

Supporting Information

Degradation Process of Lead Chromate in paintings by Vincent van Gogh studied by means of Spectromicroscopic methods. Part 5.

Effects of non-original surface coatings into the nature and distribution of chromium and sulfur species in chrome yellow paints.

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1. EXPERIMENTAL SECTION

1.1. Sampling areas of resin-embedded original paint micro-samples

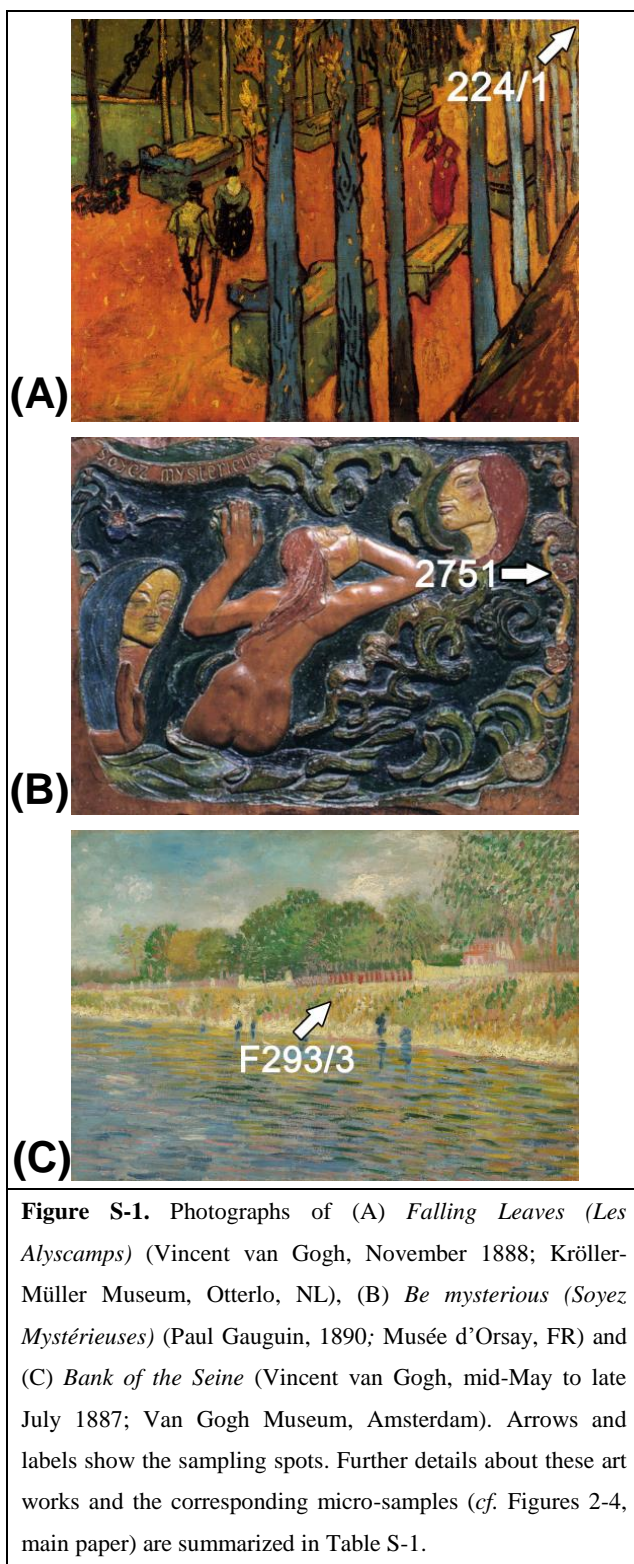


Table S-1. Details and characteristics of the original artworks and corresponding resin-embedded paint micro-samples investigated .

Painting name; corresponding sample number	Museum and inventory number	Creation date, technique and measurements	Notes on past treatments^(a)	Chrome yellow composition¹
<i>Falling Leaves (Les Alyscamps);</i> sample 224/1 (Vincent van Gogh)	Kröller-Müller Museum (Otterlo, NL) Inv. n. KM 108.668	November 1888; oil on canvas; 72.8 x 91.9 cm ²	The painting was lined, probably twice, certainly prior to 1919. The first lining was possibly a glue-paste lining; the most recent one was a wax-resin lining. Since the late 1980's cleaning tests have been performed to try to remove the oxidized and discolored varnish (application period unknown, possibly prior to 1919), which up till now have been unsuccessful.	monoclinic and possible orthorhombic PbCr _{1-x} S _x O ₄ (x~0.5)
<i>Be Mysterious (Soyez Mystérieuses);</i> sample 2751 (Paul Gauguin)	Musée d'Orsay (Paris, FR) Inv. n. RF 3405	1890; low relief, polychrome lime tree wood; 73 x 95 x 5 cm ³	The surface of the artwork is covered with a thin wax layer, that was applied before 1979	monoclinic and possible orthorhombic PbCr _{1-x} S _x O ₄ (x~0.5)
<i>Bank of the Seine;</i> sample F293/3 (Vincent van Gogh)	Van Gogh Museum (Amsterdam, NL) Inv. n. S 77 V/1962	mid-May to late July 1887; oil on linen; 32.0 x 46.0 cm ²	The painting was wax-resin lined and varnished by J. C. Traas sometime in the period 1927-1933. In 2005, the picture was cleaned and restored, ^(b) removing the deteriorated old varnish layer. No new surface coating was applied.	monoclinic PbCr _{1-x} S _x O ₄ (x~0.1)

^(a) Documentation from the conservation archives of the Kröller-Müller Museum, Van Gogh Museum, and Centre de Recherche et de Restauration des Musées de France.

^(b) Restoration performed by Ella Hendriks (head-conservator of the Van Gogh Museum).

1.2. Methods

1.2.1 Micro-Raman. Analysis of the original paint micro-samples was carried out by means of a JASCO NRS-3100 double-grating spectrophotometer equipped with a charge coupled device (CCD) detector (cooled to -47 °C) and an optical microscope (100× objective). Investigations were performed using a 785.0 nm (diode laser) excitation wavelength while keeping the laser power at the sample between 5-8 mW. A 600 lines/mm⁻¹ grating was employed. Spectra were recorded in the energy range of 1940-235 cm⁻¹; the exposure time varied between 5 and 10 s, with 10-20 accumulations. The spectral resolution was about 2 cm⁻¹.

1.2.2 Reflection mode micro-FTIR. Original paint micro-samples were investigated using a JASCO Infrared Multichannel Viewer (IMV)-4000 (Cassegrain 16× objective), interfaced with a FTIR 4100 spectrometer. Spectra were acquired from areas of *ca.* 12.5×12.5 μm², in the wavenumber range 6000-600 cm⁻¹, at a resolution of 4 cm⁻¹ and by employing 3000 scans.

1.2.3 Synchrotron μ-XANES and μ-XRF. Original paint micro-samples and varnished oil paint models were analyzed at the X-ray microscope beam line ID21 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France).²

In order to produce a highly monochromatic primary beam ($\Delta E/E = 10^{-4}$), during the Cr and S K-edges analyses, a Si(220) or Si(111) fixed-exit double-crystal monochromator was used, respectively. At the S and Cr K-edge energies, the beam size was reduced down to 0.5×0.2 μm² and 0.75×0.2 μm² (hor. × ver.), respectively by means of Fresnel zone plates. The XRF signals were collected in the horizontal plane, at 69° with respect to the incident beam direction by using an energy-dispersive silicon drift diode detector (Bruker). The software PyMca³ was employed to fit the XRF spectra in order to separate the different elemental contributions. A batch fitting procedure of the XRF profiles corresponding to each pixel of the 2D maps yielded elemental maps.

Fluorescence mode XANES spectra were acquired by scanning the primary energy around the Cr K-edge (5.96-6.09 keV) and the S K-edge (2.46-2.53 keV) with energy step sizes of 0.2 and 0.18 eV,

respectively. The position of the primary beam was maintained stable within 0.5 μm vertical and 0.3 μm horizontal. For all XANES spectra, the procedure of normalization was performed by means of the ATHENA package.⁴ The same software was also used to carry out a linear combination fitting of the XANES spectra collected from the samples against a library of XANES profiles of Cr and S reference compounds. These were chosen on the basis of the knowledge gained from XRF and vibrational spectroscopic investigations.

Cr and S K-edge chemical state map distributions were obtained by following the procedure reported in the literature.^{5,6}

2. RESULTS AND DISCUSSION

2.1. Cr and S K-edge XANES investigations of original paint micro-samples: quantitative estimation percentage of Cr and S species

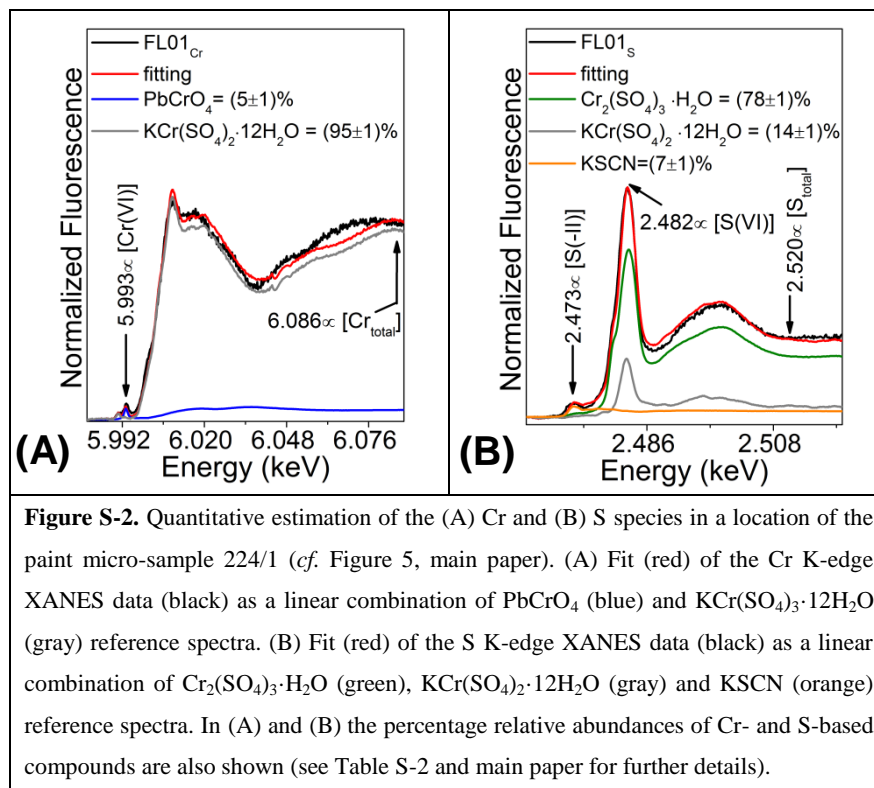


Table S-2. Quantitative estimation percentage of Cr and S species obtained by linear combination fitting of Cr and S K-edge XANES spectra collected from the original paint micro-samples.

Sample	Point analysis	Cr K-edge weight percentage fitting components (%)								S K-edge weight percentage fitting components (%)										
		PbCrO ₄ ^{**}	Cr ₂ (SO ₄) ₃ ·H ₂ O	KCr(SO ₄) ₂ ·12H ₂ O	(NH ₄) ₂ SO ₄ Cr ₂ (SO ₄) ₃ ·24H ₂ O	(CH ₃ CO ₂) ₇ Cr ₃ (OH) ₂	CrCl ₃ ·6H ₂ O	Cr(OH) ₃	Cr ₂ O ₃	[Cr(III)]/[Cr _{total}]	Cr ₂ (SO ₄) ₃ ·H ₂ O	KCr(SO ₄) ₂ ·12H ₂ O	Al ₂ (SO ₄) ₃ ·17H ₂ O	CaSO ₄ ·2H ₂ O	(NH ₄) ₂ SO ₄ Cr ₂ (SO ₄) ₃ ·24H ₂ O	(Na,K)Ca ₂ Al ₆ Si ₆ O ₂₄ (SO ₄) _{~1.5}	PbCr _{0.4} S _{0.6} O ₄ / PbSO ₄	KSCN	[S(VI)]/[S _{total}]	
224/1 (cf. Figure 5, main paper)	FL01 _{Cr/S}	5±1	-	95±1	-	-	-	-	-	95±1	78±1	14±1	-	-	-	-	-	7±1	92±1	
	FL02 _{Cr/S}	3±1	-	95±1	-	-	-	-	-	96±6	52±4	27±2	-	-	-	-	-	17±6	79±4	
		5±4	93±4	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
	FL03 _{Cr/S}	11±1	-	88±1	-	-	-	-	-	88±1	57±5	26±3	-	-	-	-	-	17±6	83±6	
	FL04 _{Cr/S}	15±3	-	85±3	-	-	-	-	-	85±4	58±2	24±2	-	-	-	-	-	14±1	82±3	
	FL05 _{Cr/S} ^(a)	27±1	-	74±1	-	-	-	-	-	72±1	-	-	35±1	-	-	-	-	35±1	35±1	
		31±1	71±1	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
	FL06 _{Cr/S}	69±1	-	-	-	-	-	-	31±1	-	30±1	-	-	-	-	-	-	-	-	
71±1		-	-	-	-	-	-	29±1	-	-		-	-	-	-	-	-	-		
FL07 _{Cr/S}	-	-	-	-	-	-	-	100	-	100	-	-	-	-	-	-	-	-		
Yellow _{Cr/S} ^(b)	100	-	-	-	-	-	-	-	-	0	-	-	-	-	-	-	90±1	-	90±1	
2751 (cf. Figure 6, main paper)	G01 _{Cr/S}	5±1	-	67±4	-	-	-	-	28±1	-	95±4	-	-	-	22±3	58±5	-	-	23±5	80±6
	G02 _{Cr/}	-	-	-	-	-	-	-	100	-	100	-	-	-	-	-	-	-	-	
	G03 _{Cr}	52±1	-	-	45±3	-	-	-	-	43±3	-	-	-	-	-	-	-	-	-	
		57±1	-	40±3	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
		52±1	45±3	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
	G04 _{Cr}	72±1	-	28±1	-	-	-	-	-	29±1	-	-	-	-	-	-	-	-	-	
		70±1	-	-	29±1	-	-	-	-		-	-	-	-	-	-	-	-	-	
		69±1	30±1	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
	G05 _S	-	-	-	-	-	-	-	-	-	-	-	-	32±1	-	26±3	-	38±1	58±3	
	G06 _S	-	-	-	-	-	-	-	-	-	-	-	-	45±5	-	25±5	-	24±2	70±7	
G07 _S	-	-	-	-	-	-	-	-	-	*										
F293/3 [§] (cf. Figure 6 of Part 2 ⁷ and Figure 4, main paper)	01	80±4	-	-	-	-	20±4	-	-	20±4	-	-	-	-	-	-	-	-	-	
	02 [†]	85±1	-	-	15±1	-	-	-	-	15±1	-	-	-	-	-	-	-	-	-	
	03	8±3	-	-	-	48±3	-	-	44±3	91±4	-	-	-	-	-	-	-	-	-	
		10±3	-	-	-	-	45±2	44±3	-		-	-	-	-	-	-	-	-	-	
		8±3	-	-	-	50±2	-	41±2	-		-	-	-	-	-	-	-	-	-	
	04	70±1	-	-	-	-	-	-	30±1	30±1	-	-	-	-	-	-	-	-	-	
		70±1	-	-	-	-	-	30±1	-		-	-	-	-	-	-	-	-	-	
	05	48±2	-	-	52±2	-	-	-	-	52±2	-	-	-	-	-	-	-	-	-	
	06	70±1	-	-	30±1	-	-	-	-	30±1	-	-	-	-	-	-	-	-	-	
		70±1	30±1	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-	
	07	12±2	-	-	-	88±2	-	-	-	88±2	-	-	-	-	-	-	-	-	-	
	BS01 _S ^(c)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	87±2	-	87±2	
	BS02 _S	-	-	-	-	-	-	-	-	-	-	-	41±2	30±2	-	-	-	23±1	71±3	
BS03 _S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	~100	-	100		
BS04 _S	-	-	-	-	-	-	-	-	-	-	-	-	-	41±2	-	-	36±2	28±1	77±3	

Best fitting results of the S K-edge XANES spectrum including as third component also: ^(a) Na₂S₄O₆·2H₂O=(26±3)%;^(b) Na₂SO₃=(10±1)%;^(c) Na₂SO₃=(12±2)%.

[†] Due to the similar spectral features of different PbCr_{1-x}S_xO₄ (0≤x≤0.8) reference compounds (cf. Figure 7C-E, main paper), similar fit results were obtained.

* no good description of the XANES spectrum by linear combination fit. However the profile resembles to that of BaSO₄ (cf. Figure 6D, main paper)

[§] Figure 6 of Part 2⁷ to see the Cr K-edge XANES spectra. For this sample Cr and S K-edge XANES profiles were not collected in the same locations.

[†] Comparable and good fitting results were obtained regardless of the Cr(III) reference compound used in the model.

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