

SUPPORTING INFORMATION

A novel photoluminescence hyperspectral camera for the study of artworks

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1. Samples description

Name	Type	Origin	Analysis method		Measurement parameters	Measurement time
Zinc White	Pigment powder dispersion	Kremer Pigmente GmbH	Hyperspectral PL micro-imaging with double fluence excitation	LF excitation	Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 0.07$ s $t_{\text{tot}} = 14$ s
				HF excitation	Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 0.28$ s $t_{\text{tot}} = 56$ s
L3	Micro cross-section embedded in epoxy resin	Mikhail Larionov painting, private collection, Archivio Gallone	Hyperspectral PL micro-imaging with double fluence excitation	LF excitation	Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 0.075$ s $t_{\text{tot}} = 15$ s
				HF excitation	Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 0.325$ s $t_{\text{tot}} = 65$ s
ALB1_01	Micro cross-section embedded in epoxy resin	<i>Allegoria in memoria di Francesca De Maestri Colleoni</i> by Arturo Albertazzi (Oil on canvas, 1909, Istituto dei Ciechi di Milano)	Time-gated PL hyperspectral micro-imaging	Nanosecond timescale	Gate = 100 ns Delay = 0 ns Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 0.38$ s $t_{\text{tot}} = 76$ s
				Microsecond timescale	Gate = 10 μ s Delay = 0.2 μ s Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 1.2$ s $t_{\text{tot}} = 4$ min
Borrelli painting	Painting, oil on panel	Private collection	Time-gated PL hyperspectral remote imaging	Nanosecond timescale	Gate = 20 ns Delay = 0 ns Scan range = ± 30 fs Scan step = 0.6 fs # images: 100	$t_{\text{exp}} = 15$ s $t_{\text{tot}} = 25$ min
				Microsecond timescale	Gate = 100 μ s Delay = 0.5 μ s Scan range = ± 30 fs Scan step = 0.6 fs # images: 100	$t_{\text{exp}} = 7$ s $t_{\text{tot}} = 12$ min
Woman portrait	Painting, oil on canvas	Private collection	Time-gated PL hyperspectral remote imaging	Nanosecond timescale	Gate = 100 ns Delay = 0 ns Scan range = ± 60 fs Scan step = 0.3 fs # images: 400	$t_{\text{exp}} = 0.8$ s $t_{\text{tot}} = 3$ min
				Microsecond timescale	Gate = 10 μ s Delay = 0.2 μ s Scan range = ± 30 fs Scan step = 0.3 fs # images: 200	$t_{\text{exp}} = 20$ s $t_{\text{tot}} = 34$ min

Table S1 – List of samples used for hyperspectral measurements. For each measurement, we report the scanning range and step of the TWINS system and the corresponding number of acquired images. In addition, we provide the gate and delay with respect to pulsed excitation used for the time-gated camera. The exposure time of the camera (t_{exp}) and the total measurements time (t_{tot}) are also shown.

2. Elemental and molecular analyses

2.1 Micro cross-section from *Allegoria in memoria di Francesca De Maestri Colleoni*

SEM-EDS system (ZEISS EVO 50EP), employed at 20 kV acceleration voltage and at chamber pressure of 60 Pa, allowed us to record images of the sample and the elemental composition of the paint layers. The sample was coated with a thin layer of carbon using an evaporative coater.

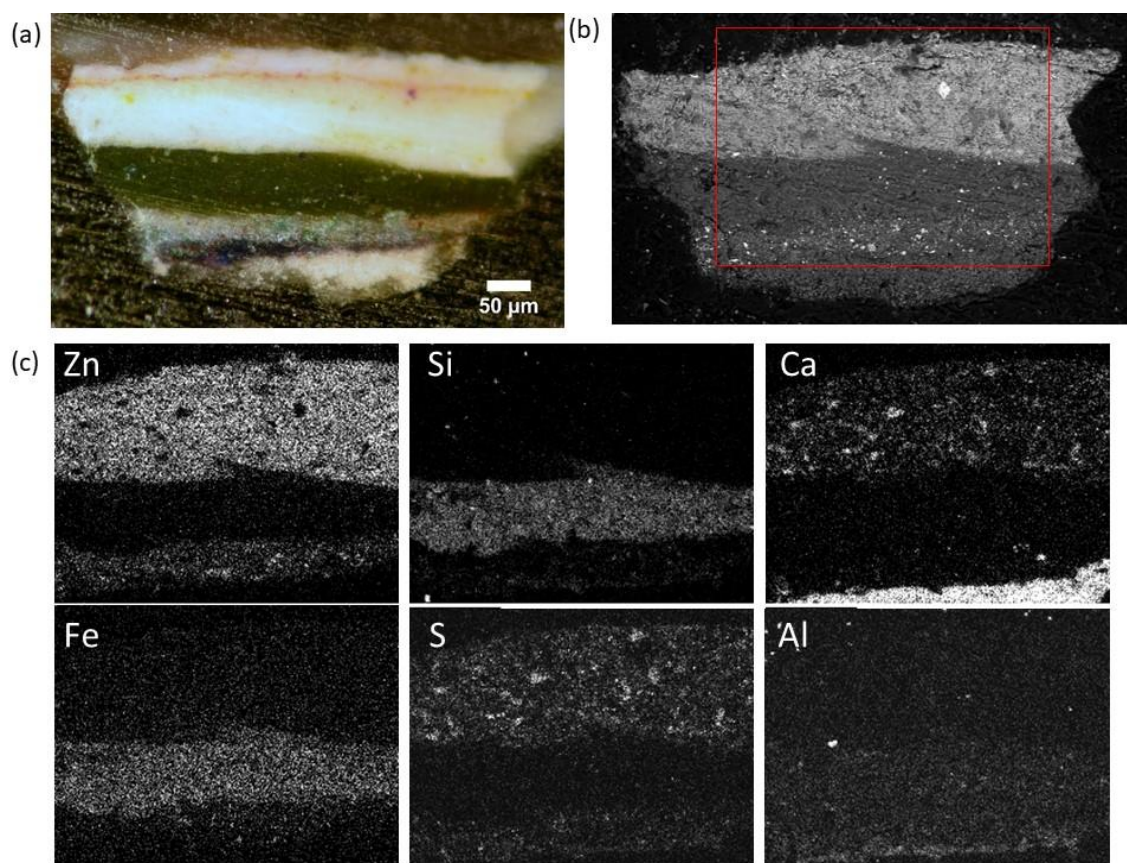


Figure S1 – (a) Visible image of the stratigraphic micro cross-section from the painting *Allegoria in memoria di Francesca De Maestri Colleoni* by Arturo Albertazzi. (b) Back-scattered image of the cross-section. (c) Maps of the elemental distribution in the paint cross-section, obtained in the area highlighted with red rectangle in panel (b).

The Raman spectroscopy device [S. Mosca *et al.*, Microchem. J. 124, 775–784 (2016)] is based on a 785 nm laser source. For the present study, measurements were performed between 180-1200 cm^{-1} , with a spectral resolution close to 10 cm^{-1} . The measurement head consists of a micro-probe for the analysis of a selected area of 50 μm diameter on the sample surface and allows estimating the main chemical composition of pigment samples based on comparison with reference Raman data from online databases and related literature.

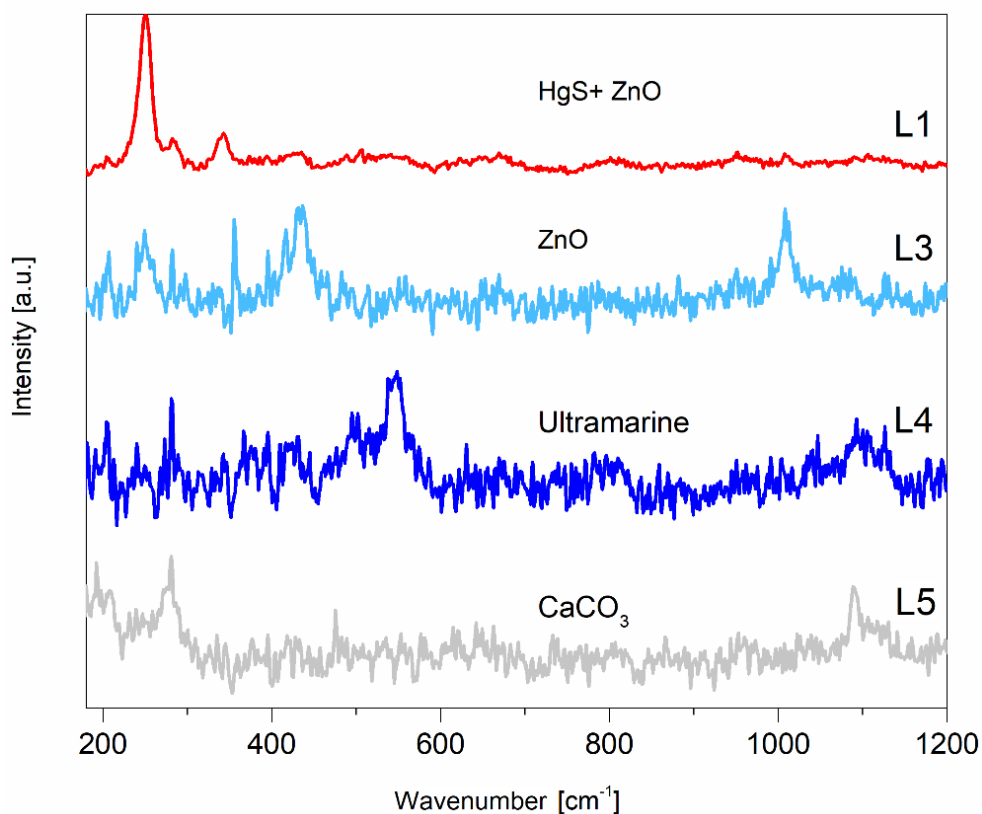


Figure S2 - Raman spectra of the different paint layers present in the micro-sample *Allegoria in memoria di Francesca De Maestri Colleoni* by Arturo Albertazzi.

2.2 Woman portrait

XRF measurements were performed in point-like mode and in raster scanning mapping mode with a portable XRF spectrometer (ELIO, XGLab srl - Bruker Nano Analytics). The instrument detects elements from Na to U with a resolution of 130 eV at Mn K α . Single point measurements were performed employing the following experimental conditions: tube voltage = 50 kV, tube anode current = 80 μ A, acquisition time = 120 s. XRF maps have been performed over several parts of the painting with the following instrument settings: acquisition time per point = 1 s, tube voltage = 50 kV, tube anode current = 80 μ A, pixel size = 1x1 mm² and distance from the sample = 1.4 cm.

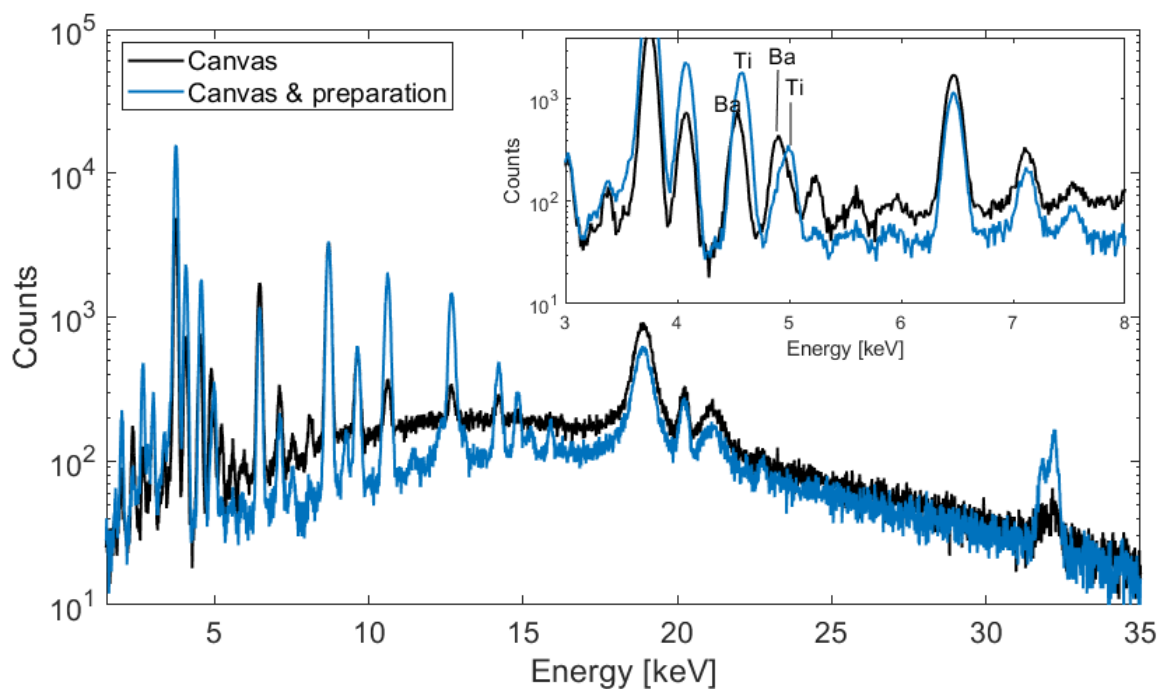


Figure S3 - Point-like measurements performed on the border of the painting, in an area with only the canvas and in an area with the canvas and the preparation. On the basis of the result found, it is possible to assume that the canvas is an industrially prepared one with probably lithopone (presence of Zn and Ba) and calcium based compound. The preparation layer is instead composed of lead white based pigment and titanium white. It is particularly difficult to distinguish the Ba-L and Ti-K lines (4.5 keV region) due to their superimposition, but from the Ba-Ka lines it is possible to clearly identify the presence of Ba-K lines (32 keV region) more intense in the canvas and preparation layer.