Supporting Information

Application of synchrotron radiation-based micro-analysis on cadmium yellows in Pablo Picasso’s *Femme*

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**S1. Preliminary laboratory characterization**

Details of the preliminary laboratory characterization are largely reported in (Comelli et al., 2019), while details of the Raman micro-spectroscopy are new. The results are briefly summarized here.

The multi-analytical study showed that the Cd-based yellow paints of the two samples have a different chemical composition. Raman micro-spectroscopy identified the vibrant yellow as a mixture of lead white, cadmium sulfide (CdS) and barium sulfate (BaSO4). Small, isolated vermilion (HgS) particles dispersed in the yellow layer were also detected. The now-brownish yellow is instead composed of cadmium sulfide pigment (inferred based on the co-localization of Cd and S through SEM-EDX) and finely divided barium sulfate.

Different degradation compounds, residues and fillers were also detected in the two yellows by µFTIR measurements, including sulfate, oxalate, and carbonate species. These chemical species are more abundant in the now-brownish yellow. However, the chemical speciation of sulfates and carbonates is rather unclear due to the many different compounds present, thus requiring further investigations.

**Table S1.** Summary of the chemical composition and PL properties of the two microsamples based on previous analysis reported in (Comelli et al., 2019) and new Raman micro-spectroscopy analysis.

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| **Sample** | **Description** | **SEM-EDS** | **µFTIR** | **Raman micro-spectroscopy** | **PL emission peak and average lifetime of the emission at the microsecond timescale**  |
| Vibrant yellow | Preserved yellow | Cd, Ba, Pb, *S*, *Si*, *Al*, *Hg* | Sulfate species | CdSBaSO4HgSPb3(CO3)2(OH)2 | 870 nm, 1.3 µs |
| Now-brownish yellow | Degraded yellow | Cd, Ba, S, *Al*, *Cl* | Sulfate species, increased carbonates and oxalates contents and depletion of fatty acids | BaSO4 | 660 nm, 0.6 µs |

**Raman micro-spectroscopy**

Raman micro-spectroscopy was used to identify pigments in the removed paint cross-section (with examinations both prior and after mounting). The vibrational signatures in the resulting Raman spectra allow pigment identification through comparison to known or reported spectra (Burgio & Clark, 2001; Bell et al., 1997; Lee et al., 2008), and can be acquired from individual pigment grains since the Raman spectrometer is coupled to a microscope. Raman spectra were collected using a Renishaw inVia Raman microscope using 785 nm laser excitation (calibrated using the 520.5 cm-1 silicon Raman line); a 50X-L microscope objective (N.A. 0.50, 8 mm working distance) was used to direct laser light onto the sample and collect the resulting Raman signal. In all cases, laser power and collection times for each area were chosen to optimize the signal while avoiding sample degradation.

**S2. SR µPL measurements**

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**Figure S1.** Reconstructed PL emission spectra of the now-brownish (black trace) and vibrant (red trace) yellow paints. For a better comparison, the spectra are also shown normalized (panel (b)). The mean intensity of the selected region of interest (ROI) in the band-pass filters is plotted versus the filter central wavelength, with error bars reporting the ROI standard deviation. The intensity is corrected for the overall spectral detection efficiency.

**S3. S K-edge XANES spectra of reference compounds**

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**Figure S2.** S K-edge XANES spectra of sulfur reference compounds employed for the linear combination fit of the S K-edge XANES spectra recorded from the historical samples (see Table S2 for details).

**S4. Quantitative estimation percentage of S and Cd species**

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| **Table S2.** Quantitative estimation percentage of S species obtained by linear combination fitting of S K-edge XANES spectra collected from now-brownish yellow sample. Fit errors are also reported. |
| **Now-brownish yellow sample** | **Component weight (%)** | **Average S-species (%)** | **Fit error** |
| **Analysed area** | **S K-edge XANES spectrum** | **CdS** | **BaSO4** | **CdSO4/CdSO4·nH2O** | **PbSO4** | **Na2SO3** | **[S-II]/[ Stotal]** | **[SVI]/[ Stotal]** | **[SIV]/[ Stotal]** | **R-factor** | **Reduced chi-square** | **chi-square** |
| Area II(Figure 1c) | Bulk yellow paint | 47±1 | - | 12±1 | 35±2 | 6±2 | **47±1** | **47±2** | **6±2** | 0.0022 | 0.0031 | 0.995 |
| Average 4.8-8.0 µm | 27±1 | 22±2 | 11±1 | 35±2 | 5±2 | **27±1** | **68±2** | **5±2** | 0.0020 | 0.0030 | 0.998 |
| Average 8.4-10.0 µm | 37±1 | 21±2 | 13±1 | 23±2 | 6±1 | **37±1** | **57±3** | **6±1** | 0.0026 | 0.0038 | 1.27 |
| Average 10.4-12.00 µm | 23±1 | 45±2 | 13±1 | 14±1 | 5±1 | **23±1** | **72±2** | **5±1** | 0.0021 | 0.0034 | 1.10 |
| Average 12.4-14.0 µm | 31±2 | 27±2 | 22±1 | 14±1 | 6±2 | **31±2** | **63±2** | **6±2** | 0.0031 | 0.0048 | 1.62 |
| Average 14.4-16.0 µm | 42±2 | 15±1 | 28±2 | 7±2 | 8±1 | **42±2** | **50±3** | **8±1** | 0.0034 | 0.0057 | 1.86 |
| Surface | 26±1 | 49±2 | 9±2 | 10±1 | 6±2 | **26±1** | **68±2** | **6±2** | 0.0012 | 0.0016 | 0.531 |
| Area III (Figure S2c) | Bulk yellow paint | 46±1 | 13±2 | 13±1 | 20±2 | 8±1 | **46±1** | **46±3** | **8±1** | 0.0026 | 0.0038 | 1.07 |
| Average 3.3-4.5 µm | 37±1 | 27±2 | 7±1 | 19±2 | 10±1 | **37±1** | **53±3** | **10±1** | 0.0028 | 0.0037 | 1.09 |
| 4.8 µm depth | 47±1 | 19±2 | 8±1 | 17±2 | 9±1 | **47±1** | **44±3** | **9±1** | 0.0020 | 0.0026 | 0.769 |
| Average 5.1-10.5 µm | 69±1 | 2±1 | 12±1 | 10±1 | 7±1 | **69±1** | **24±2** | **7±1** | 0.0014 | 0.0018 | 0.578 |
| Average 10.9-14.9 µm | 50±1 | 26±2 | 16±2 | - | 8±1 | **50±1** | **42±3** | **8±1** | 0.0012 | 0.0018 | 0.512 |
| Average 15.3-16.8 µm | 63±1 | 10±1 | 12±1 | 8±1 | 7±1 | **63±1** | **30±2** | **7±1** | 0.0016 | 0.0022 | 0.614 |
| Average 17.2-20.0 µm | 70±1 | 10±1 | 8±1 | 7±2 | 5±1 | **70±1** | **25±2** | **5±1** | 0.0021 | 0.0028 | 0.782 |
| Average 20.4-20.8 µm | 52±1 | 16±2 | 11±1 | 13±2 | 8±1 | **52±1** | **40±3** | **8±1** | 0.0029 | 0.0036 | 1.21 |
| Surface | 43±1 | 28±2 | 12±1 | 8±2 | 9±1 | **43±1** | **49±3** | **9±1** | 0.0028 | 0.0040 | 1.12 |

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| **Table S3.** Quantitative estimation percentage of Cd species obtained by linear combination fitting of Cd L3-edge XANES spectra collected from now-brownish yellow sample. Fit errors are also shown. |
| **Now-brownish yellow sample** | **Component weight (%)** | **Fit error** |
| **Analysed area** | **Cd L3-edge XANES spectrum** | **CdS** | **CdCO3** | **CdCl2/CdCl2·nH2O/Cd(OH)Cl** | **CdC2O4** | **CdSO4/CdSO4·nH2O** | **R-factor** | **Reduced chi-square** | **chi-square** |
| Area II(Figure 1c) | Bulk yellow paint | 60±6 | - | 24±3 | 4±2 | 12±4 | 0.00045 | 0.00031 | 0.0780 |
| Average 2.5-9.50 µm | 43±4 | 11±2 | 18±2 | 13±1 | 6±3 | 0.00024 | 0.00017 | 0.0407 |
| Surface | 51±5 | - | 17±2 | 32±2 | - | 0.00021 | 0.00015 | 0.0365 |
| Area III (Figure S2c) | Bulk yellow paint | 79±6 | 2±1 | 5±3 | 14±4 | - | 0.00069 | 0.00047 | 0.117 |
| Average 1.5-25.2 µm | 69±7 | - | 18±3 | 13±1 | - | 0.00020 | 0.00014 | 0.035 |
| Average 25.5-27.30 µm | 60±7 | - | 19±4 | 21±1 | - | 0.00021 | 0.00015 | 0.037 |
| Surface | 52±7 | - | 22±4 | 26±2 | - | 0.00025 | 0.04366 | 0.00018 |

**S5. Now-brownish yellow sample: additional SR µXRF and µXANES investigations**

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**Figure S3.** Now-brownish yellow sample. (a) Visible light microscopy image of the cross section. The black rectangle corresponds to the region where SR µXRF analysis of panels (b,c) was performed. RGB composite SR µXRF maps of (b) Ba/Pb and (c) Cd/Cl/S [step size (h × v), 0.25 × 0.25 µm2; exp. time, 50 ms/pixel; energy, 7.2 keV]. Series of µXANES spectra (black) recorded at (d) S K-edge, (e) Cd L3-edge and (f) Cl K-edge and LCF results (cyan) of different S-/Cd-based reference compounds (for details see Tables S2-S3). In blue, spectral profiles of selected references. In (d-f), spectra were recorded across the line shown in (c) with steps of 0.4-0.5 µm and averaged within the depth values reported in each panel.

**S6. Vibrant yellow sample: further SR µXRF mapping results**

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**Figure S4.** Vibrant yellow sample. (a) Visible light microscopy image of the cross section. Area marked in black corresponds to the SR µXRF map in panel (b). (b) RGB composite SR µXRF maps of Ba/Pb/S [step size (h × v), 0.5 × 0.25 µm2; exposure time, 50 ms/pixel; energy, 7.2 keV].

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