before and (red) after aging. The reduction of the original Cr(VI) is demonstrated by the decrease of the pre-edge peak intensity at ca. 5.993 KeV and the shift of the edge absorption toward lower energies. The relative abundance of Cr(III) and Cr(VI) was estimated by means of a linear combination fitting procedure of the XANES spectra of a series of Cr(VI) and Cr(III) reference compounds.

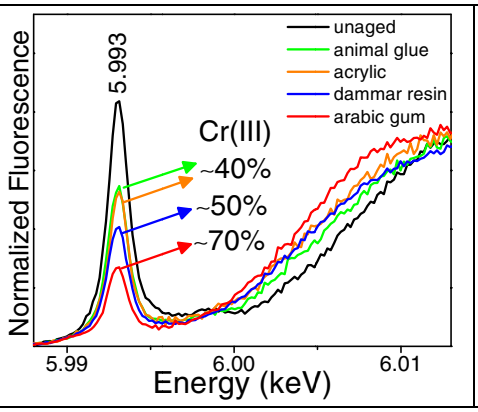


Figure 2. Cr K-edge XANES spectra recorded from the top layer of cross-sectioned photochemical aged model samples prepared by mixing the in-house synthesized powder S_{3D} (orthorhombic $PbCr_{0.25}S_{0.75}O_4$) and different organic binders. The quantitative estimation of the relative abundance of Cr(III) and Cr(VI) is also reported.

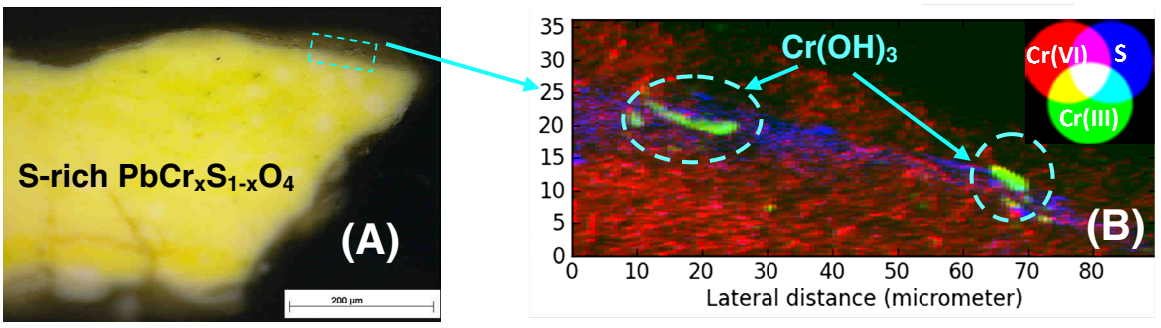


Figure 3. (A) Visible light microscopy image and (B) composite images of µ-XRF chemical state maps of Cr(VI), Cr(III) and S of sample F458-3b taken from the "Table area" of *Sunflowers* (Van Gogh Museum, Amsterdam). [Map size: 89.6×36.2 µm^2; pixel size: 0.7×0.2µm^2; dwell time: 300 ms]. In (B) cyan arrows and rounded shapes illustrate the areas where Cr-K edge XANES spectra (not reported) were acquired. The Cr(III)-rich particles located at the surface show XANES spectral features similar to that of the Cr(III)-hydroxide reference compound. In the surrounding areas a mixture of Cr(III) and Cr(VI)-species was found.

https://doi.org/10.1017/S1431927613009112 Published online by Cambridge University Press