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ESRF	**Experiment title: XANES and XRD mapping of a series of paint samples obtained from Van Gogh paintings: understanding the factors that influence the darkening of chrome yellow.**	**Experiment number**: EC-1051
Beamline: ID21	**Date of experiment**: from: 05/12/2012 to: 11/12/2012	**Date of report**: 19/02/2013
Shifts: 18	**Local contact(s)**: Marine Cotte	*Received at ESRF:*

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1. INTRODUCTION The darkening of lead chromate-based compounds, commonly known as *chrome yellows*, is a problematic often encountered in several late 19th-early 20th century paintings, such as those by Vincent van Gogh.[1] Chrome yellows belong to a class of pigments that are characterized by 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). Previous SR µ-XANES and µ-XRF investigations at the Cr K-edge (experiments EC-504 and EC-799) were performed on photochemically aged model paints made up of different chrome yellow varieties [2,3] and paint microsamples from Van Gogh paintings.[4] This allowed us to demonstrate that the presence of Cr(III) species at the exposed altered layer is ascribable to a photo-reduction of the original Cr(VI) [2-4] and that the darkening behavior of lead chromate-based materials is critically influenced by their chemical composition and crystalline structure.[4] Among the paint models prepared by employing historical and in-house chrome yellows, only those composed of a sulfate-rich orthorhombic $PbCr_{1-x}S_xO_4$ featured a significant darkening after the aging, revealing the formation of up to 60% of Cr(III) at the exposed surface [4]. By employing SR µ-XRD, 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].

2. EXPERIMENTAL XANES spectra were acquired in XRF mode by scanning the primary energy around the Cr K-edge (5.96-6.09 keV) with energy step of 0.2 eV. Investigations under vacuum (10-6 mbar) were performed both in unfocused mode (collimated beam, 0.2 mm diameter) and by means of a focused X-ray beam [0.7 x 0.2 μm^2 diameter (hxv)]. Energy calibration was performed with respect to the first inflection point of the Cr metal foil, which was determined by its first derivative and set to 5.989 keV. During the µ-XRF mapping experiments, the fluorescence signals were generated by employing a monochromatic primary beam of fixed energy (around the Cr K-edge). 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 6.088 keV to obtain a Cr−Kα fluorescence intensity map that is proportional to the total Cr content at a given position (i.e., irrespective of its oxidation state). The program PyMca was used to fit the fluorescence spectra and separate the different elemental contributions [6].

3. RESULTS A summary of the embedded paint micro-samples and the corresponding SR µ-XANES and µ-XRF results collected during the experiment is reported in Table I. Among the 9 samples investigated, only for the sample coming from the painting *Grapes* (F603/3, S-poor monoclinic $PbCr_{1-x}S_xO_4$) and one fragment taken from the version of *Sunflowers* conserved at the National Gallery of London (F454/13, monoclinic

$PbCrO_4$) the presence of Cr(III)-species was not identified. For all the remaining samples, SR μ-XANES investigations allowed us to reveal a mixture of Cr(III) and Cr(VI) species at the exposed surface. The additional presence of Cr(III) hydroxide/oxide "islands" was identified in the outer yellow paint and/or inside the superficial varnish layer of the samples coming from *The bedroom* (F482/8), *Portrait of Gauguin* (X448_2) and two cross-sections (F458/3b and F458/4) taken from the "Table area" of the version of *Sunflowers* conserved at the Van Gogh Museum in Amsterdam.

Table I. List of the original embedded paint microsamples investigated and corresponding Cr-speciation results obtained *via* SR-based μ-XRF and μ-XANES.

Origin of paint sample	Sample's number/name	Chrome yellow type		Cr-speciation[§]			
		$PbCrO_4$	$PbCr_{1-x}S_xO_4$*	Cr(VI)	Cr(III)	Mixture Cr(VI)/Cr(III)	Location
Grapes, 1887 (VGM)	F603/3	-	monoclinic	Y	N	N	Cr(VI): entire yellow layer. No evidence of presence of Cr(III)-species
The bedroom, 1888 ((VGM)	F482/8	monoclinic	-	Y	Y	Y	Cr(VI): middle-bottom yellow layer. Cr(III)/mixture: yellow-greenish areas of the upper yellow layer covered by a varnish layer. Identification of Cr(III) hydroxide.
Portrait of Gauguin, 1888 (VGM)	X448_2	-	monoclinic and possible orthorhombic	Y	Y	Y	Cr(VI): yellow brush-strokes below the exposed surface. Cr(III): single grain at the exposed surface [Cr(III) hydroxide]. Mixture: exposed surface of the yellow paint
Sunflowers, 1889 (VGM)	F458/3	-	monoclinic and possible orthorhombic	Y	N	Y	Cr(VI): middle-bottom yellow layer. mixture exposed surface of the yellow paint
	F458/1	monoclinic	monoclinic	Y	N	Y	Cr(VI): middle-bottom yellow layer. mixture exposed surface of the yellow paint
	F458/4	-	monoclinic and possible orthorhombic	Y	Y	Y	Cr(VI): yellow paint inside Cr(III)/mixture: superficial varnish; between the upper yellow area and the varnish layer. Identification of Cr(III) oxide
	F458/3b	-	monoclinic and possible orthorhombic	Y	Y	Y	Cr(VI): yellow paint inside Cr(III)/mixture: superficial varnish; between the upper yellow area and the varnish layer. Identification of Cr(III) hydroxide
Sunflowers, 1888 (National Gallery of London)	F454/13	monoclinic	-	Y	N	N	Cr(VI): entire yellow layer. No evidence of presence of Cr(III)-species
	F454/15	-	monoclinic[#]	Y	N	Y	Cr(VI): yellow-orange paint inside. Identification of $BaCrO_4$ particles at the exposed surface. Mixture: exposed surface of the yellow paint.

*"monoclinic": $PbCr_{1-x}S_xO_4$ more simiar to those model samples having a monoclinic phase and an amount of SO_4^{2-} < 0.5; "monoclinic and possible orthorhombic": $PbCr_{1-x}S_xO_4$ more similar to those reference samples having an orthorhombic phase and an amount of SO_4^{2-} ~ 0.5. [§]"Y": yes; " N": no. [#]Mixture of chrome yellow and chrome orange [phoenicochroite − (1−x)$PbCrO_4$·xPbO].

In Figure 1, as an example, the SR-based results obtained from the embedded sample F458/4 and the cotton swab n.5 (both coming from the "Table area") are reported. Figure 1VL illustrates the cross-section of sample F458/4, while panel A show the corresponding SR μ-XRF map acquired around the Cr K-edge. Consistent with the results obtained by means of preliminary benchtop FTIR and Raman spectroscopy and SR μ-XRD the presence of a PbCr1-xSxO4 compound in the yellow layer is confirmed by the fact that Pb, Cr and S appear as main constituents of this region. The varnish layer appears to be somewhat depleted in Cr and richer in S (Figure 1A). Al, Ca, K and Si (maps not shown for these elements) are also observed and their presence can be associated to aluminum-silicate compounds. XANES measurements at the Cr K-edge were performed inside a number of selected areas, such as those indicated in Figure 1A (Area A and Area B). In Figure 1D, the XANES spectra were acquired from the locations illustrated in the images of panels B-C. In a location inside the varnish layer (Figure 1B, 01) Cr appears to be completely reduced to the Cr(III) state, the corresponding XANES spectra resembling that of Cr2O3. In another region of the varnish layer, the original lead chromate-based compound is partially reduced (Figure 1B, 02), as demonstrated by the decrease of the a Cr pre-edge peak intensity at ca. 5.993 keV and a shift of the absorption edge toward lower energies. Similar spectral feature were obtained for the data collected at the interface between the yellow paint and the superficial varnish layer (Figure 1C, 03). In the underneath bright yellow paint (Figure 1C, 04), XANES spectra similar to that of $PbCrO_4$ are obtained, suggesting the presence of unaltered chrome yellow pigment. The Cr chemical state maps of Figures 1B and 1C show a good agreement with the data obtained from the XANES investigations of Figure 1D. Consistent with the results obtained from the embedded sample, the XANES spectra acquired from the cotton swab n.5 (Figure 1D, blue line) demonstrated the partial reduction of the original Cr(VI) ($[Cr(III)]/[Cr_{total}]$~40%).

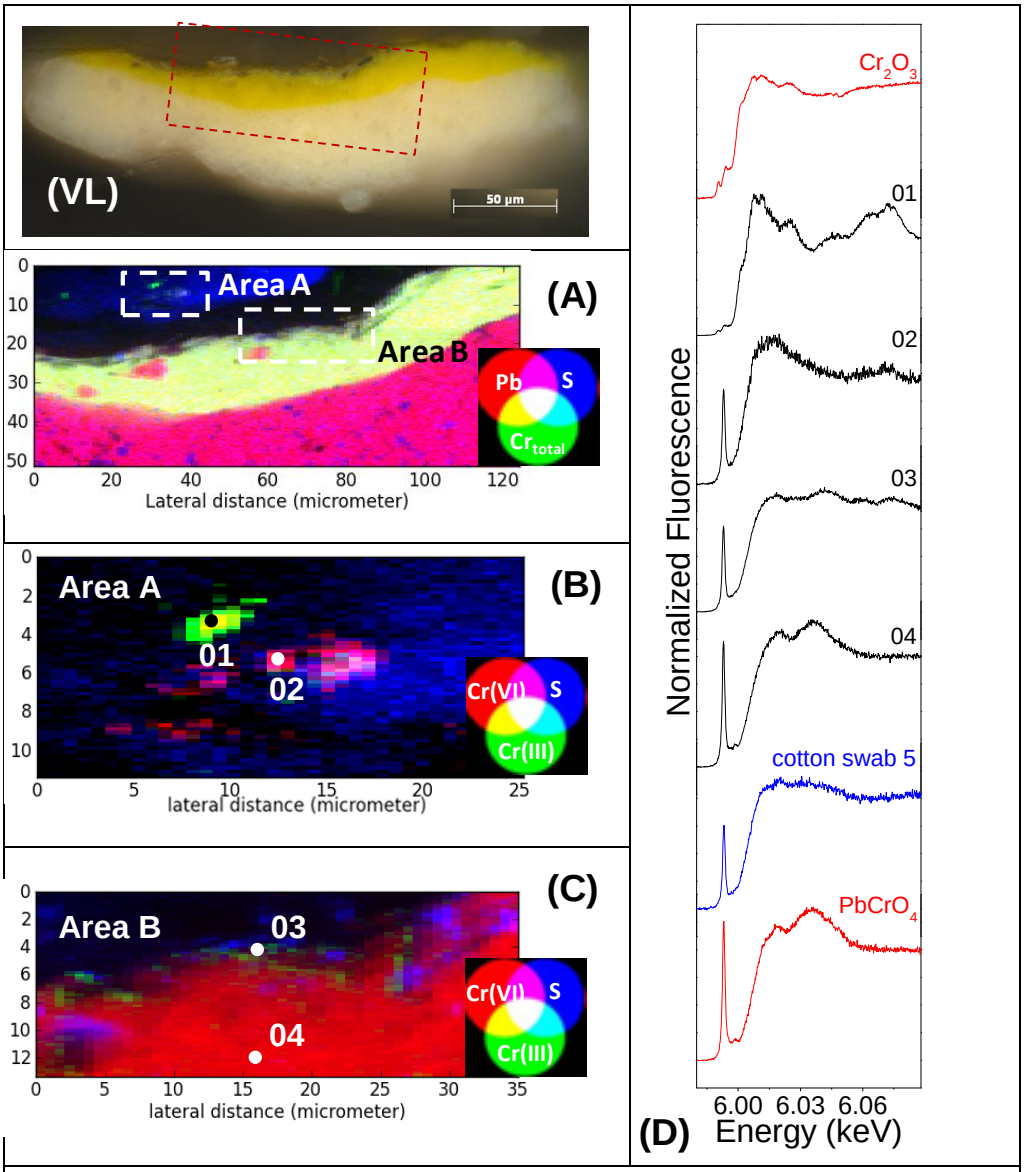

Figure 1.(VL) Visible light microscopy image and (A) RGB composite images of Pb, Cr and S of sample F458/4 taken from the "Table area" of *Sunflowers* (Van Gogh Musuem, Amsterdam).[Map size: 124 × 51.25 µm^2; pixel size: 1 × 0.25µm^2; dwell time: 100 ms]. (B-C) Composite images of chemical state maps of Cr(VI) and Cr(III) obtained by µ-XRF. In blue color, elemental distribution of S. [Map size $_{\text{Area A}}$: 25.5 × 11.2 µm^2; Map size $_{\text{Area B}}$: 35 × 13.2 µm^2; pixel size: 0.7 × 0.2µm^2; dwell time: 100 ms]. In (VL), the red rectangle shows the location of map of panel A; in (A), white rectangles illustrate the map positions of panels B-C. (D) Cr K-edge XANES spectra. Analysis positions are indicated in panels B-C. In (D) the blue line show the spectrum collected from the cotton swab n.5 employed to remove the superficial varnish layer in the area indicated in Figure 2D.

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