Electronic supplementary information

Full spectral XANES imaging using the Maia detector array as a new tool for the study of the alteration process of chrome yellow pigments in paintings by Vincent van Gogh

Letizia Monico,[1,2,] Koen Janssens,[2] Matthias Alfeld,[3] Marine Cotte,[4,5] Frederik Vanmeert,[2] Chris G. Ryan,[6] Gerald Falkenberg,[3] Daryl L. Howard,[7] Brunetto Giovanni Brunetti,[1] Costanza Miliani.[1]*

[1] Institute of Molecular Science and Technologies (ISTM), National Research Council (CNR) and Centre SMAArt, c/o Department of Chemistry, Biology and Biotechnologies, University of Perugia, via Elce di Sotto 8, 06123 Perugia, Italy.

[2] University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, 2020 Antwerp, Belgium.

[3] Deutsches Elektronen-Synchrotron, Notkestrasße 85, 22603 Hamburg, Germany.

[4] European Synchrotron Radiation Facility, Avenue des Martyrs 71, 38000 Grenoble, France.

[5] Laboratoire d'Archéologie Moléculaire et Structurale, CNRS-UPMC, UMR 8220, place Jussieu 4, 75005 Paris, France.

[6] Commonwealth Scientific and Industrial Research Organisation, Minerals Research Flagship, Normanby Road, Clayton, Victoria 3168, Australia.

[7] Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia.

* Correspondance: letizia.monico@uantwerpen.be

1. EXPERIMENTAL

1.1. *Sampling areas of original paint micro-samples*

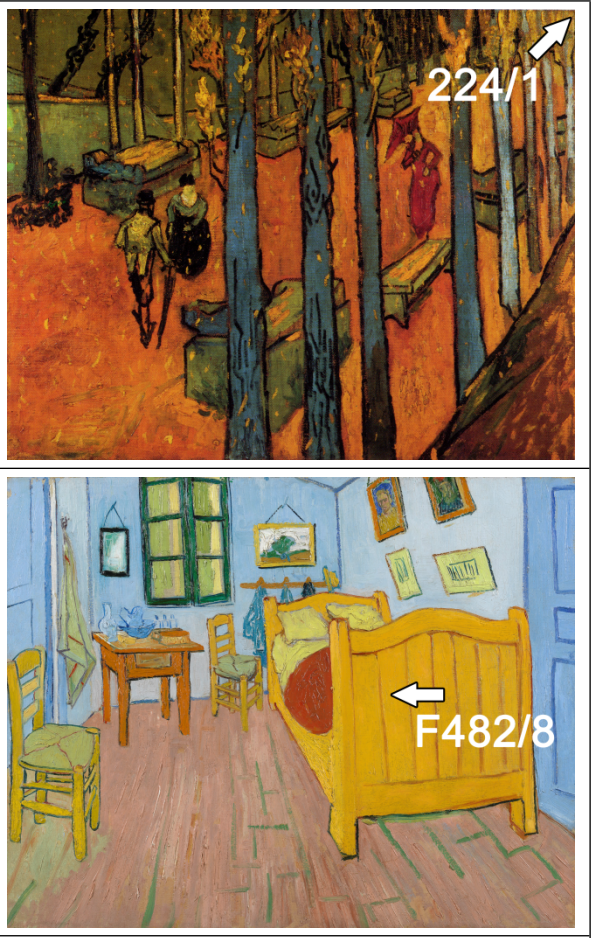

Figure S1. Photographs of (A) *Falling leaves (Les Alyscamps)* (Vincent van Gogh, November 1888; Kröller-Müller Museum, Otterlo, NL) and (B) *The Bedroom* (Vincent van Gogh, October 1888, Van Gogh Museum, Amsterdam, NL). Arrows and labels show the sampling spots (see Figures 1A-2A, main paper).

2. RESULTS AND DISCUSSION

2.1. *Cr K-edge XANES investigations of original paint micro-samples: least squares linear combination fitting results*

Table S1. Least squares linear combination fitting results of the XANES spectra obtained from sample 224/1 [from *Falling leaves (Les Alyscamps)*] (see Figures 3D-E and 4A, main paper).

XANES spectrum	Component weight (%)					Fit error		
	$PbCr_{0.5}S_{0.5}O_4$ [a]	$Cr_2(SO_4)_3 \cdot H_2O$	$KCr(SO_4)_2 \cdot 12H_2O$	$Cr(OH)_3$	[Cr(III)]/[Cr_{total}]	chi-square	R-factor	Reduced chi-square
$FL01_{A\text{-}XFM}$ [b]	3±2	97±1	-	-	97±1	0.044	0.0009	0.0005
$FL01_{A\text{-}ID21}$	5±1	-	95±1	-	95±1	0.560	0.002	0.0014
$FL02_{XFM}$ [b]	30±1	66±4	-	4±2	70±4	0.035	0.0006	0.0004
$FL02_{ID21}$	5±2	-	95±2	-	95±2	0.389	0.001	0.0010
$FL03_{A\text{-}XFM}$	12±1	-	-	88±1	88±1	0.040	0.0008	0.0004
$FL03_{A\text{-}ID21}$	5±1	-	-	95±1	95±1	0.040	0.0002	0.0001
$Yellow_{XFM}$	83±1	-	-	17±1	17±1	0.035	0.0005	0.0003
$Yellow_{ID21}$	~100	-	-	-	~0	(e)		
$FL01_{B\text{-}XFM}$-$FL01_{D\text{-}XFM}$ [c],*	10±1	90±1	-	-	90±1	0.043	0.0008	0.0005
$FL03_{B\text{-}XFM}$-$FL03_{C\text{-}XFM}$ [d],*	14±1	-	-	86±1	86±1	0.060	0.001	0.0006
$FL04_{XFM}$*	59±4	41±4	-	-	41±4	0.098	0.002	0.0011
$FL05_{XFM}$*	67±2	29±6	-	4±2	33±4	0.112	0.002	0.0011

Due to the similar spectral features, acceptable fit results were obtained also including in the fitting model:

[a] $PbCrO_4$ rather than $PbCr_{0.5}S_{0.5}O_4$; [b] $KCr(SO_4)_2 \cdot 12H_2O$ rather than $Cr_2(SO_4)_3 \cdot H_2O$.

XANES profile obtained from different Cr(III)-rich grains by averaging:

[c] ~20 pixels; [d] ~60 pixels.

[e] Fit not performed. The spectrum resembles to that of the $PbCr_{0.5}S_{0.5}O_4$ reference compound.

* equivalent spectrum not collected at the beamline ID21.

Table S2. Least squares linear combination fitting results of the XANES spectra obtained from sample F482/8 (from *The Bedroom*) (see Figures 6D-F and 7D-F, main paper).

XANES spectrum	Component weight (%)			Fit error		
	$PbCrO_4$	$Cr(OH)_3$	$[Cr(III)]/[Cr_{total}]$	chi-square	R-factor	Reduced chi-square
$B01_{ID21}$	0	100	100	(a)		
$B01_{XFM}$	6±1	94±1	94±1	0.063	0.001	0.0007
$B01_{P06}$	0	100	100	(a)		
$B02_{ID21}$	0	100	100	(a)		
$B02_{XFM}$	6±1	94±1	94±1	0.033	0.0006	0.0004
$B02_{P06}$	0	100	100	(a)		
$B03_{ID21}$	75±3	25±3	25±3	0.231	0.0006	0.0005
$B03_{XFM}$	80±1	20±1	20±1	0.036	0.0005	0.0004
$B03_{P06}$	77±1	23±1	23±1	0.046	0.0007	0.0005
$B04_{ID21}$	72±2	28±3	28±3	0.145	0.0004	0.0003
$B04_{XFM}$	71±2	29±1	29±1	0.066	0.001	0.0006
$B04_{P06}$	68±1	32±1	32±1	0.064	0.0009	0.0006
$B05_{ID21}$	66±3	34±3	34±3	0.512	0.002	0.0012
$B05_{XFM}$	74±1	26±1	26±1	0.081	0.001	0.0008
$B05_{P06}$	73±2	27±1	27±1	0.099	0.002	0.0010
$B06_{ID21}$	75±3	25±2	25±2	0.233	0.002	0.0009
$B06_{XFM}$	72±1	28±1	28±1	0.16	0.003	0.002
$B06_{P06}$	76±1	24±1	24±1	0.075	0.001	0.0007
$B07_{ID21}$	63±2	37±1	37±1	0.218	0.0006	0.0004
$B07_{XFM}$	67±1	33±1	33±1	0.052	0.001	0.0006
$B07_{P06}$	71±1	29±1	29±1	0.177	0.003	0.0018
$B08_{ID21}$	70±1	30±1	30±1	0.206	0.0006	0.0004
$B08_{XFM}$	70±1	30±1	30±1	0.073	0.001	0.0007
$B08_{P06}$	70±1	30±1	30±1	0.092	0.001	0.0009
$B09_{ID21}$	75±1	25±1	25±1	0.215	0.0007	0.0005
$B09_{XFM}$	73±2	27±2	27±2	0.121	0.002	0.0013
$B09_{P06}$	77±1	23±1	23±1	0.075	0.001	0.0008

[(a)] Fit not performed. The spectrum resembles to that of the $Cr(OH)_3$ reference compound.