

**Analytical and Bioanalytical Chemistry**

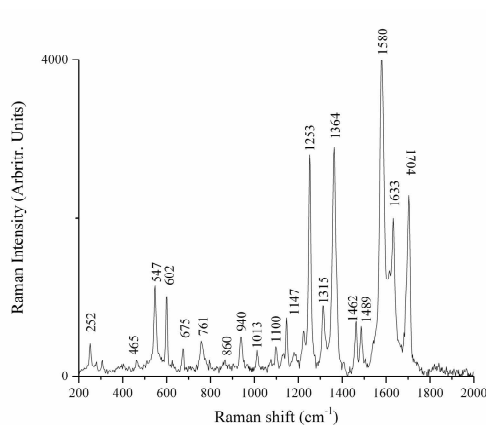
**Electronic Supplementary Material**

**Tailored micro-extraction method for Raman/SERS detection of indigoids in ancient textiles**

Elena Platania, Cristiana Lofrumento, Elisabetta Lottini, Elena Azzaro, Marilena Ricci, Maurizio Becucci

## 1. Raman spectrum of indigo

The spectrum of reference indigo's powder is reported below in order to better visualize the relative intensity of its fundamental bands, whose corresponding wavenumbers are showed in the Table 1 of the main text.



**Fig. S1** Raman spectrum obtained on the powder of reference indigo ( $\lambda_{\text{exc}} = 514.5 \text{ nm}$ )

## 2. Control of the *leuco*-methodology on the textile

Additionally there are reported the results referred to colorimetric (Table S1) and XRF analyses (Fig. S2), carried out on the reference dyed textiles after the application of the dye extraction procedure, in order to demonstrate the minimal invasiveness of the used methodology.

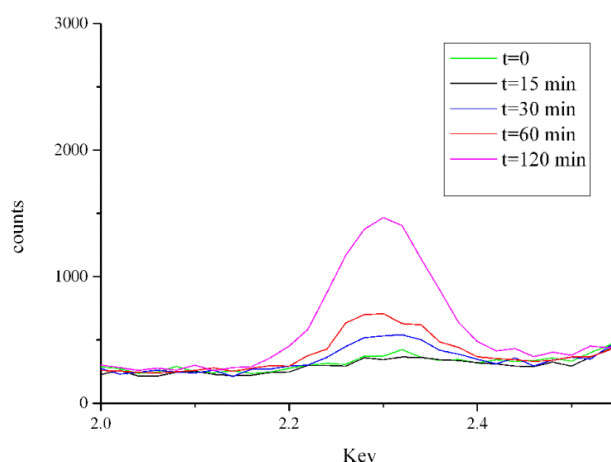
Colorimetric analyses were performed using CM-2600d Konica-Minolta portable spectrophotometer equipped with the integrative sphere inside the apparatus and a Xenon lamp to pulse the light on the sample surface. The measurement aperture is 3 mm and light is reflected by surface with an angle of 8°. Color coordinates are based on CIEL\*a\*b\* system using an illuminant D65 with an observer angle of 10°.

X-Ray fluorescence analyses were performed with a Bruker portable XRF spectrometer TRACeR III-SD provided by a rhodium X-ray tube and a SSD 10 mm<sup>2</sup> energy dispersion spectrometer (EDS) cooled by thermoelectric cooling. XRF spectra were acquired in 50s at a voltage of 40kV and 15  $\mu\text{A}$  current.

There are no evidences of color changes due to dye extraction, as demonstrated by colorimetric data, while a little of sulfur release occurs for times by far greater than the ones necessary for the extraction procedure (30 minutes).

Extraction with Ag-agar gel and <i>leuco</i> -reagents							
	L*	a*	b*	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$
Point 1 t = 0 min	34,47	-0,84	-23,03	0,8	-0,43	0,19	0,93
Point 1 t = 15 min	35,27	-1,27	-22,84				
Point 2 t = 0 min	36,34	-1,55	-22,14	-0,8	0,4	-0,62	1,18
Point 2 t = 30 min	35,54	-1,15	-22,76				
Point 3 t = 0 min	36,36	-1,59	-22,51	0	0,11	-0,42	0,43
Point 3 t = 60 min	36,36	-1,48	-22,93				
Point 4 t = 0 min	37,29	-1,77	-22,30	-0,16	-0,03	0,18	0,24
Point 4 t = 120 min	37,13	-1,80	-23,12				

**Table S1** Colorimetric CIEL\*a\*b\* coordinates on four different points of mock up before and after the extraction with Ag-agar gel and *leuco*-reagents at different extraction times

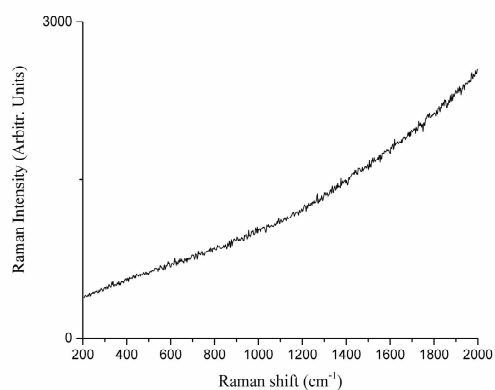


**Fig. S2** XRF spectra of mock up textile after the Ag-agar gel extraction with *leuco*-reagents at different extraction times (0, 15, 30, 60, 120 minutes) in the region of sulphur ( $K\alpha = 2.31$  Kev)

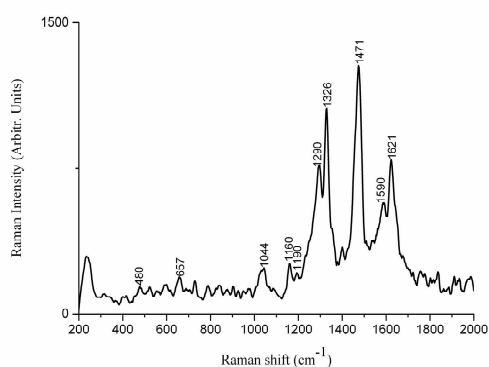
### 3. SERS test on the selectivity of extraction procedures

In order to confirm the specificity of the extraction procedure proposed for the vat dyes, we tried to use the same extraction protocol on reference textile dyed with alizarin. (Fig. S3). Also we report the alizarin and indigo's extraction on the cotton cloth mock-up, adopting as a solvent an aqueous solution with a chelant agent, 0.1% EDTA (ethylenediaminetetraacetic acid).(Fig.S4, Fig.S5).

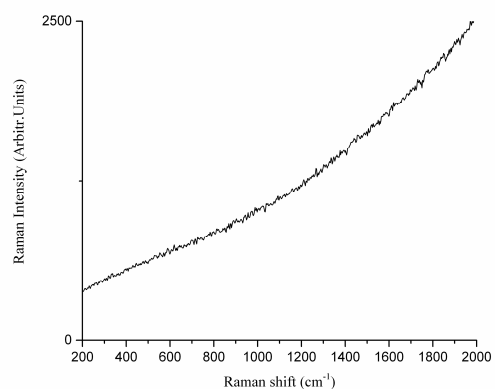
The Raman spectra registered on three dry Ag-agar gel cubes are reported below.



**Fig. S3** Raman/SERS spectrum collected on Ag-agar gel following *leuco*-extraction on the cotton cloth mock up dyed with alizarin ( $\lambda_{\text{exc}} = 514.5 \text{ nm}$ )



**Fig. S4** Raman/SERS spectrum collected on Ag-agar gel following extraction on the cotton cloth mock up dyed with alizarin, adopting as a solvent an aqueous solution of EDTA ( $\lambda_{\text{exc}} = 514.5 \text{ nm}$ )



**Fig. S5** Raman/SERS spectrum collected on Ag-agar gel following extraction on the cotton cloth mock up dyed with indigo, adopting as a solvent an aqueous solution of EDTA ( $\lambda_{\text{exc}} = 514.5 \text{ nm}$ )