

Supplementary data

Towards the non-destructive analysis of multilayered samples: a novel XRF-VNIR-SWIR hyperspectral imaging system combined with multiblock data processing

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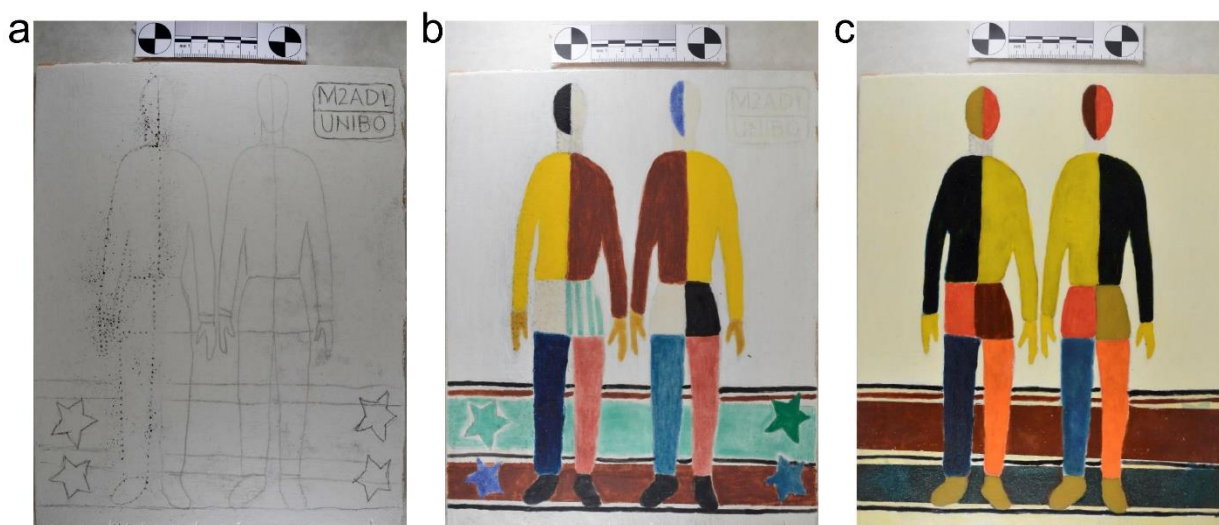


Fig. S1. The painting at the different stages of preparation: (a) preparatory drawing over the gypsum-based ground layer; (b) first painting layer; (c) second painting layer

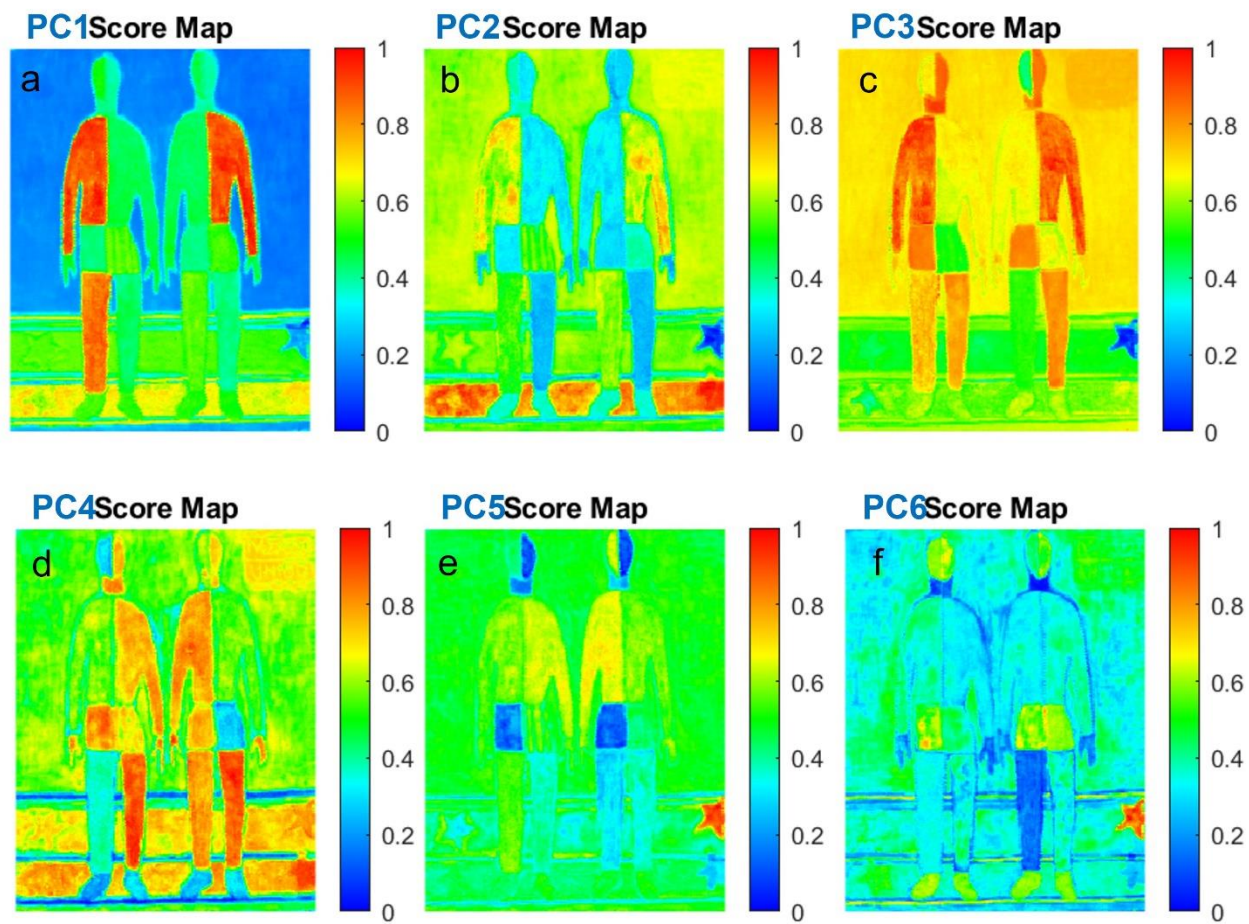


Fig. S2. PC1 to PC6 score maps: (a) PC1(explained variance: 38.1%); (b) PC2 (explained variance: 10.7%); (c) PC3 (explained variance: 7.2%); (d) PC4 (explained variance: 5.5%); (e) PC5 (explained variance: 4.6%); (f) PC6 (explained variance: 4.3%).

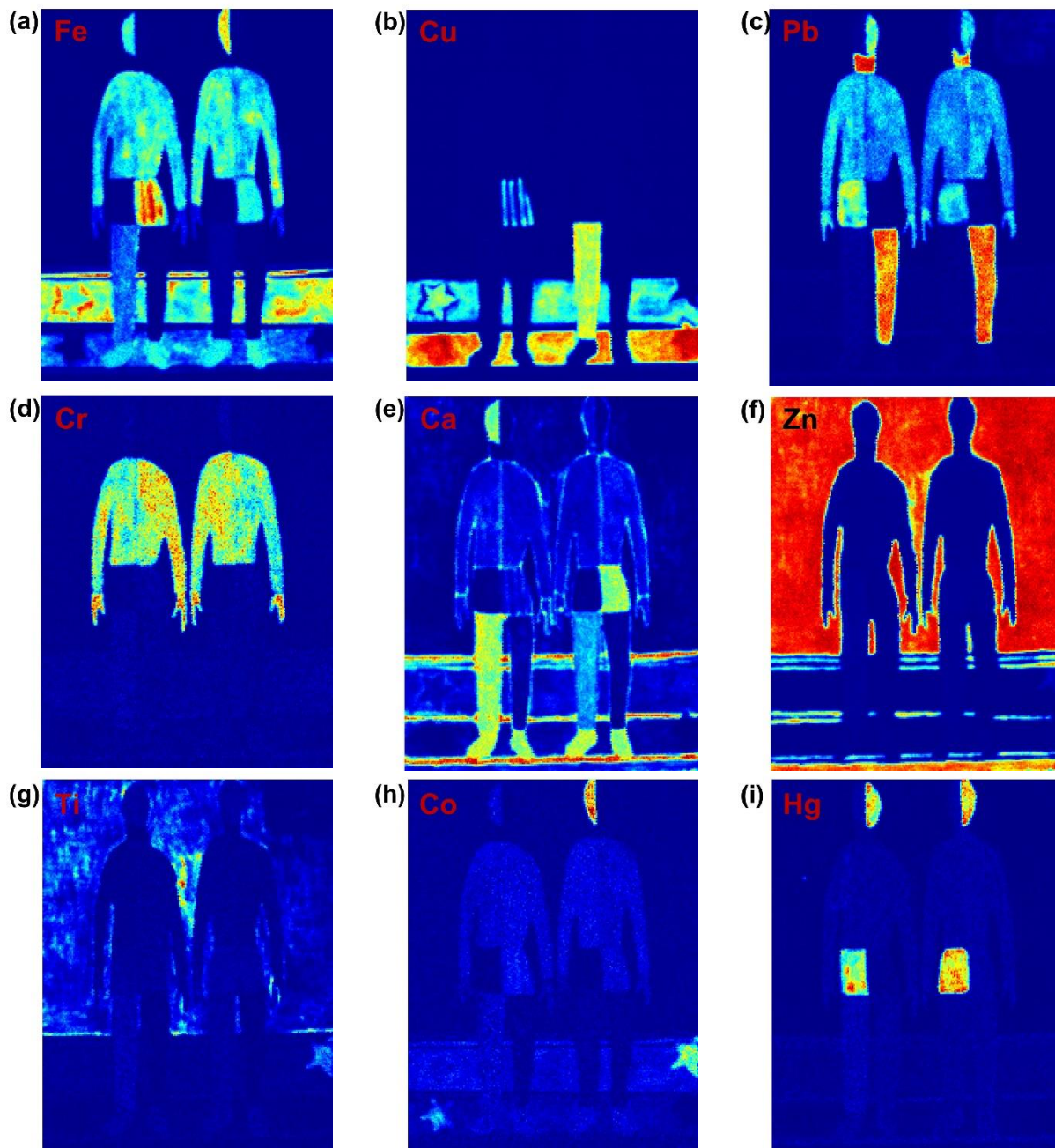


Fig.S3. Distribution maps obtained from the “classical” univariate XRF data analysis. (a) Iron; (b) Copper; (c) Lead; (d) Chromium; (e) Calcium; (f) Zinc; (g) Titanium; (h) Cobalt; (i) Mercury.

Table S1. Assignment of the electronic and vibrational bands employed to recognize pigments and binders from the spectra of the painting.

Compound	Band position (nm)	Assignment (Ref. [37-42])
Proteinaceous materials (P)	2173	1st overtone $\nu(\text{CO})$ amide I + amide II
	2042	$\nu(\text{NH})+\delta(\text{NH})$
Lipidic material (L)	2347	$\nu(\text{CH}_2)+\delta(\text{CH}_2)$
	2303	$\nu(\text{CH}_2)+\delta(\text{CH}_2)$
	1724	1st overtone $\nu(\text{CH}_2)$
	1206	2nd overtone $\nu(\text{CH}_2)$
Iron-based pigment	580	Inflection point
	850-900	Ligand field transition
Yellow ochre	545	Inflection point
	900	Ligand field transition
Gypsum (Gy)	1941	$\nu(\text{OH})+\delta(\text{OH})$
	1532	1st overtone $\nu(\text{OH})$
	1490	1st overtone $\nu(\text{OH})$
	1446	1st overtone $\nu(\text{OH})$
Verdigris (V)	500	Reflectance minimum
	2310	$\nu(\text{CH})+\delta(\text{CH})$
	2255	$\nu(\text{CH})+\delta(\text{CH})$
	2286	$\nu(\text{CH})+\delta(\text{CH})$
Azurite (Az)	1497	$2\nu(\text{OH})$
	2285	$(\nu + \delta) \text{OH}$ and $3\nu(\text{CO}_3^{2-})$
Malachite	2267	$2\nu \text{CO}_3^{2-}$
Co-based pigment	1500-1300	
Vermilion	600 (inflection point)	Semiconductor transition

Table S2. Within- and between-block spectral correlation of the selected areas														
Region selected	Description	Within-block correlation								Between-block correlation				Comments (P.C. = positively correlated)
		VNIR-SWIR				XRF				VNIR-SWIR vs. XRF				
		positive correlation		negative correlation		positive correlation		negative correlation		positive correlation		negative correlation		
		selected band	correlated band(s)	selected band	correlated band(s)	selected element	correlated element(s)	selected element	correlated element(s)	selected element	correlated band(s)	selected element	correlated band(s)	
A	White background	2ν(OH)	ν(OH)+δ(OH)			Ca	Ti	Zn	Ti, Ca	Ti	ν(NH)+δ(NH)/ 2ν(CO) amide I+ II			Ti pigment P.C. to proteinaceous binder and Zn P.C. to lipidic binder- Ca P.C. with OH of gypsum and proteinaceous materials
		3ν(CH)	2ν(CH)/ ν(NH)+δ(NH)/ ν(CH ₂)+δ(CH ₂)							Zn	3ν(CH)/ 2ν(CH)/ ν(CH ₂)+δ(CH ₂)			
		ν(NH)+δ(NH)	2ν(CO) amide I+ II							Ca	2ν(OH)/ ν(OH)+δ(OH)/ ν(NH)+δ(NH)/ 2ν(CO) amide I+ II			
B	Upper-right background area	2ν(OH)	ν(OH)+δ(OH)					Pb	Zn	Pb	ν(NH)+δ(NH)/ 2ν(CO) amide I+ II			Pb pigment P.C. to proteinaceous binder Zn pigment P.C. to lipidic binder
		3ν(CH)	2ν(CH)/ ν(CH ₂)+δ(CH ₂)							Zn	2ν(CH) / ν(CH ₂)+δ(CH ₂)			
		ν(NH)+δ(NH)	2ν(CO) amide I+ II / ν(OH)+δ(OH)											
C	Two men's external shirt	2ν(OH)	ν(OH)+δ(OH)			Fe	K	Fe/K	Ca, Cr, Pb	Fe	2ν(CH) / ν(NH)+δ(NH) / ν(CH ₂)+δ(CH ₂)			Fe pigment P.C. to lipidic binder; Ca P.C. with OH of gypsum
		2ν(CH)	ν(NH)+δ(NH)/ ν(CH ₂)+δ(CH ₂)			Cr	Pb	Cr/Pb	Ca, Fe, K	Ca	2ν(OH)/ν(OH)+δ(OH)			
		ν(NH)+δ(NH)	2ν(CO) amide I+II					Ca	Fe, K, Cr, Pb					
D	Left man's left leg	2ν(OH)	2ν(CH)	2ν(OH)	ν(OH)+δ(OH)			Ca	Fe	Fe	ν(NH)+δ(NH)/ 2ν(CO) amide I+ II	Fe	2ν(CH) / ν(NH)+δ(NH) /ν(CH ₂)+δ(CH ₂)	Fe pigment P.C. to proteinaceous binder
		2ν(CH)	ν(CH ₂)+δ(CH ₂)					Ca	Fe	ν(OH)+δ(OH)				
		ν(NH)+δ(NH)	2ν(CO) amide I+ II / ν(OH)+δ(OH)											
E	Two men's internal shirt	2ν(OH)	ν(OH)+δ(OH)			Cr	Pb	Cr/Pb	Fe, Ca	Cr/Pb	2ν(CH) / ν(CH ₂)+δ(CH ₂)			Fe pigment P.C. to proteinaceous binder Cr and Pb pigment P.C. to lipidic binder
		3ν(CH)	2ν(CH)/ ν(CH ₂)+δ(CH ₂)					Fe	Ca	Fe	ν(NH)+δ(NH)/ 2ν(CO) amide I+ II			
		ν(NH)+δ(NH)	2ν(CO) amide I+ II											
F	Right man's left face	2ν(OH)	ν(OH)+δ(OH)					Fe	Ca	Ca	2ν(OH)/ν(OH)+δ(OH)			No clear correlation
		3ν(CH)	2ν(CH)/ ν(CH ₂)+δ(CH ₂)					Ca	Fe, Co					
		ν(NH)+δ(NH)	2ν(CO) amide I+ II					Co	Ca					
G+H	Right star on upper stripe	ν(NH)+δ(NH)	2ν(CO) amide I+ II / ν(OH)+δ(OH)			Co	Ni, Ti, Zn	Co/Ni /Ti/Zn	Ca, Fe	Co/Ni /Ti/Zn	2ν(CH) / ν(CH ₂)+δ(CH ₂)			Co P.C. with lipidic binder
		3ν(CH)	2ν(CH)/ ν(CH ₂)+δ(CH ₂)					Fe	Ca	Fe	ν(OH)+δ(OH)			
		ν(NH)+δ(NH)	2ν(CO) amide I+ II							Ca	2ν(OH)/ ν(OH)+δ(OH)			
I	Left man's left face.	2ν(OH)	ν(OH)+δ(OH) / 2ν(CH)					Fe	Ca	Fe	2ν(CH) / ν(CH ₂)+δ(CH ₂)			No clear correlation

	right man's right shorts, shoes													
J	Two men's right face, two men's left shorts	2v(OH) 3v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) 2v(CH)/ v(CH ₂)+δ(CH ₂) 2v(CO) amide I+ II					Pb Hg	Hg Ca	Pb	v(NH)+δ(NH)/ 2v(CO) amide I+ II			Pb pigment P.C. to proteinaceous binder
K	Right star on bottom stripe	2v(OH) 2v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) v(CH ₂)+δ(CH ₂) 2v(CO) amide I+II			no enough variables for correlation			no enough variables for correlation					
L	Left star on bottom stripe	2v(OH) 3v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) 2v(CH)/ v(CH ₂)+δ(CH ₂) 2v(CO) amide I+ II					Fe Cu Ca	Cu Fe, Ca, Co Cu	Fe Cu	3v(CH)/ 2v(CH)/ v(CH ₂)+δ(CH ₂) 2v(OH)/ v(OH)+δ(OH)/ v(NH)+δ(NH)/ 2v(CO) amide I+ II			Correlation not in accordance with recipe
M	Bottom stripe	2v(OH) 2v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) v(CH ₂)+δ(CH ₂) 2v(CO) amide I+II					Fe Cu Ca	Cu, Ca Fe, Ca Fe, Cu	Fe Cu Ca	v(NH)+δ(NH)/ 2v(CO) amide I+ II 2v(CH) / v(CH ₂)+δ(CH ₂) 2v(OH)/ v(OH)+δ(OH)			Fe pigment P.C. to proteinaceous binder and Cu P.C. to lipidic binder- Ca P.C. with OH of gypsum
N	Upper stripe, left man's right shorts	2v(OH) 2v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) v(CH ₂)+δ(CH ₂) 2v(CO) amide I+II					Fe Cu Ca	Cu, Ca Fe, Ca Fe, Cu	Fe Cu Ca	2v(CH) / v(CH ₂)+δ(CH ₂) v(NH)+δ(NH)/ 2v(CO) amide I+ II 2v(OH)/ v(OH)+δ(OH)			Cu pigment P.C. to proteinaceous binder and Fe P.C. to lipidic binder- Ca P.C. with OH of gypsum
O	Right man's left leg	2v(OH) 2v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) v(CH ₂)+δ(CH ₂) 2v(CO) amide I+II / 2vCO ₃ ²⁻ of malachite					Cu	Ca	Cu	v(NH)+δ(NH)/ 2v(CO) amide I+ II			Cu pigment P.C. to proteinaceous binder
P	Two men's right legs	2v(OH) 3v(CH) v(NH)+δ(NH)	v(OH)+δ(OH) 2v(CH)/ v(CH ₂)+δ(CH ₂) 2v(CO) amide I+ II					Pb	Ca	Fe Ca	2v(CH) / v(CH ₂)+δ(CH ₂) 2v(OH)/ v(OH)+δ(OH)			Fe pigment P.C. to lipidic binder Ca P.C. with OH of gypsum