SUPPLEMENTARY INFORMATION: ADDITIONAL FIGURES AND TABLES

A Multi-Analytical Study of the Palette of Impressionist and Post-Impressionist Puerto Rican Artists

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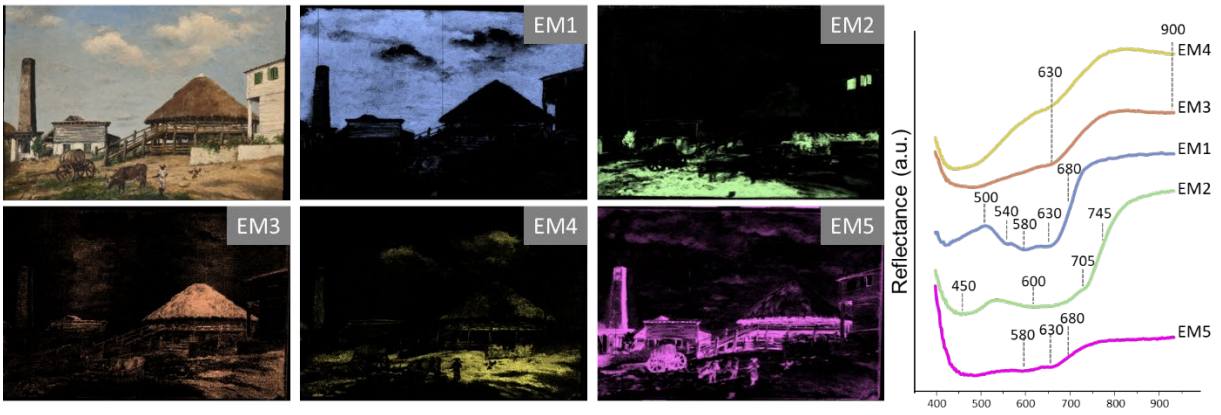
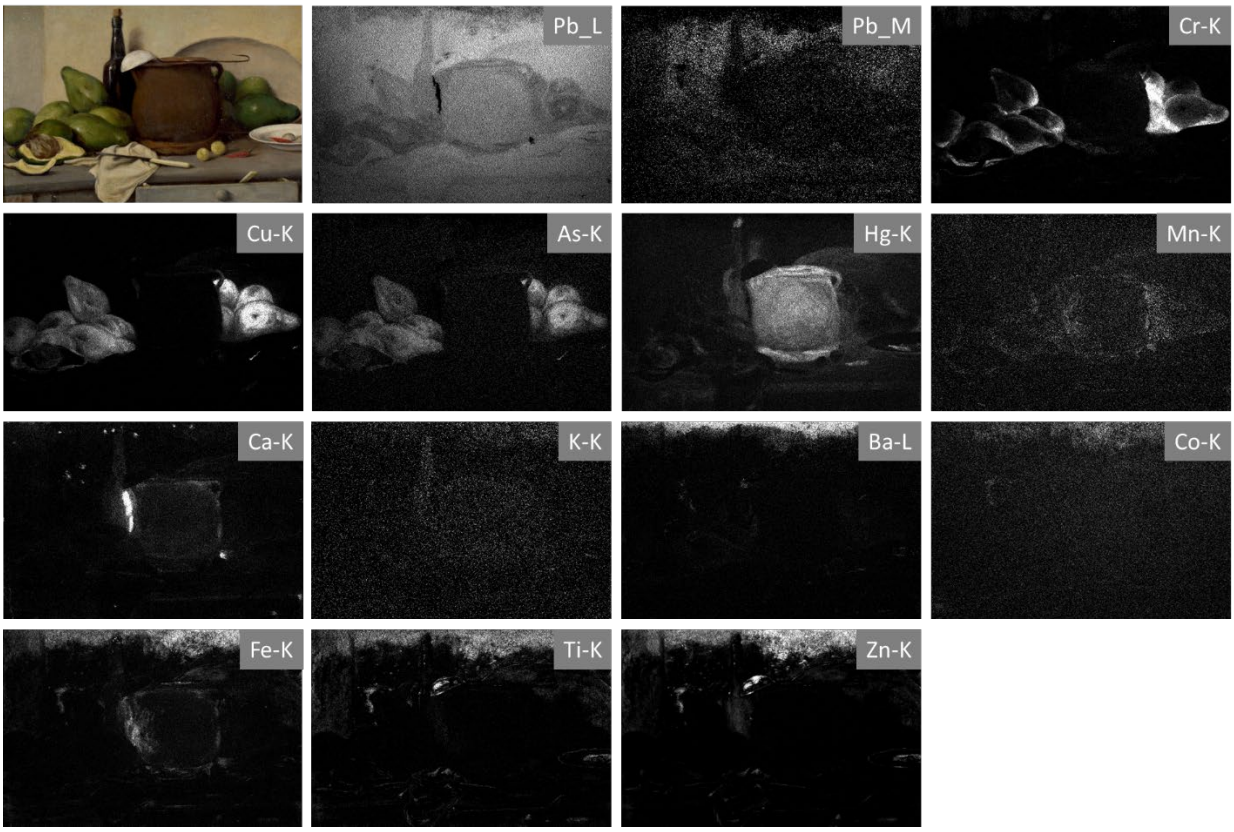
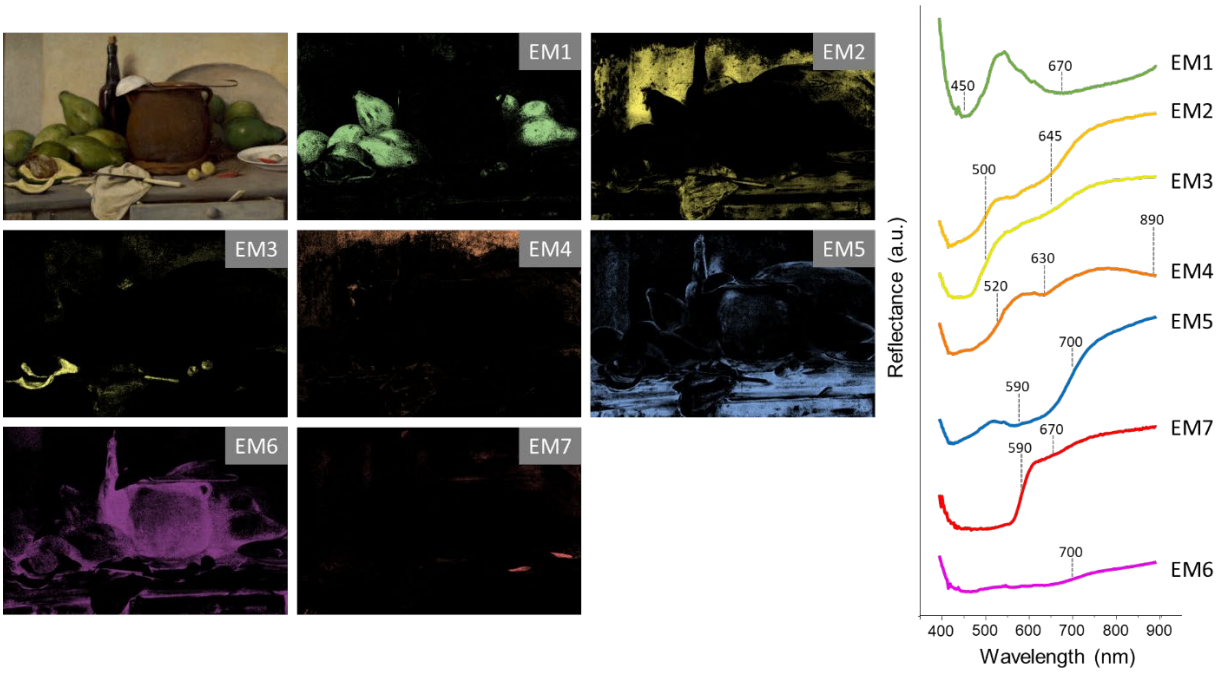
Table S1. *Per pixel acquisition time (s), step size (mm) and number of scans associated with all paintings analyzed.*

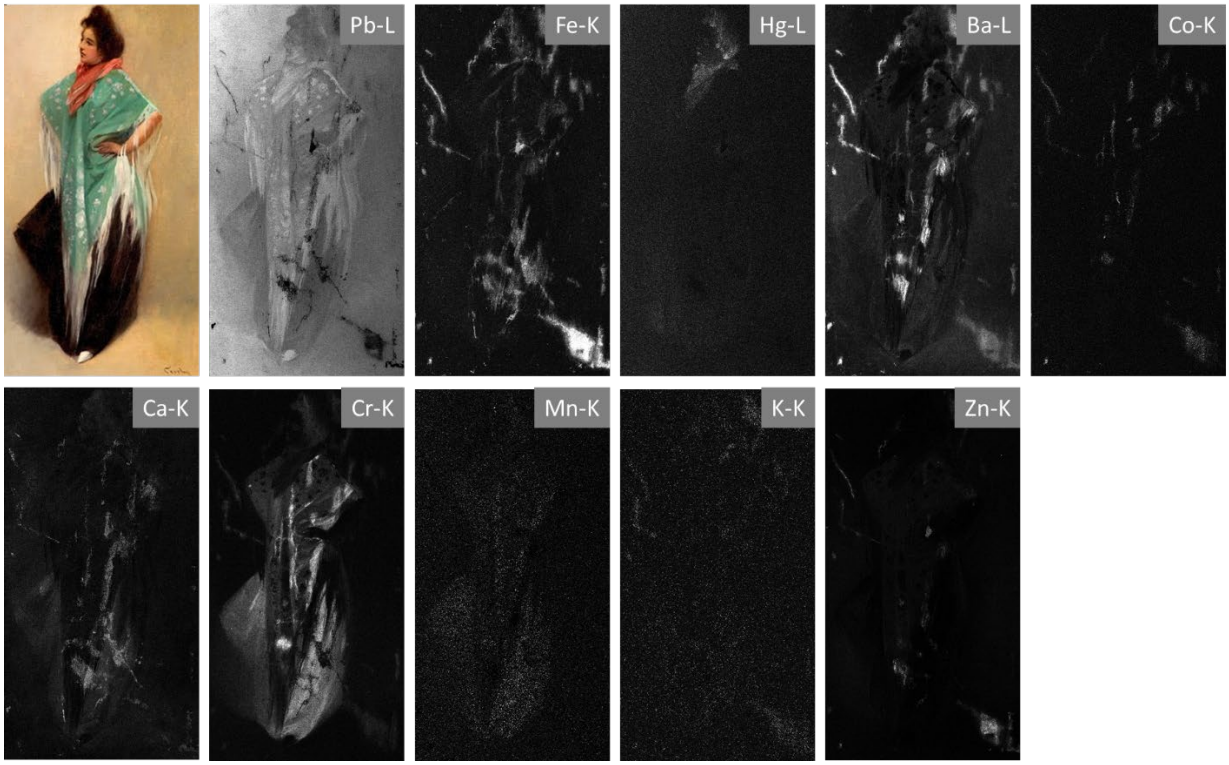
	MA-XRF			RIS		
Object number	per pixel acquisition times (s)	step size (mm)	Number of scans	Integration time (s)	Spatial resolution	Number of scans
Trapiche	0.100	0.7	2	1	0.5 x 0.5 mm^2	2
CAM-1328	0.100	1.5	1	1	0.3 x 0.3 mm^2	12
CAM-1329	0.200	2	1	1	0.3 x 0.3 mm^2	10
2004-005	1.200	0.23	1	1	0.5 x 0.5 mm^2	12
2004-007	0.100	0.5	2	1	0.3 x 0.3 mm^2	3
2003-05-02	0.200	0.8	1	1	0.3 x 0.3 mm^2	4

Non-invasive imaging techniques: MA-XRF and RIS

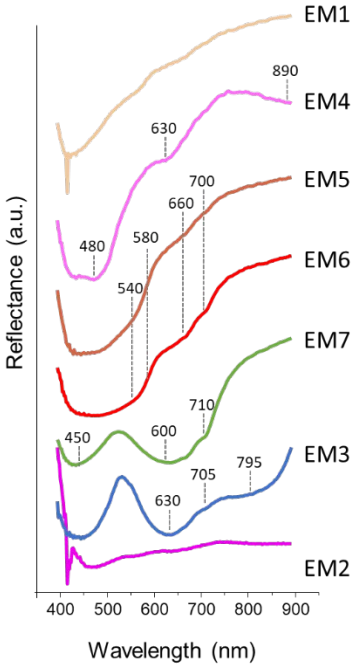


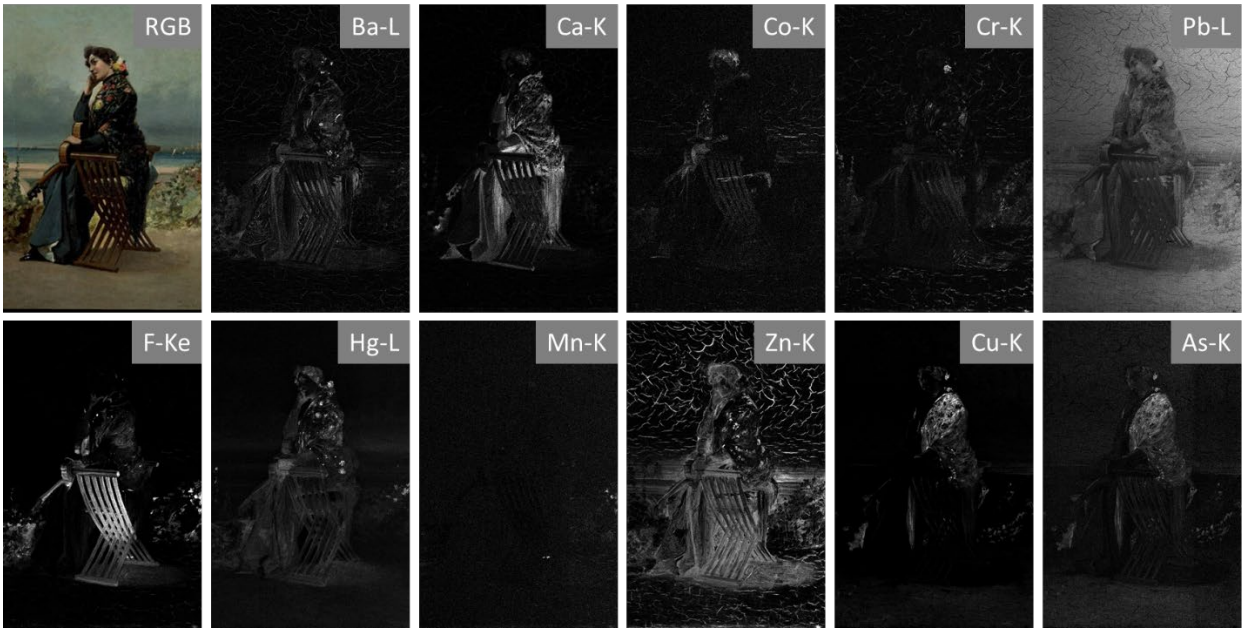

Pb_L
Pb_M
Cr-K
Cu-K
As-K
Hg-K
Mn-K
Ca-K
K-K
Ba-L
Co-K
Fe-K
Ti-K
Zn-K

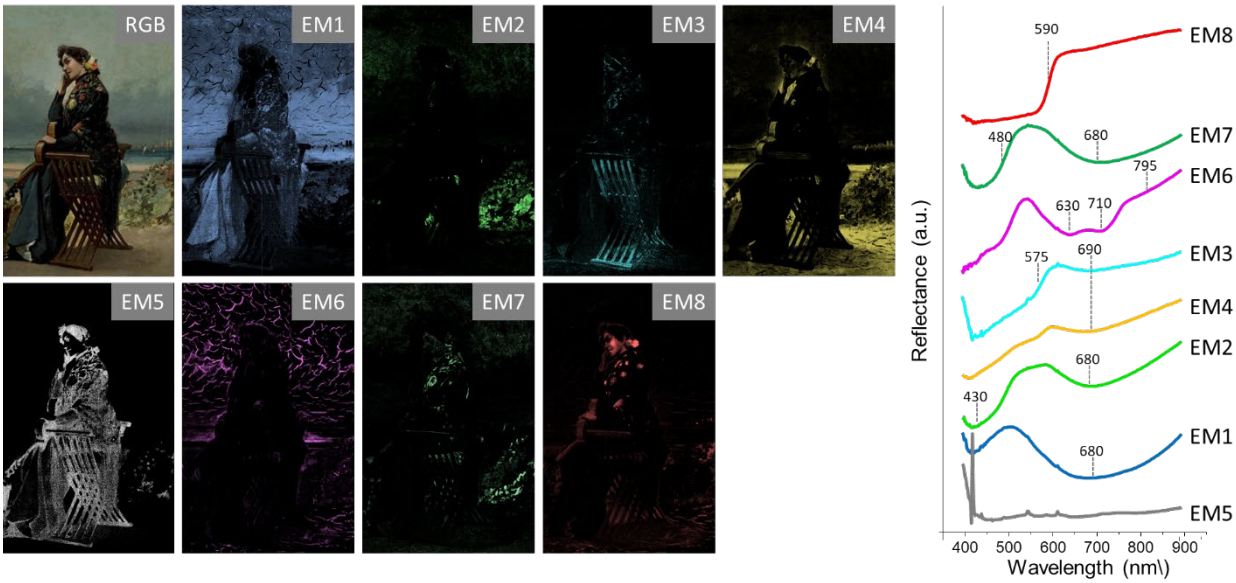

EM1
EM2
EM3
EM4
EM5
EM6
EM7
Reflectance (a.u.)
450
670
645
500
890
630
520
700
590
670
590
700
EM1
EM2
EM3
EM4
EM5
EM7
EM6
400
500
600
700
800
900
Wavelength (nm)

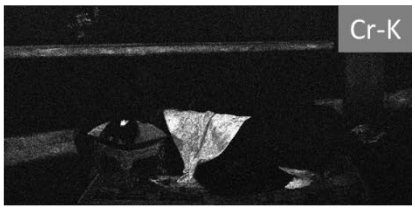
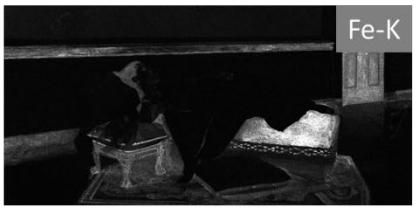

Pb-L
Fe-K
Hg-L
Ba-L
Co-K
Ca-K
Cr-K
Mn-K
K-K
Zn-K


EM1
EM2
EM3
EM4
EM5
EM6
EM7


EM1
890
EM4
630
700
660
EM5
480
580
EM6
540
EM7
710
450
600
EM3
705
795
630
EM2
Reflectance (a.u.)
400
500
600
700
800
900
Wavelength (nm)


RGB
Ba-L
Ca-K
Co-K
Cr-K
Pb-L
F-Ke
Hg-L
Mn-K
Zn-K
Cu-K
As-K

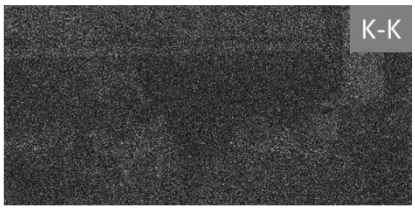
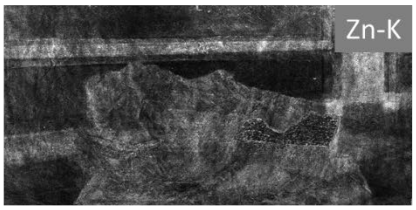

RGB
EM1
EM2
EM3
EM4
EM5
EM6
EM7
EM8
590
EM8
480
680
EM7
795
EM6
630
710
575
690
EM3
EM4
EM2
680
430
EM1
680
EM5
Reflectance (a.u.)
400
500
600
700
800
900
Wavelength (nm\)


RGB

Cr-K

Fe-K

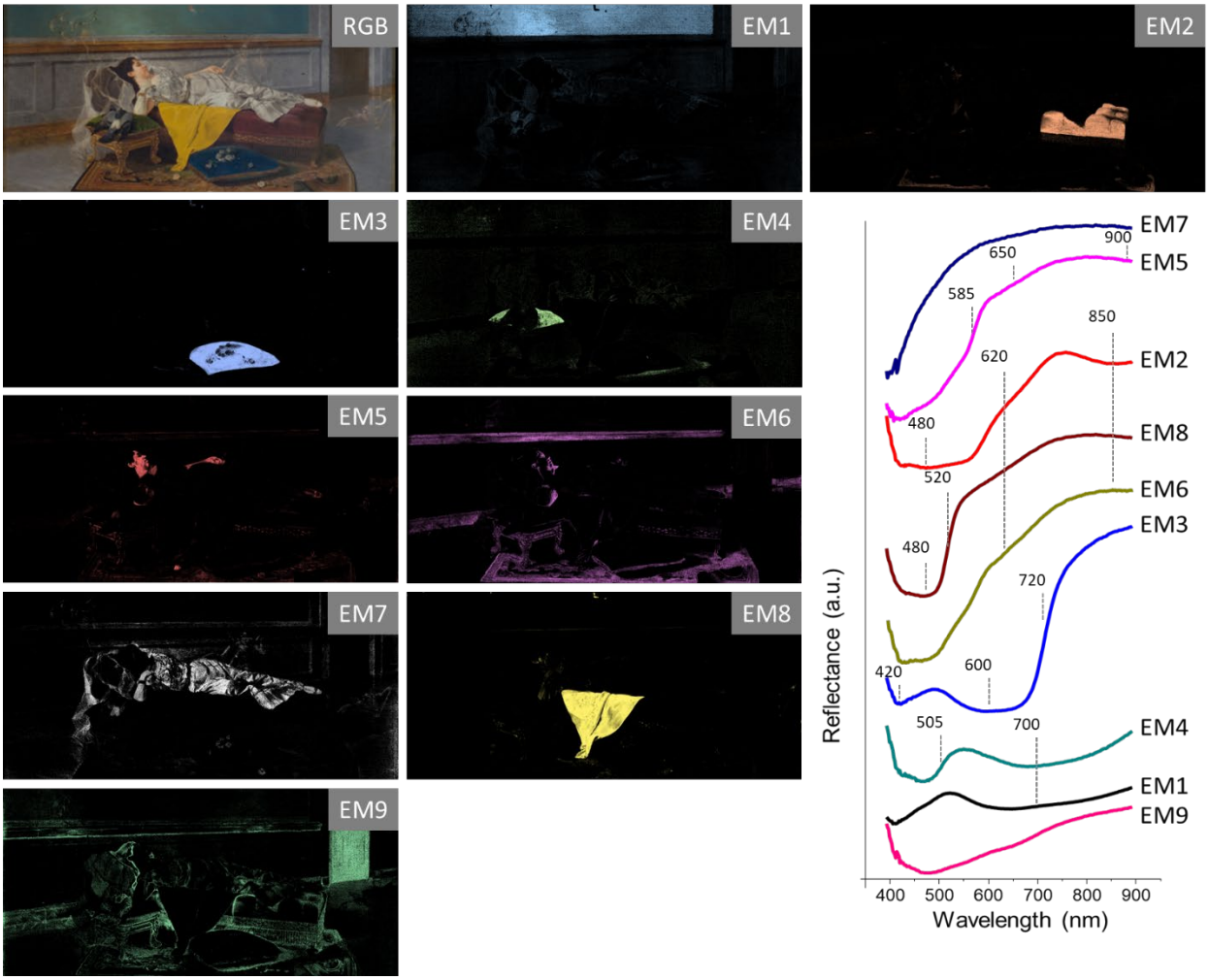
Mn-K

Ca-K

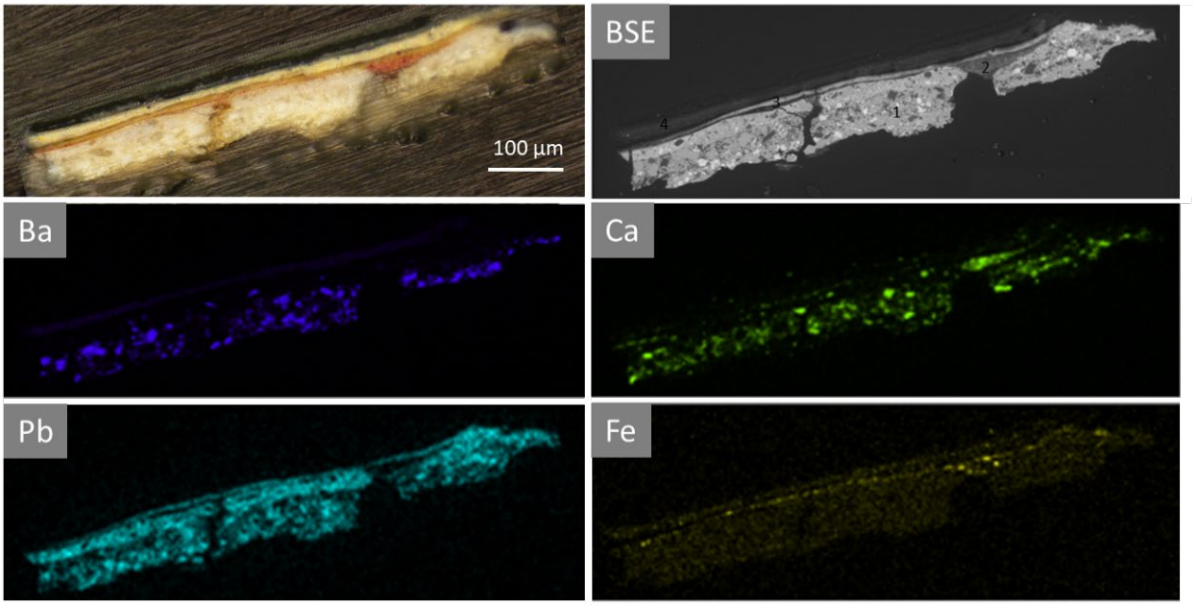
Hg-L

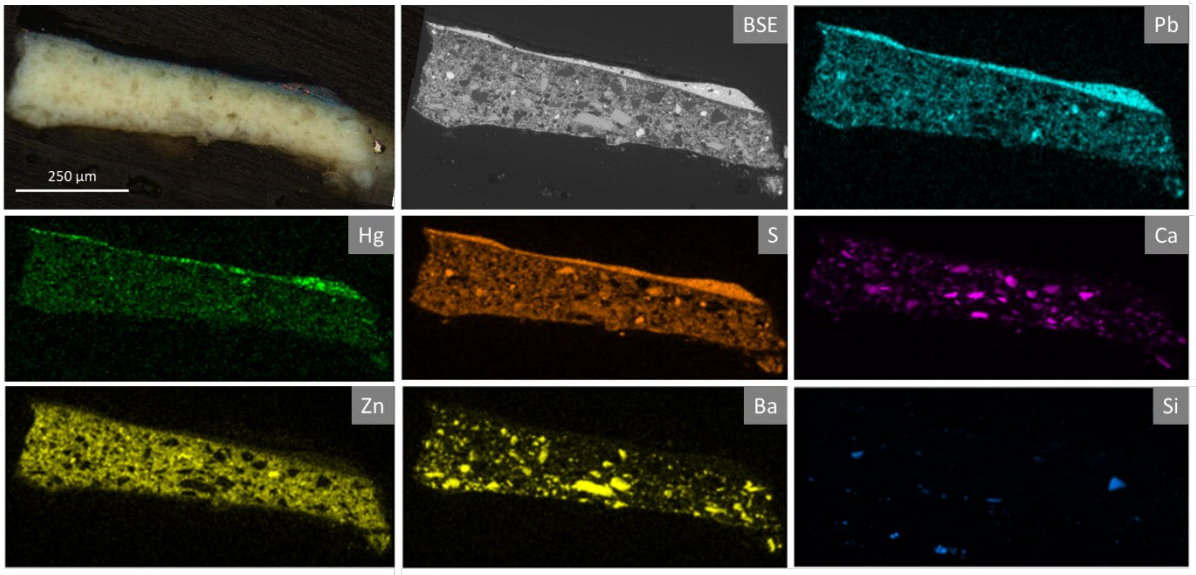
Pb-L

K-K

Zn-K

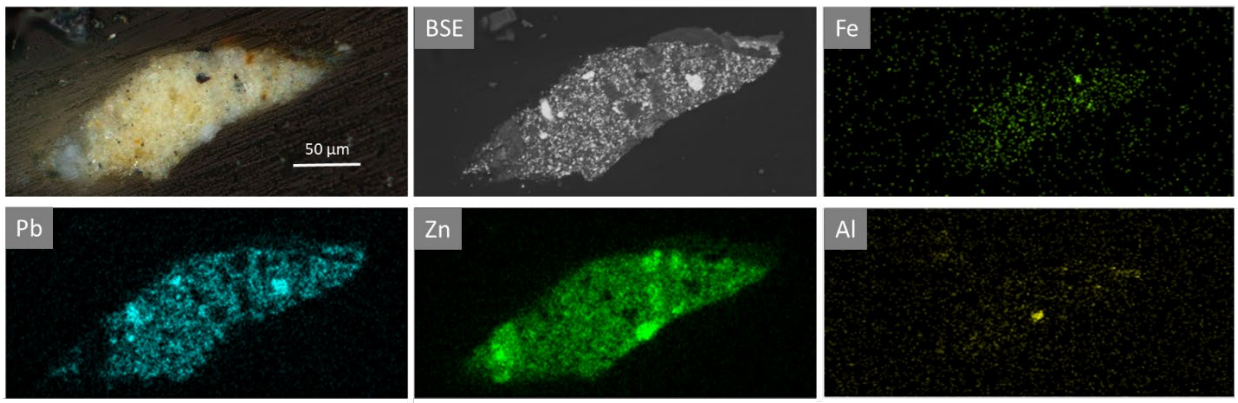
Cu-K

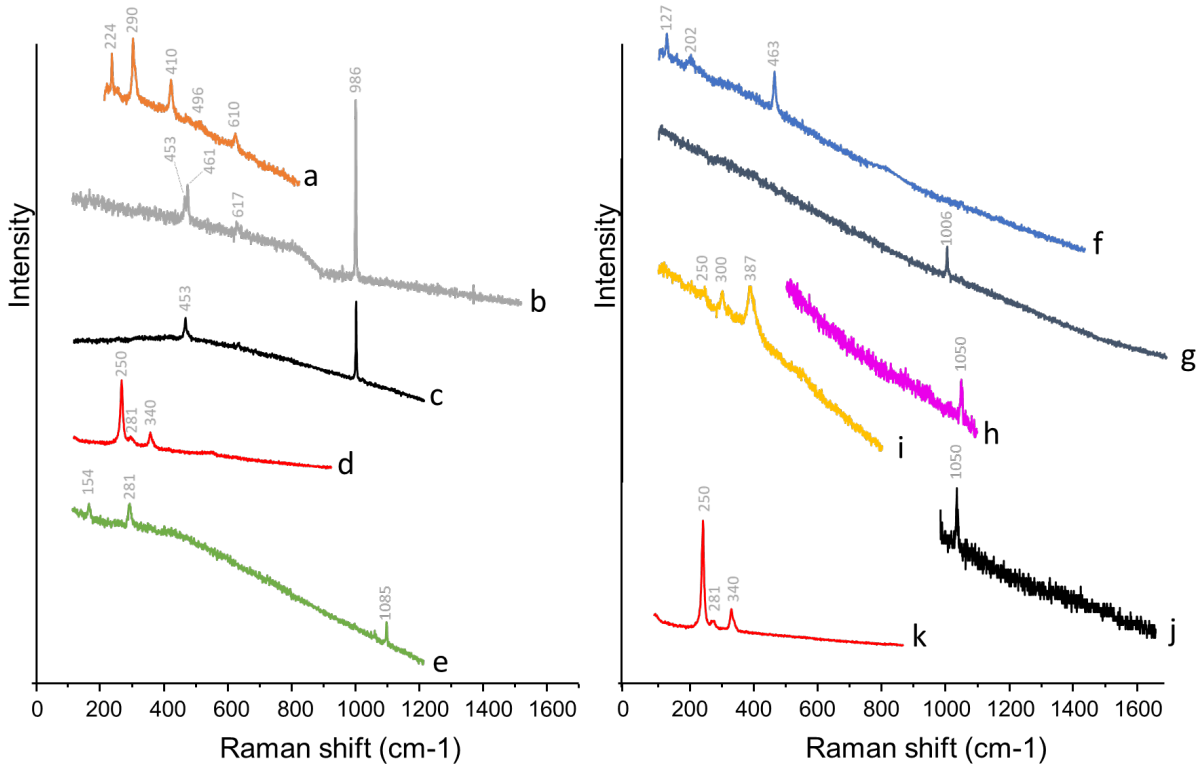

RGB
EM1
EM2
EM3
EM4
EM5
EM6
EM7
EM8
EM9
EM7
EM5
EM2
EM8
EM6
EM3
EM4
EM1
EM9
900
650
585
850
620
480
520
480
720
420
600
505
700
Reflectance (a.u.)
400 500 600 700 800 900
Wavelength (nm)

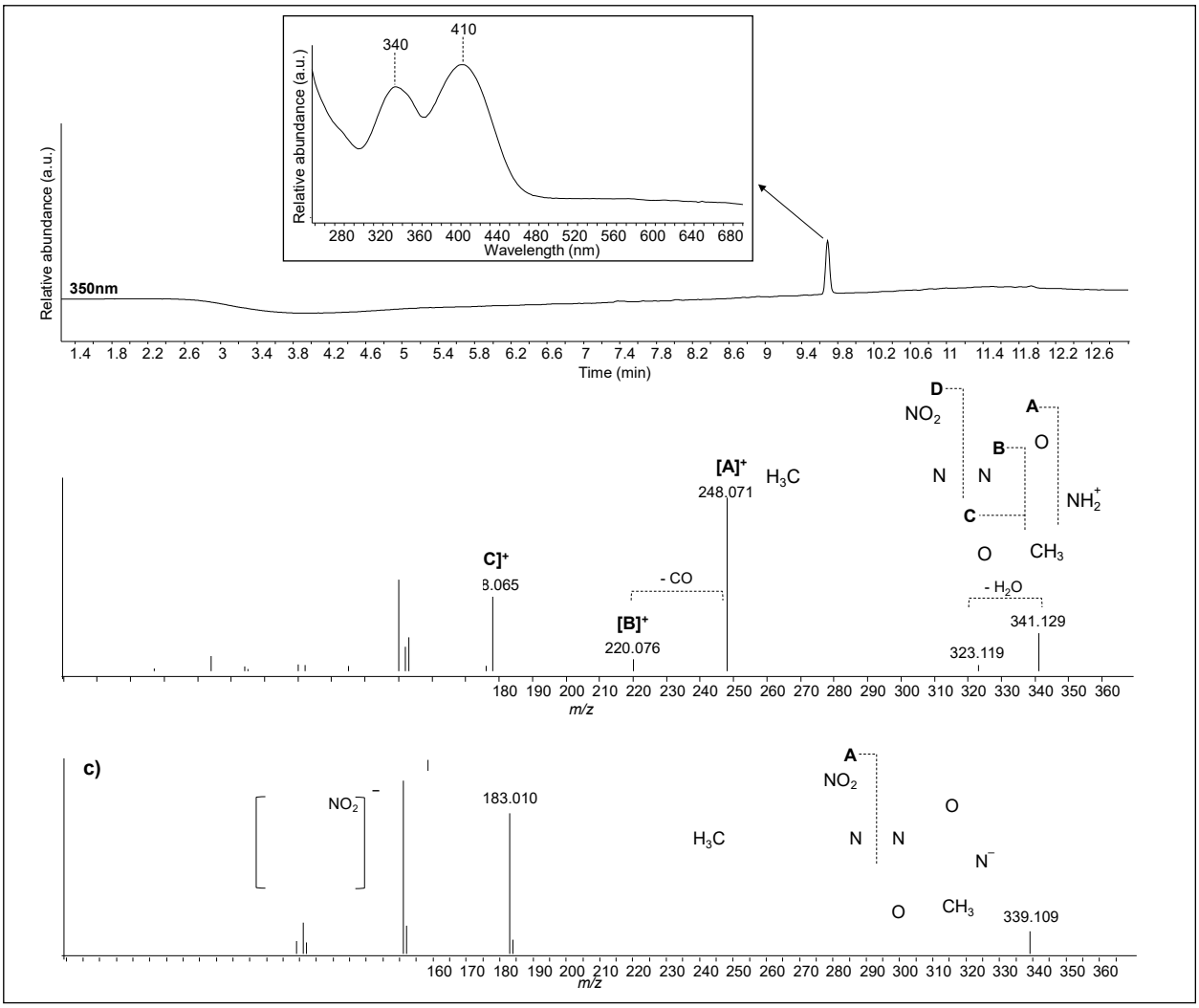
Micro-invasive investigation: optical microscopy, SEM-EDX, and Raman spectroscopy.





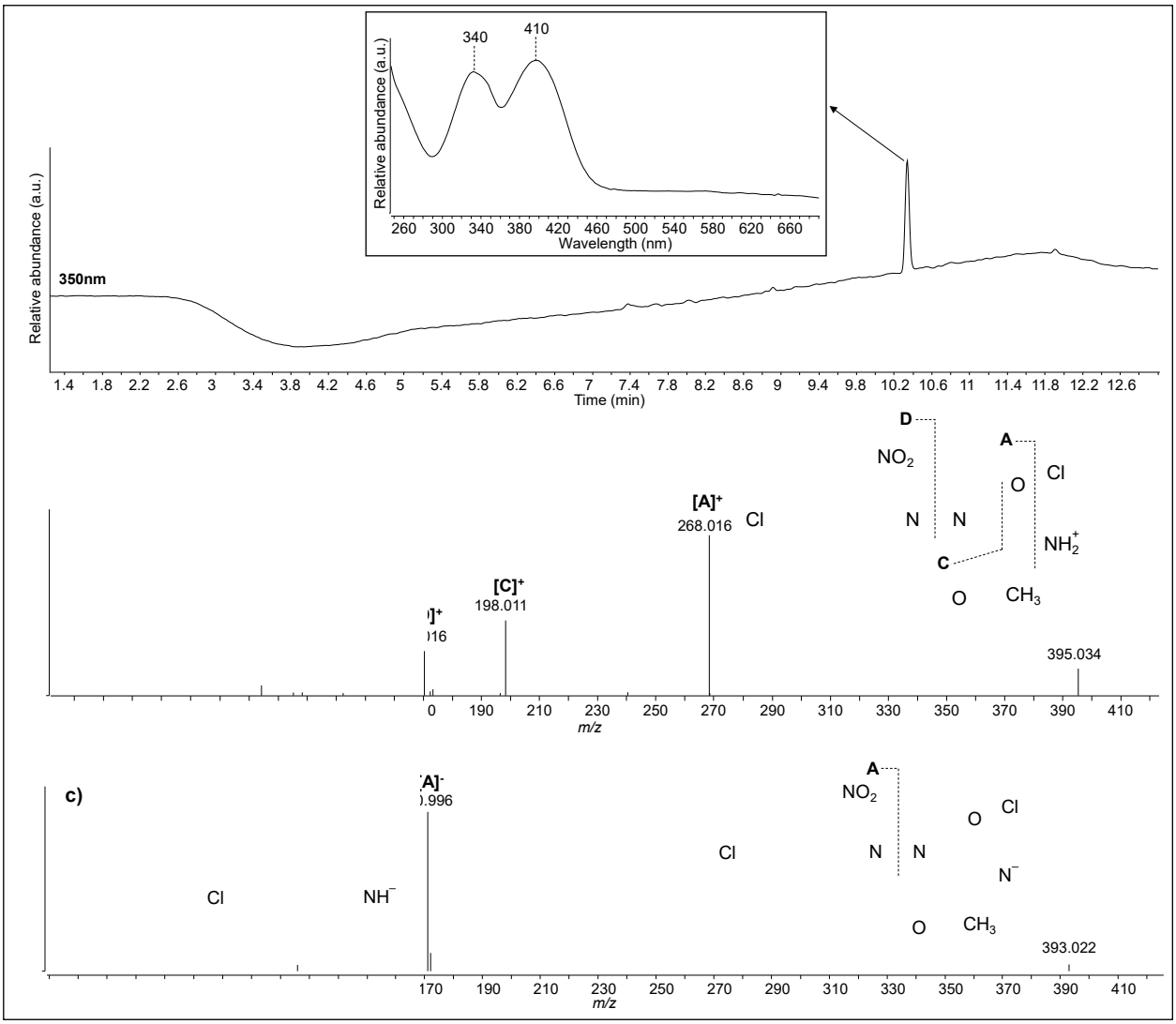

50 µm
BSE
Fe
Pb
Zn
Al


Intensity
Raman shift (cm-1)
0
200
400
600
800
1000
1200
1400
1600
224
290
410
496
610
986
453
461
617
a
b
453
c
250
281
340
d
154
281
1085
e
127
202
463
f
1006
g
250
300
387
i
1050
h
1050
250
281
340
k
j



In positive ionization, the mass fragmentation is dominated by the cleavage of the amide functionality, generating the $[A]^+$ ion, followed by successive losses of the molecular components linked to the diazo group in β position, generating $[B]^+$ and $[C]^+$ ions. The $[D]^+$ ion is produced by the N=N scission.

In negative ionization, a few fragment ions are observed. For diazo compounds, the fragmentation is generally dominated by the cleavage of the N=N group [F. Sabatini, I. Degano, Investigating the fragmentation pathways of β-naphthol pigments by Liquid Chromatography – Electrospray Ionization Quadrupole Time-of-Flight Mass Spectrometry, Rapid Communications in Mass Spectrometry, 34 (2020) e8789.]. Although the $[A]^-$ ion is likely to derive from this fragmentation, the ion at 183.010 *m/z* is difficult to justify without considering molecular rearrangements. The negative ion corresponding to nitrobenzene is also detected.



Very similar considerations to those presented for PY1 can be drawn from the fragmentation spectra.