SUPPLEMENTARY INFORMATION

Jazz Colors: Pigment Identification in the Gouaches Used by Henri Matisse.

Spectra and summary of the analyses carried out on the *Jazz* colors using transmitted and reflectance infrared, Raman, SERS, and X-ray fluorescence spectroscopies

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Table S1: All pigments and auxiliary compounds detected and identified across three copies of *Jazz* using a multi-analytical approach

Color		Prints (P)	Pigment(s) identified	MFT	p-XRF	r-FTIR	p-Raman	µ-FTIR	Confocal Raman	SERS	Plates sampled
Black 1 (Bk1)		1, 2, 4, 5, 7, 10, 11,	Bone black/carbon black	>3	P, Ca		T		T		P1
		13, 14, 15, 17, 18,	Prussian blue		K, Fe	X		X			
		19, 20	Silicates and metal oxides		Si	X		P	P	*	
					(Al, K, S, Ca, Ti,						
					Cr, Mn, Fe, Zn)						
Black 2 (Bk2)		8, 12, 16	Bone black/carbon black	>3	P, Ca	X	T	X	T		P8
			Prussian blue		K, Fe			X			
			Silicates and metal oxides		Si	X		X		*	
					(Al, K, S, Ca, Ti,						
					Cr, Mn, Fe, Zn)						
Violet (V)		20	Crystal violet/methyl violet	3						X	P20
			Rhodamine 6G							X	
			Copper ferrocyanide		Cu, Fe	X		X			
			Barium sulfate		S, Sr, Ba			X	X		
					Al, P (Si, K)						
Magenta (M)		5, 6, 10, 11, 13, 15,	Rhodamine 6G	2.5						X	P5
		16, 17, 18	Rhodamine 3B						X		P11
			Copper ferrocyanide		Cu, Fe	X					
			Phototungstic (acid)		P, W						
			Barium sulfate		S, Sr, Ba	X	X		X		
					Al, Ca						
Pink 1 (Pk1)		7, 10, 16	Crystal violet/methyl violet	2.5						X	P7,
			Rhodamine 6G							X	P10
			Copper ferrocyanide		Cu, Fe						P16
			Barium sulfate		S, Sr, Ba						
					Al						
Pink 2 (Pk2)		20	PR49:2	2	S, Ca		X		X	X	P20
					Al						
Blue 1 (B1)		1 ,2 ,3 ,4 ,5 ,6 ,8 ,9,	Synthetic ultramarine	2	Al, Si, S (K, Ca)	X	X	X	X		P1
		10, 11, 13, 14, 15,								*	
		16, 17, 18, 20									
Blue 2 (B2)		19	Synthetic ultramarine	3	Al, Si, S (K, Ca)	X	X	X	X		P19
			Titanium white		Ti		X		X		
			Calcium carbonate		Ca	X		X		*	
			Zinc white		Zn						
Blue 3 (B3)		6	Synthetic ultramarine	3	Al, Si, S (K, Ca)	X	X	X	X		P6
			Zinc white /		Zn					*	
			Barium sulfate /lithopone		S, Ba						
Blue 4 (B4)		12	Synthetic ultramarine	2	Al, Si, S (K, Ca)	X	*	X	X	*	P12
Blue 5 (B5)		15	Synthetic ultramarine	2	Al, Si, S (K, Ca)	X	*	X	X	*	P15
Green 1 (G1)		14, 16, 20	PG7	2	Cl, Cu		X		X		P14,
			PY3		Cl	X		X		*	P20
			Barium sulfate		S, Ba	X		X			
			Aluminum Hydrate		Al			X			

Color		Prints (P)	Pigment(s) identified	MFT	p-XRF	r-FTIR	p-Raman	µ-FTIR	Confocal Raman	SERS	Plates sampled
Green 2 (G2)		5, 12, 17, 18, 19	PG7	>3	Cl, Cu		X		X		P5
			PY3		Cl	X	X	X		*	P19
			Barium sulfate		S, Ba	X		X			
Green 3 (G3)		6, 7, 11, 18	PG7	2.5	Cl, Cu		X	X	X		P6
			Synthetic ultramarine		Al, Si, S, K				X	*	P18
			Barium sulfate		S, Ba	X		X			
Yellow 1 (Y1)		10, 14	PY5	>3		X	X	X	X	*	P14
					Al, S						
Yellow 2 (Y2)		4	PY5	>3		X	*	X	X	*	P4
			PY10		Cl	X		X	X		
Yellow 3 (Y3)		12, 16	PY5	3		X		X	X		P12
			PY6		Cl		*	X	X	*	
			Barium sulfate/zinc white/Lithopone		S, Zn, Ba						
Yellow 4 (Y4)		1, 2, 5	PY3	3	Cl	X	X	X	X		P1
			PY6		Cl	X	X	X	X	*	
			Barium sulfate		S, Sr, Ba		X	X	X		
Yellow 5 (Y5)		11	PY3	>3	Cl	X	X	X	X		P11
			PY10		Cl		X	X	X	*	
			Lead chromate		Cr, Pb				X		
			Calcium sulfate		S, Ca	X	X	X	X		
Yellow 6 (Y6)		1, 2, 20	PY3	>3	Cl	X	X	X	X		P1,
			Gypsum		S, Ca, Sr	X	X	X	X	*	P20
			Barium sulfate		S, Ba, Sr						
Yellow 7 (Y7)		3, 8, 11	PY5	>3		X	X	X	X		P8
			PY3		Cl	X	X	X	X	*	
			Barium sulfate		S, Sr, Ba	X	X	X	X		
Orange 1 (O1)		6, 11	PY5	2.5		X	X	X	X		P6
			PR4			X	X	X	X	*	
					Al,S						
Orange 2 (O2)		3	PY5	3		X	X	X	X		P3
			PY10		Cl	X	X	X	X		
			Lead chromate		Cr, Pb					*	
			Calcium sulfate		S, Ca		X	X			
Orange 3 (O3)		10	PY5	3		X	*	X	X	*	P10
			PY10		Cl	X		X	X		
Orange 4 (O4)		2	Iron oxide (yellow ochre)	>3	Al, Si, K, Fe	X		X	X		P2
			Lithopone		S, Zn, Ba		*		X	*	
			Calcium carbonate		Ca						
					P						
Orange 5 (O5)		20	Iron oxide (yellow ochre)	2.5	Al, Si, K, Mn, Fe, Ti	X		X	X	*	P20
Orange 6 (O6)		20	PR4	2				X	X		P20
			PY5			X		X	X		
			Iron oxide (Mars red)		Al, Si, K, Mn, Fe				X		
			Iron oxide (ochre)				*	X	X	*	
			Calcium sulfate		S, Ca	X		X			
			Lead chromate		Cr, Pb						

Color		Prints (P)	Pigment(s) identified	MFT	p-XRF	r-FTIR	p-Raman	µ-FTIR	Confocal Raman	SERS	Plates sampled
Red 1 (R1)		1, 2, 20	PR3	2.5		X	X	X	X		P2
			PR49:2		S ,Ca	X	X	X	X		
			Vermilion		S, Hg		X		X	*	
			Barium sulfate		S, Ba			X			
					Al						
Red 2 (R2)		4, 10, 12	PR3	>3		X					
			PR49:2		S, Ca	X					
			Lead chromate		Cr, Pb		*	*	*	*	
			Barium sulfate		S, Ba						
					Al						
Red 3 (R3)		7, 11, 17, 19	PR49:2	>3	S, Ca	X	X	X	X		P7
					Al					*	
Red 4 (R4)		6, 8, 13	PR3	3		X	X	X	X		P6
			PR49:2		S, Ca	X	X	X	X	*	
					Al						
Brown (Br)		2, 20	Iron oxide (Sienna/Mars Red)	>3	Al, Si, K, Mn, Fe	X	X	T	X		P2,
			Lead chromate		Cr, Pb	X				*	P20
			Calcium sulfate		S, Ca	X	X	X	X		
Tan 1 (T1)		10	Possibly iron oxide	2.5	Al, Si, Fe						P10
			Barium sulfate/zinc		S, Zn, Ba					*	
			white/Lithopone								
Tan 2 (T2)		11	Iron oxide	*	Al, Si, Fe		*			*	
White 1 (W1)		12	Barium sulfate/zinc	≈3	S, Zn, Ba	X	X	X	X	*	P12
			white/Lithopone								
White 2 (W2)		17	Zinc white		Zn					*	P17
			Barium sulfate /Lithopone		S, Ba	X	X	X	X		
Gray 1 (Gy1)		18	Zinc white	2.5	Zn						P18
			Barium sulfate/zinc		S, Sr,Ba	X	X	X	X	*	
			white/Lithopone Prussian blue		Fe	X					
Gray 2 (Gy2)		7,15, 17, 19	Titanium white (anatase)	2.5	Ti	X	X		X		P7,
			Calcium carbonate		Ca	X	X	X	X		P19
			Ultramarine blue		Al, Si, S	X	X	X	X	*	
			Prussian blue		Fe		X				
			Barium sulfate/zinc		S, Zn, Ba	X	X		X		
			white/Lithopone								
Gray 3 (Gy3)		9	Titanium white (anatase)	*	Ti	X	*		*		P9
			Calcium carbonate		Ca	X		X		*	
			Ultramarine blue		Al, Si, S						
			Prussian blue		Fe						
Paper		all	Low mineral content	2	Al, Si, P, S, K, Ca, Fe, Zn					*	

(X) present, (T) tentatively identified - Raman cannot distinguish bone black from carbon black, and differentiation of iron oxide pigments with FTIR is very challenging (*) not analyzed

Table S2: Gouaches identified in each *Jazz* plate.

	Bx1	Bk2	V	M	Pk1	Pk2	B1	B2	B3	B4	B5	G1	G2	G3	Y1	Y2	Y3	Y4	Y5	Y6	Y7	O1	O2	O3	O4	O5	O6	R1	R2	R3	R4	Br	T1	T2	W1	W2	Gy1	Gy2	Gy3
P1	X						X											X		X								X											
P2	X						X											X		X					X			X				X							
P3							X														X		X																
P4	X						X									X													X										
P5	X			X			X						X					X																					
P6				X			X		X					X								X									X								
P7	X				X									X																X								X	
P8		X					X														X										X								
P9							X																																X
P10	X			X	X		X								X									X					X				X						
P11	X			X			X							X					X		X	X								X				X					
P12		X								X			X				X												X						X				
P13	X			X			X																								X								
P14	X						X					X			X																								
P15	X			X			X				X																											X	
P16		X		X	X		X					X					X																						
P17	X			X			X						X																	X						X		X	
P18	X			X			X						X	X																							X		
P19	X							X					X																	X								X	
P20	X		X			X	X					X								X						X	X	X				X							

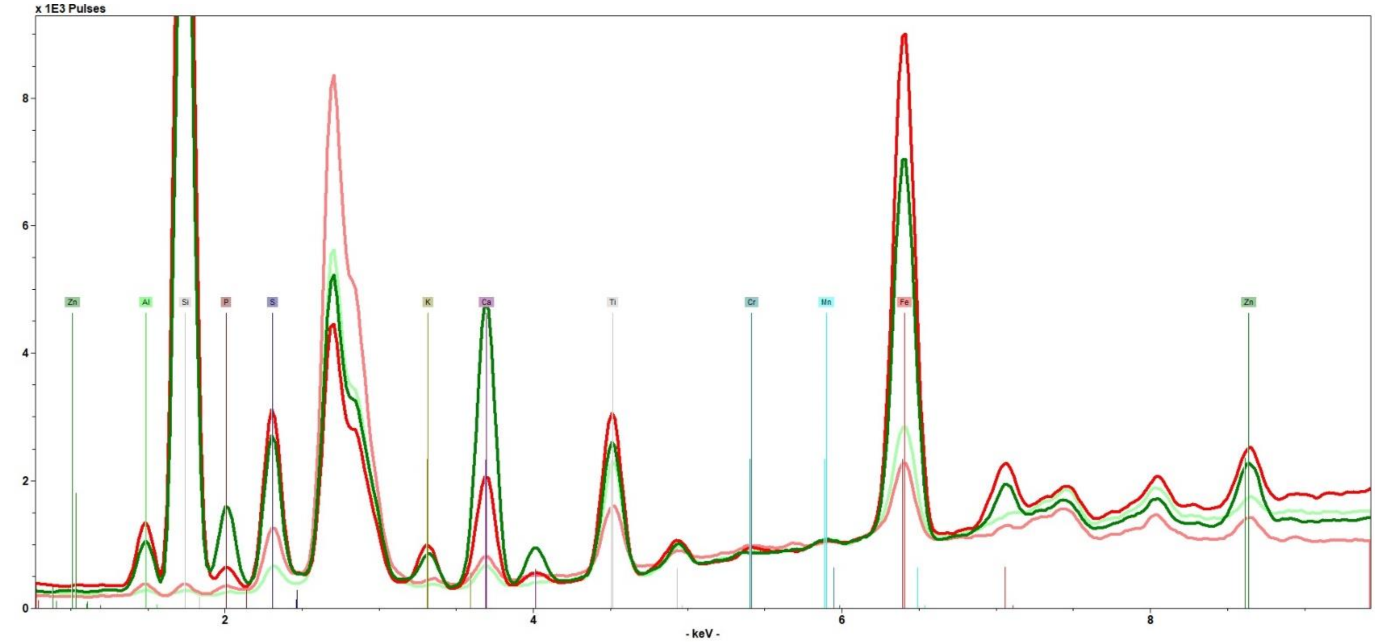

Figure S1: p-XRF spectra for the black gouaches (red and light red): Bk1 and paper support (plate P1) and (green and light green): Bk2 an paper support (plate P8). Elements present in both gouaches: Al, Si, P, S, K, Ca, Ti, Cr, Mn, Fe and Zn.

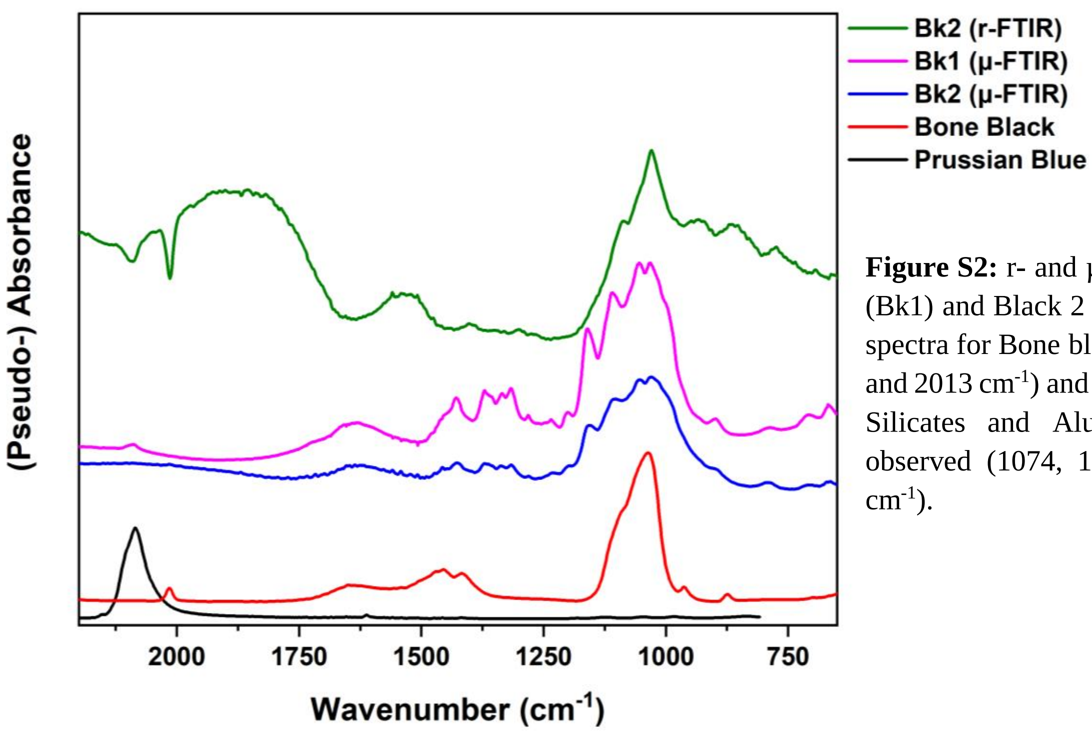

Figure S2: r- and μ-FTIR spectra of Black 1 (Bk1) and Black 2 (Bk2) alongside reference spectra for Bone black (875, 962, 1038, 1087 and 2013 cm^{-1}) and Prussian blue (2094 cm^{-1}). Silicates and Aluminosilicates were also observed (1074, 1031, 1001, 794 and 470 cm^{-1}).

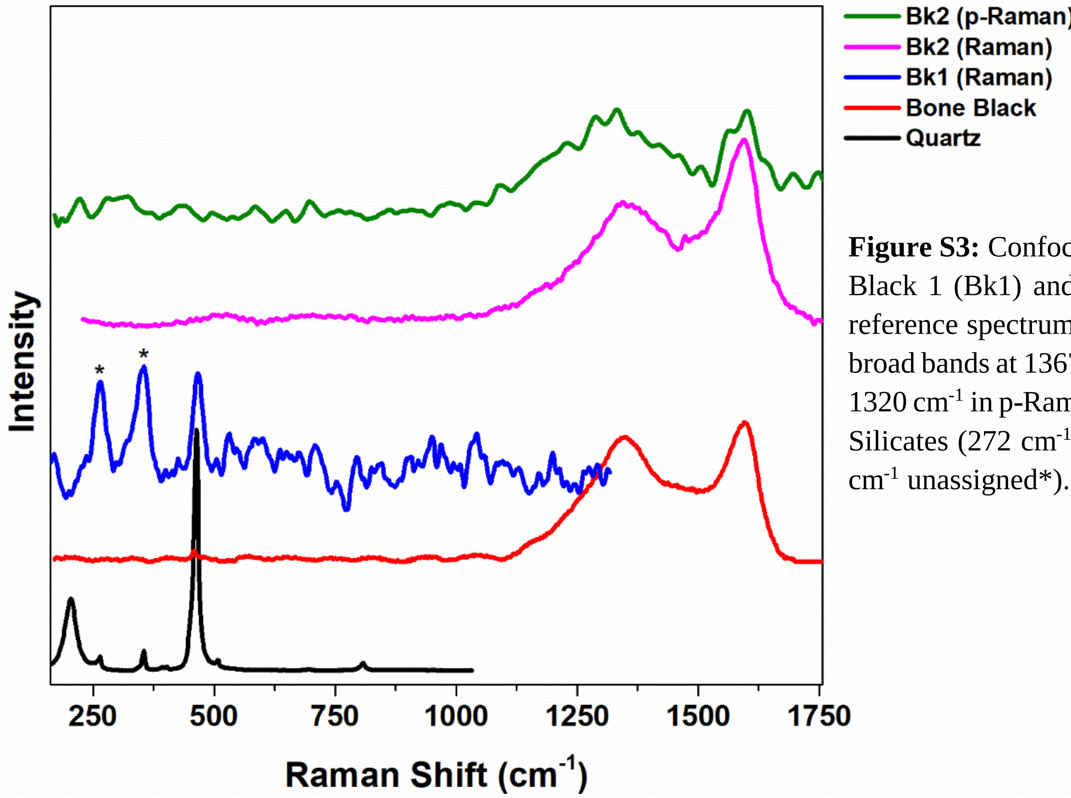

Figure S3: Confocal and p-Raman spectra of Black 1 (Bk1) and Black 2 (Bk2) alongside reference spectrum for Bone black (D and G broad bands at 1367 and 1590 cm^{-1} - shifted to 1320 cm^{-1} in p-Raman). Quartz (468 cm^{-1}) and Silicates (272 cm^{-1}) were also observed (355 cm^{-1} unassigned*).

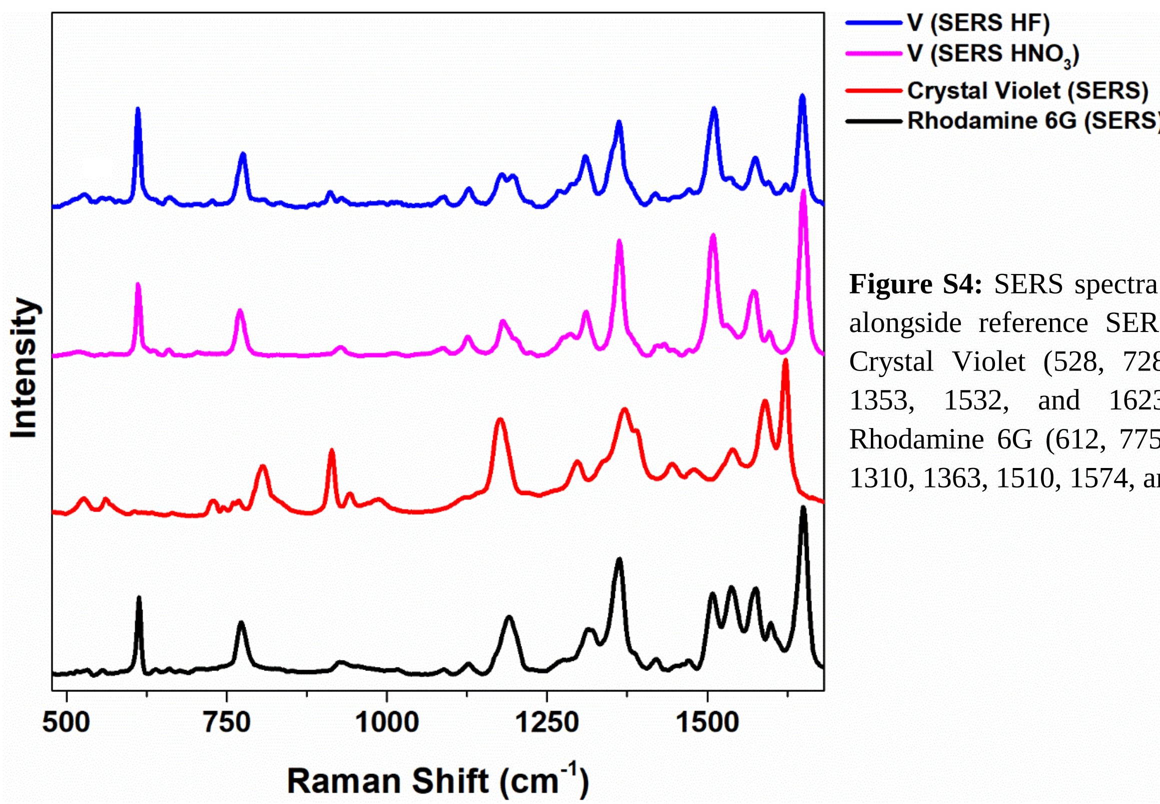

Figure S4: SERS spectra of Violet (V) alongside reference SERS spectra for Crystal Violet (528, 728, 912, 1180, 1353, 1532, and 1623 cm^{-1}) and Rhodamine 6G (612, 775, 1090, 1179, 1310, 1363, 1510, 1574, and 1679 cm^{-1}).

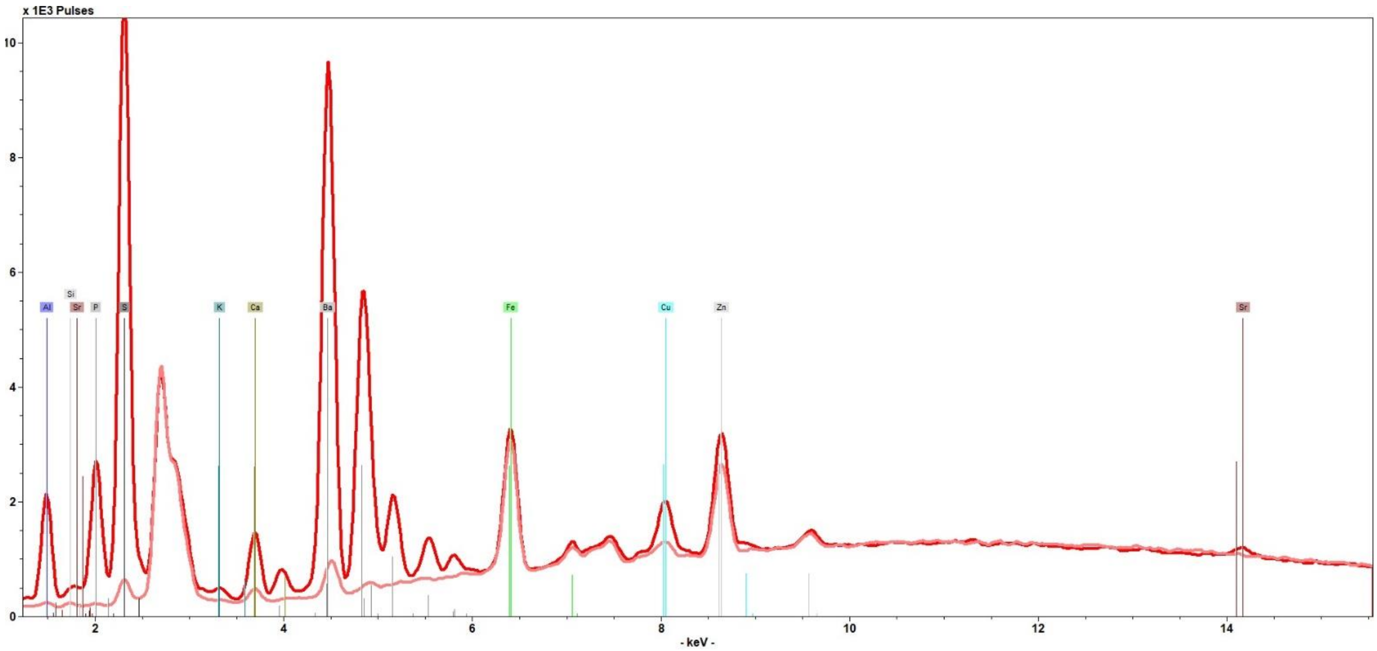

Figure S5: p-XRF spectrum for the (red) violet gouache V and (light red) paper support (plate P20). Elements present in the gouache: Al, Si, P, S, K, Ca, Fe, Cu, Zn, Sr and Ba.

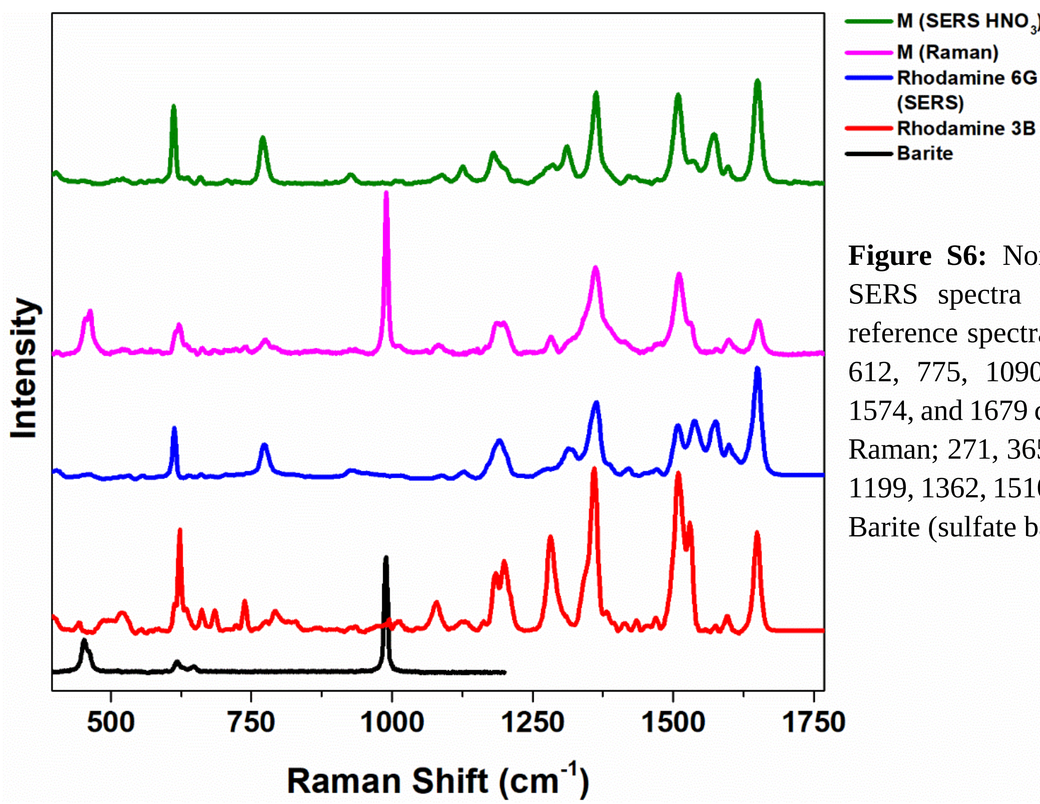

Figure S6: Normal (confocal) Raman and SERS spectra of Magenta (M) alongside reference spectra for Rhodamine 6G (SERS; 612, 775, 1090, 1179, 1310, 1363, 1510, 1574, and 1679 cm^{-1}), Rhodamine 3B (normal Raman; 271, 365, 620, 633, 662, 1082, 1187, 1199, 1362, 1510, 1530, 1599, 1650 cm^{-1}) and Barite (sulfate band at 988 cm^{-1}).

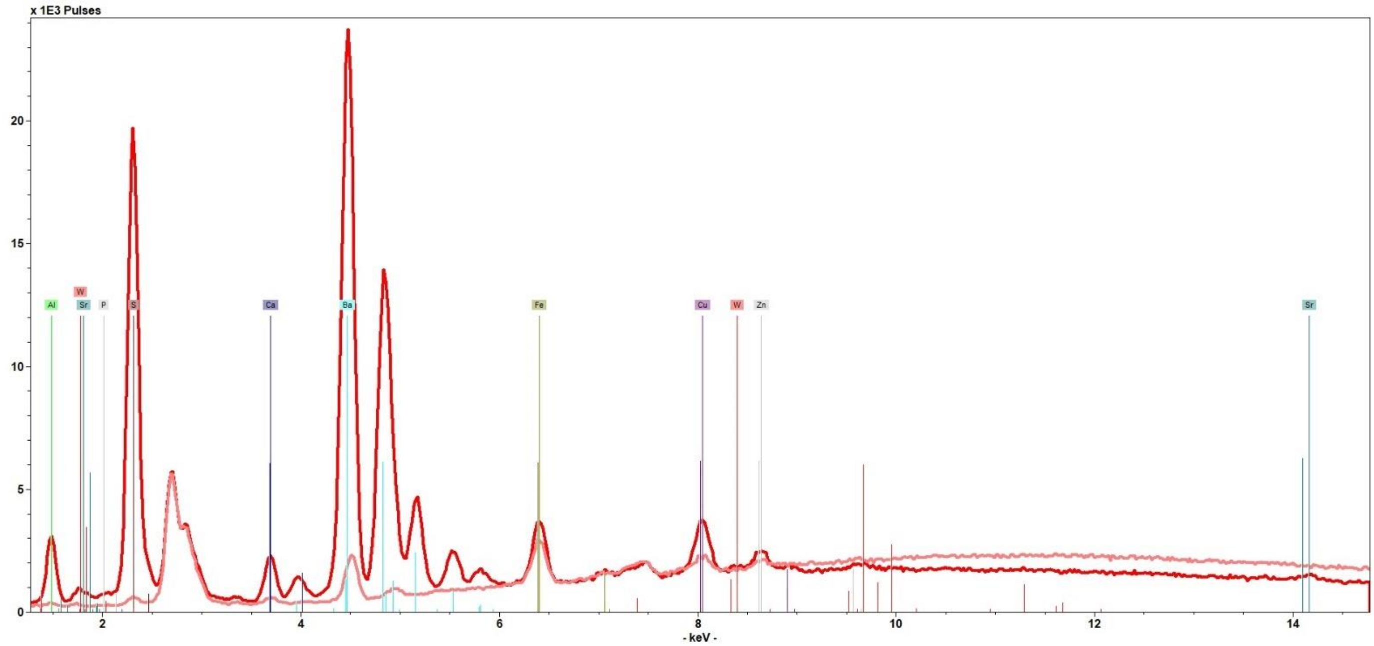

Figure S7: p-XRF spectrum for the (red) magenta gouache M and (light red) paper support (plate P6). Elements present: Al, P, S, Ca, Fe, Cu, Zn, Sr, Ba and W.

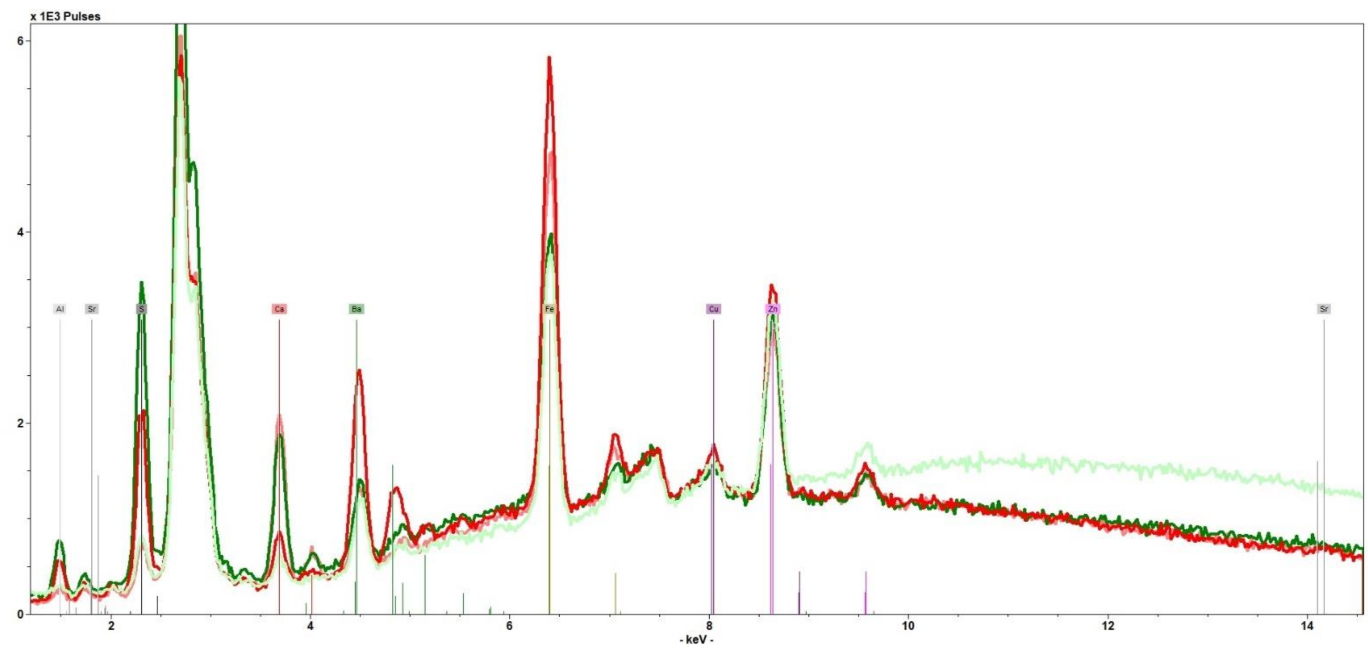

Figure S8: p-XRF spectrum for the pink gouaches: (red and light red) Pk1 and paper support (plate P16) and (green and light green) Pk2 (plate P20). Elements present in the gouaches: Al, S, Ca, Fe, Cu, Zn, Sr and Ba.

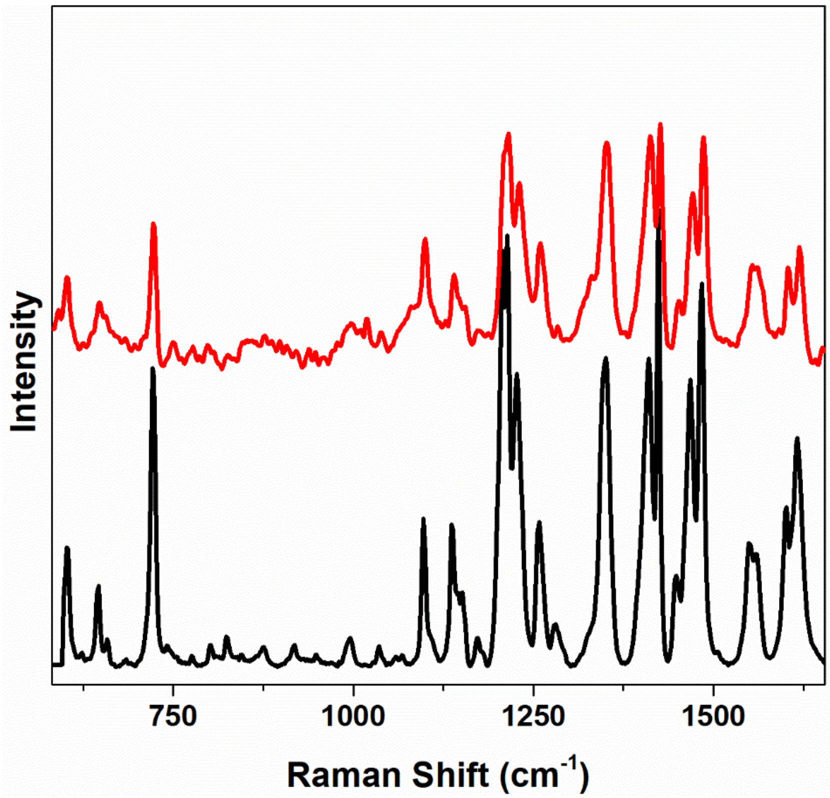

Figure S9: Confocal Raman spectrum of Pink 2 (Pk2) alongside reference spectrum for PR 49:2 (602, 648, 655, 723, 997, 1039, 1000, 1140, 1155, 1260, 1283, 1330, 1351, 1412, 1426, 1452, 1470, 1485, 1554, 1560, 1603, 1619 cm^{-1}).

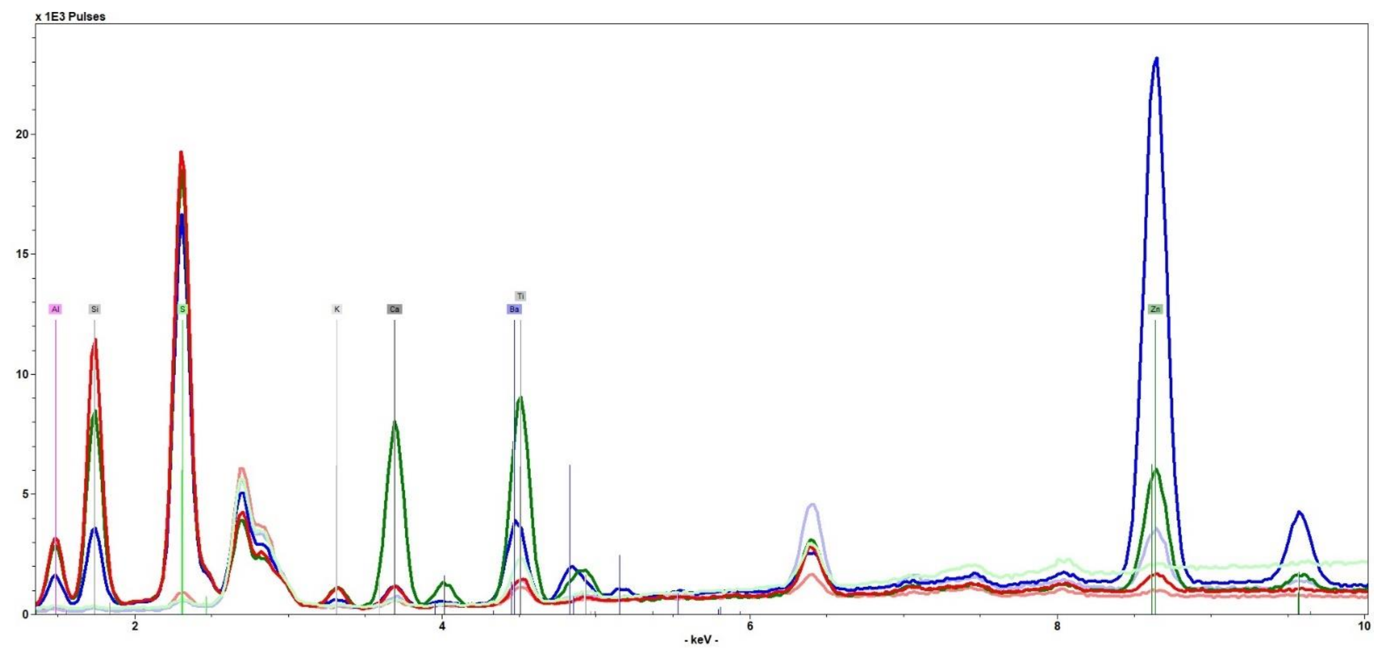

Figure S10: p-XRF spectrum for the blue gouaches: (red and light red) B1 and paper support (plate P1), (green and light green) B2 (plate P19), (blue and light blue) B3 and paper support (plate P6). Elements present in the gouaches: Al, Si, S, K, Ca, Ti, Zn and Ba.

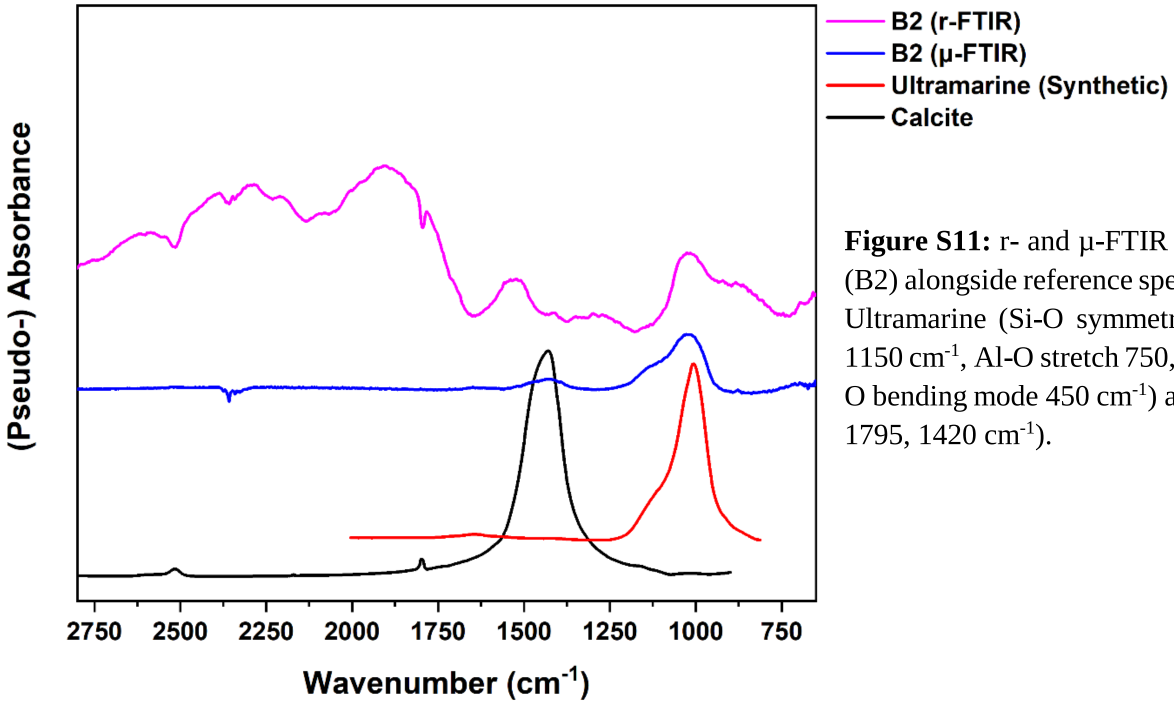

Figure S11: r- and μ-FTIR spectra of Blue 2 (B2) alongside reference spectra for Synthetic Ultramarine (Si-O symmetric stretch (1010, 1150 cm^{-1}, Al-O stretch 750, 650 cm^{-1}, and Si-O bending mode 450 cm^{-1}) and Calcite (2514, 1795, 1420 cm^{-1}).

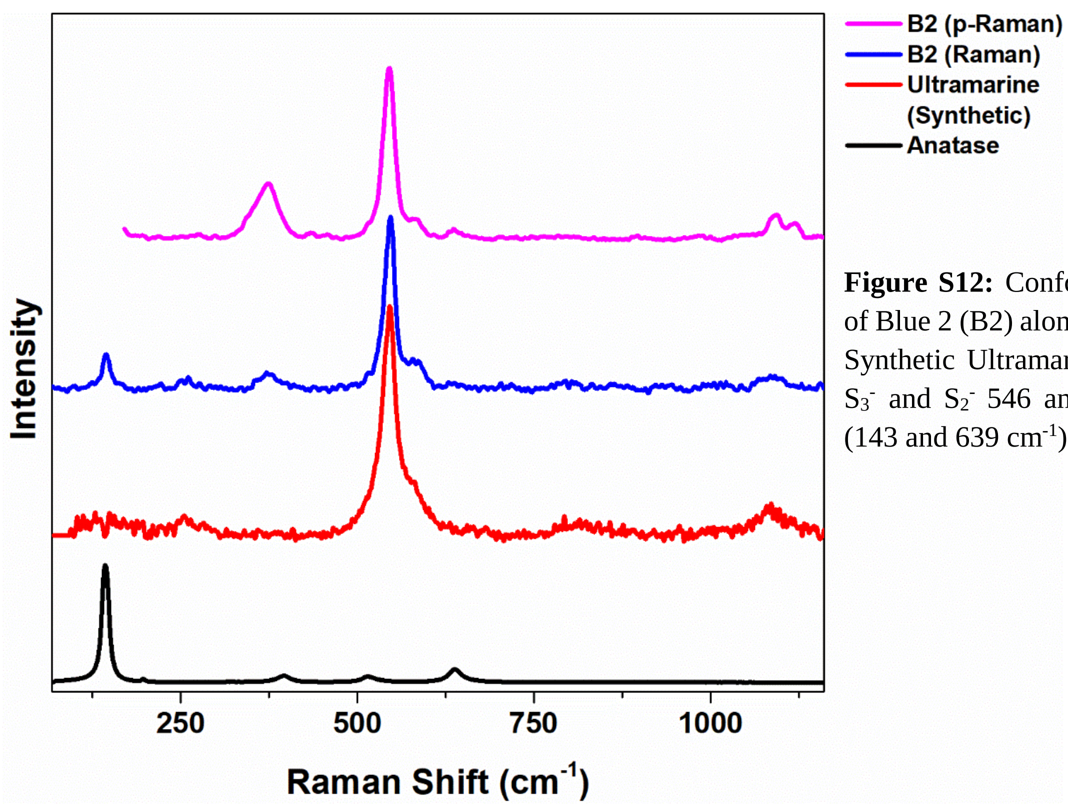

Figure S12: Confocal and p-Raman spectra of Blue 2 (B2) alongside reference spectra for Synthetic Ultramarine (sulfur radical anions S_3^- and S_2^- 546 and 580 cm^{-1}) and Anatase (143 and 639 cm^{-1}).

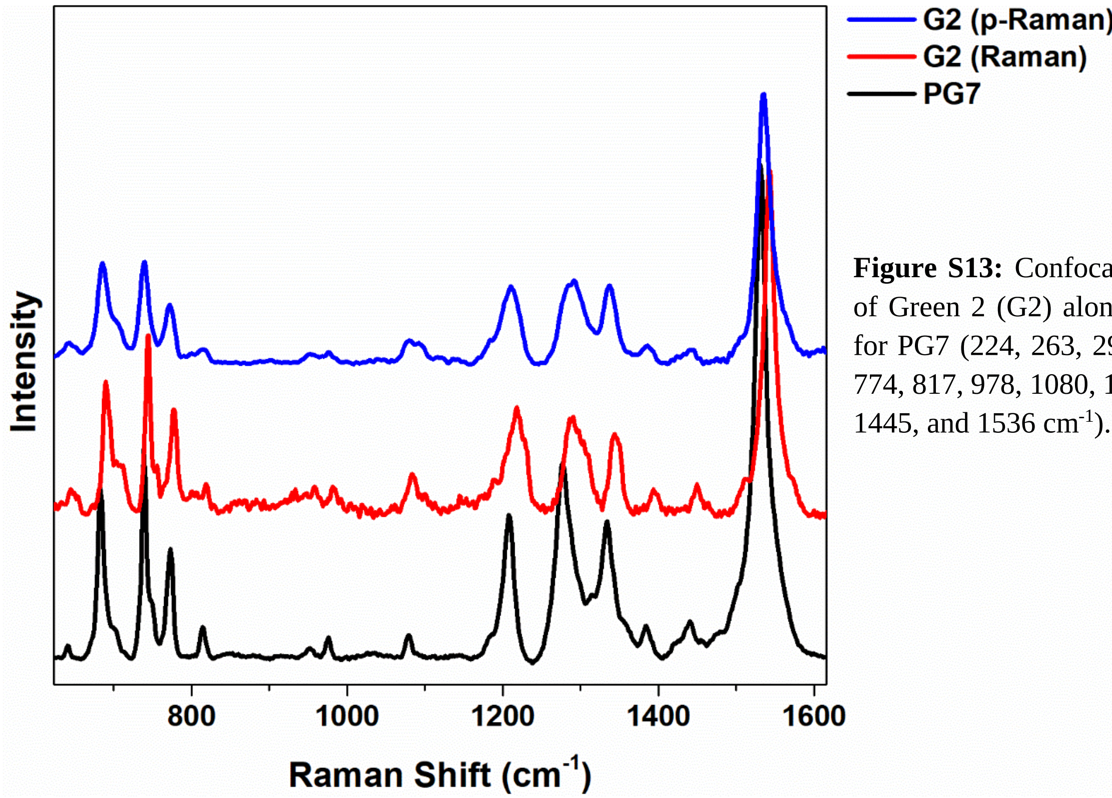

Figure S13: Confocal and p-Raman spectra of Green 2 (G2) alongside reference spectra for PG7 (224, 263, 291, 644, 682, 705, 739, 774, 817, 978, 1080, 1212, 1281, 1338, 1387, 1445, and 1536 cm^{-1}).

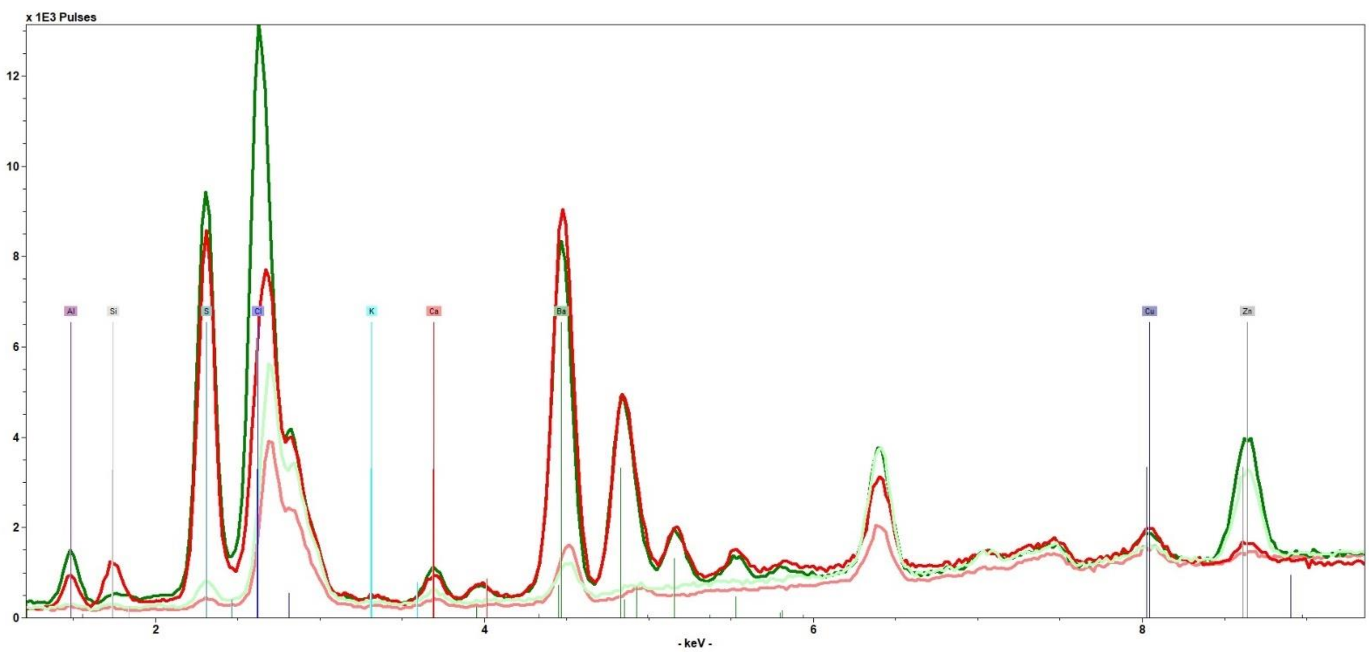

Figure S14: p-XRF spectrum for the green gouaches: (red and light red) G1 and paper support (plate P20), (green and light green) G3 (plate P6). Elements present in the gouaches: Al, Si, S, Cl, K, Ca, Cu, Zn and Ba.

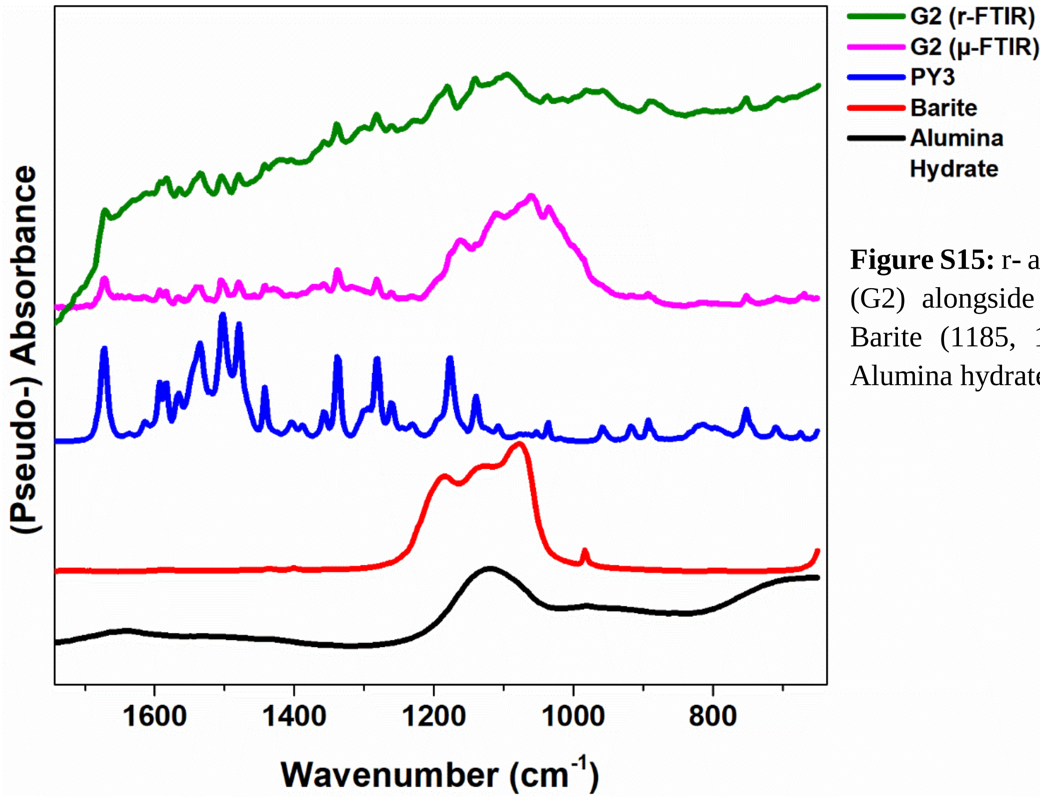

Figure S15: r- and μ-FTIR spectra of Green 2 (G2) alongside reference spectra for PY3, Barite (1185, 1114, 1077, 984 cm^{-1}) and Alumina hydrate (1122, 982, 940 cm^{-1}).

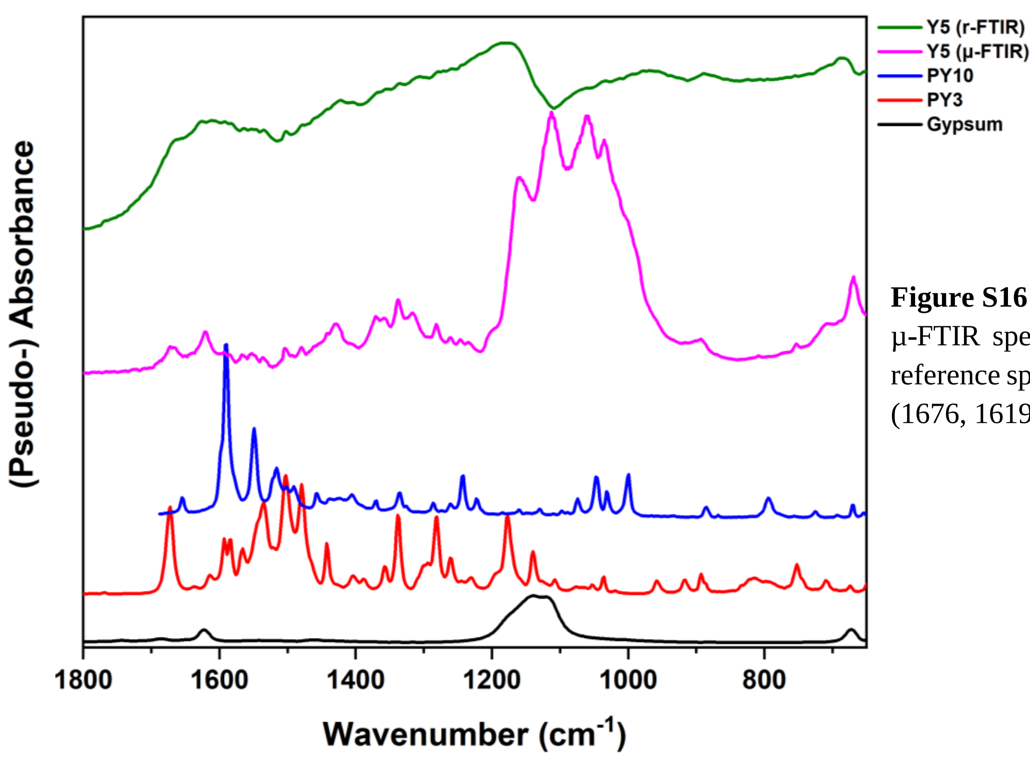

Figure S16: r- (with KK transformation) and μ-FTIR spectra of Yellow 5 (Y5) alongside reference spectra for PY10, PY3 and Gypsum (1676, 1619, 1112, and 675 cm^{-1}).

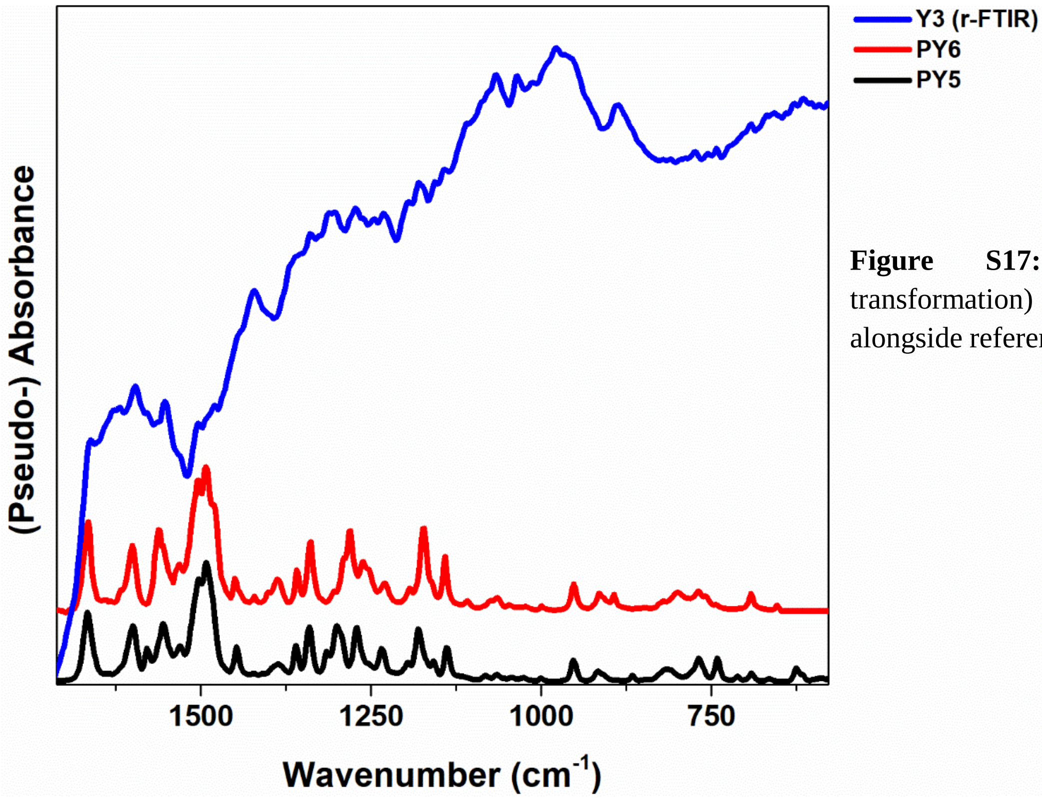

Figure S17: r-FTIR (with KK transformation) spectrum of Yellow 3 (Y3) alongside reference spectra for PY6 and PY5.

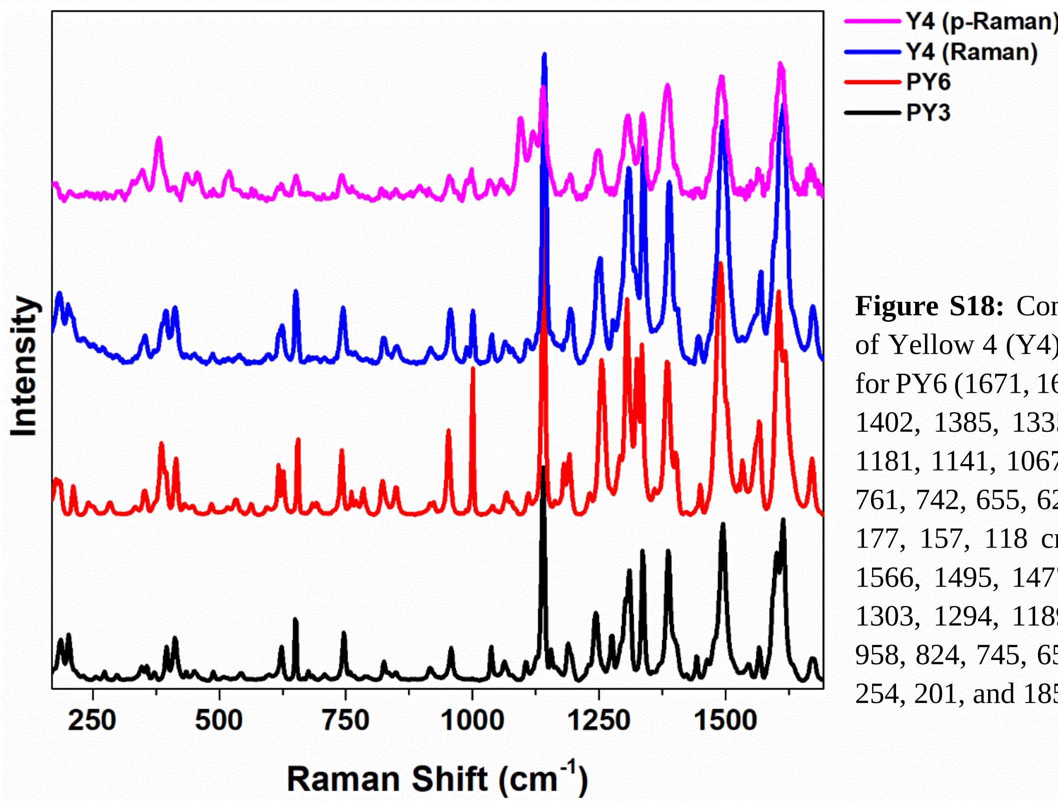

Figure S18: Confocal and p-Raman spectra of Yellow 4 (Y4) alongside reference spectra for PY6 (1671, 1605, 1576, 1533, 1490, 1451, 1402, 1385, 1335, 1325, 1306, 1255, 1192, 1181, 1141, 1067, 1000, 953, 849, 822, 784, 761, 742, 655, 626, 617, 414, 386, 352, 212, 177, 157, 118 cm^{-1}) and PY3 (1614, 1594, 1566, 1495, 1477, 1440, 1387, 1337, 1310, 1303, 1294, 1189, 1139, 1104, 1060, 1034, 958, 824, 745, 650, 622, 395, 356, 346, 270, 254, 201, and 185 cm^{-1}).

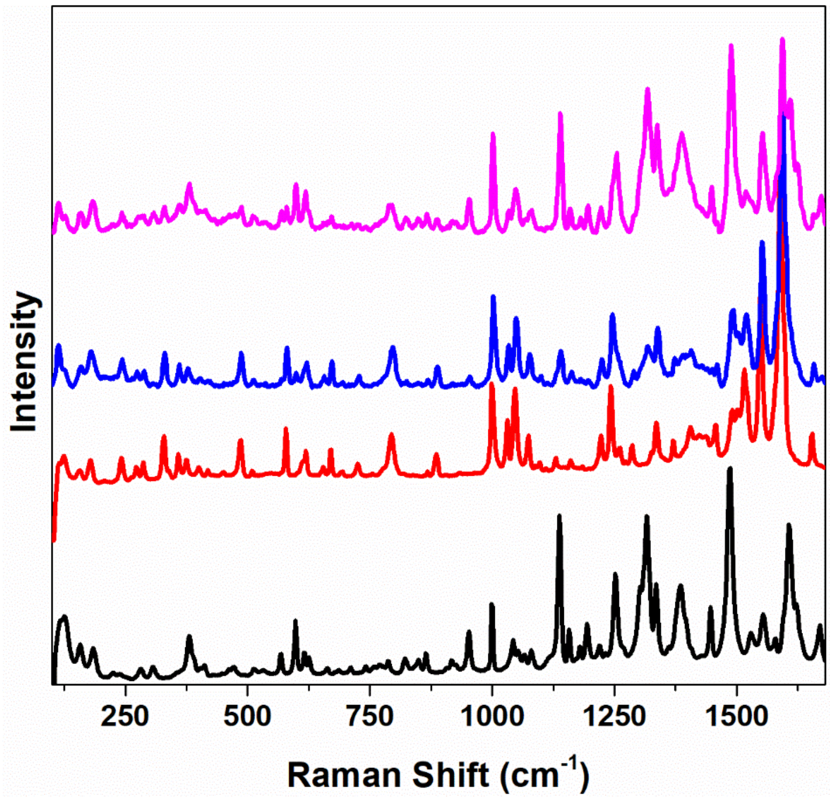

Figure S19: Confocal and p-Raman spectra of Yellow 1 (Y1) and Yellow 2 (Y2) alongside reference spectra for PY10 (1590, 1549, 1516, 1501, 1491, 1457, 1405, 1335, 1243, 1222, 1074, 1046, 1031, 1000, 885, 794, 670, 619, 578, 485, 400, 375, 358, 329, 286 cm^{-1}) and PY5 (1667, 1598, 1575, 1532, 1500, 1460, 1434, 1411, 1368, 1338, 1302, 1243, 1204, 1153, 1079, 1050, 1030, 1001, 893, 839, 795, 758, 715, 674, 626, 583, 457, 443, 397, 313, 245, 213, and 112 cm^{-1}).

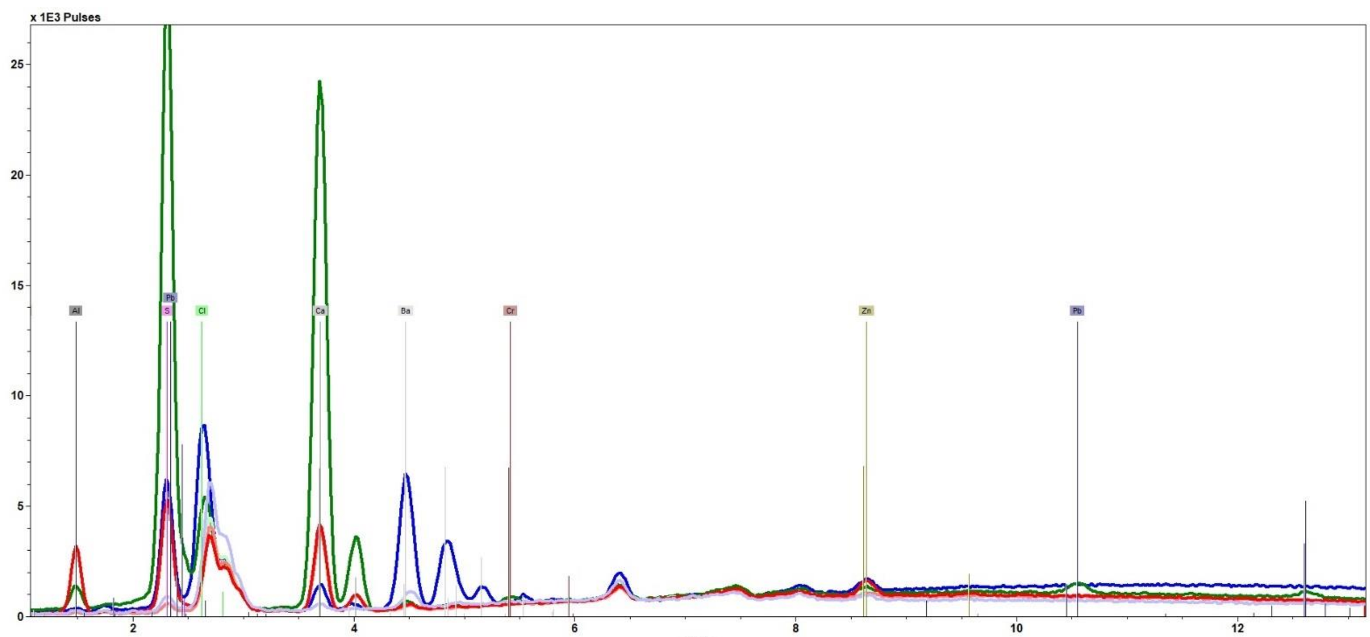

Figure S20: p-XRF spectrum for the yellow gouaches: (red and light red) Y1 and paper support (plate P10), (blue and light blue) Y4 (plate P1) and (green and light green) Y5 (plate P11). Elements present in the gouaches: Al, S, Cl, Ca, Cr, Zn, Ba and Pb.

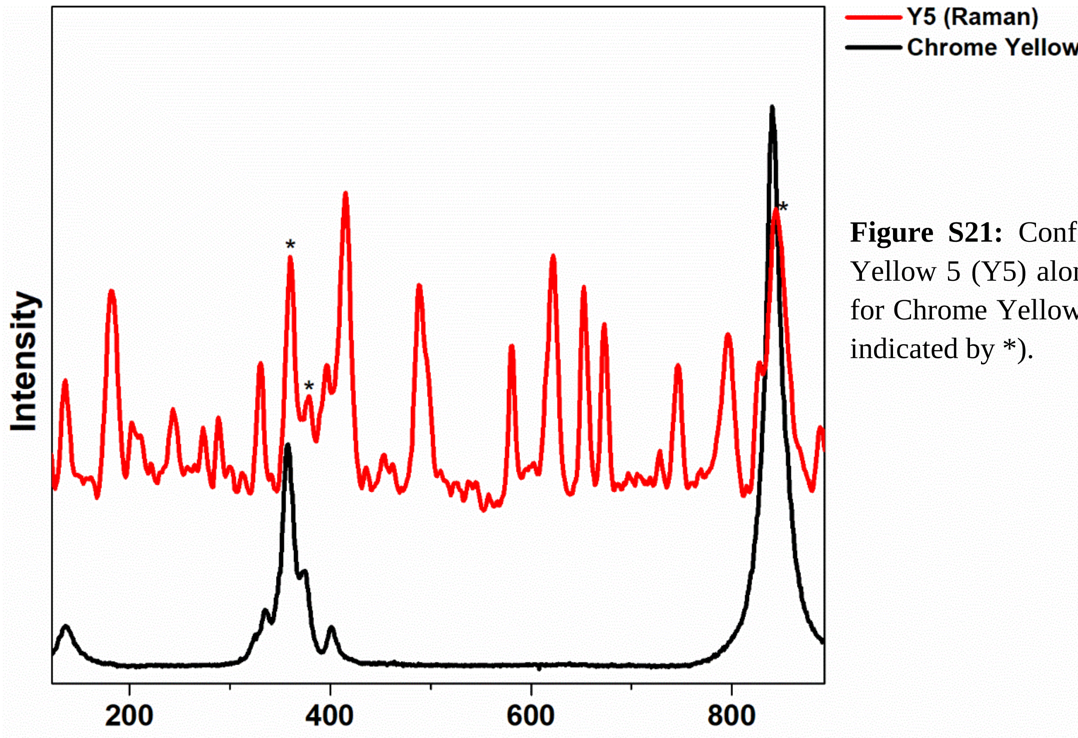

Figure S21: Confocal Raman spectrum of Yellow 5 (Y5) alongside reference spectrum for Chrome Yellow (360, 378, and 844 cm^{-1}; indicated by *).

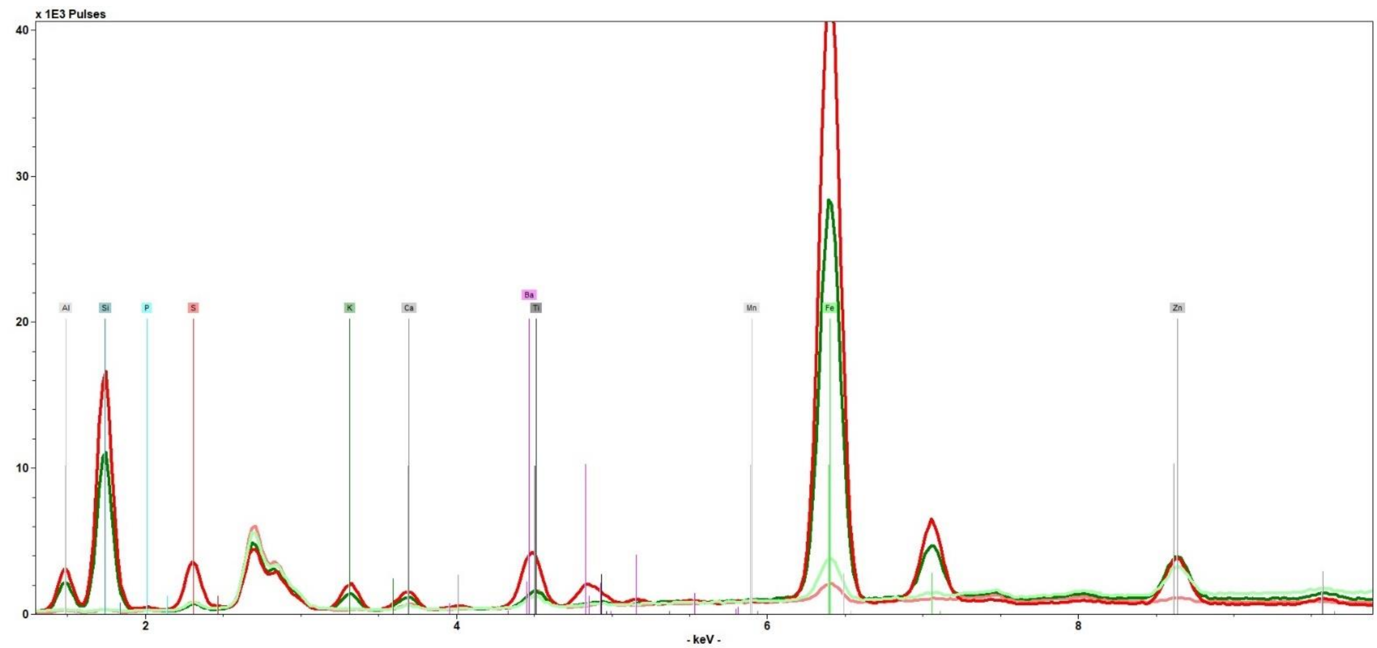

Figure S22: p-XRF spectrum for the orange gouaches: (red and light red) O4 and paper support (plate P2) and (green and light green) O5 (plate P20). Elements present in the gouaches: Al, Si, P, S, K, Ca, Ti, Mn, Fe, Zn and Ba.

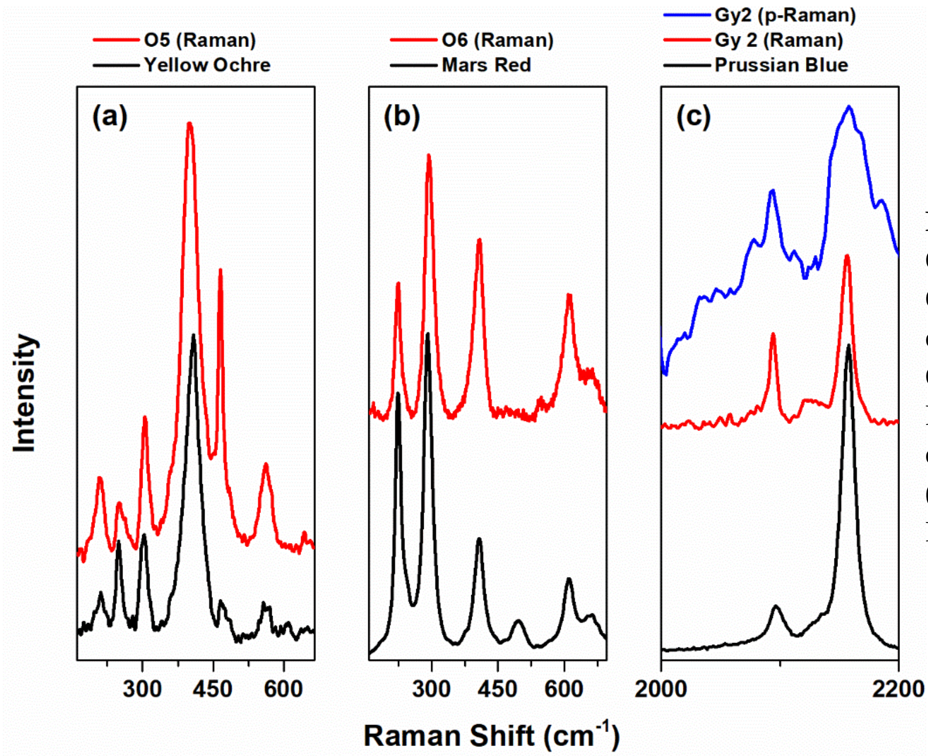

Figure S23: (a) Confocal Raman spectrum of Orange 5 (O5) alongside reference for Yellow Ochre (207, 248, 305, 357, 400, 464, and 561 cm^{-1}); (b) confocal Raman spectrum of Orange 6 (O6) alongside reference for Mars Red (223, 293, 408, and 510 cm^{-1}) ; (c) confocal and p-Raman spectrum of Gray 2 (Gy2) alongside reference spectrum of Prussian Blue (2092 and 2160 cm^{-1}).

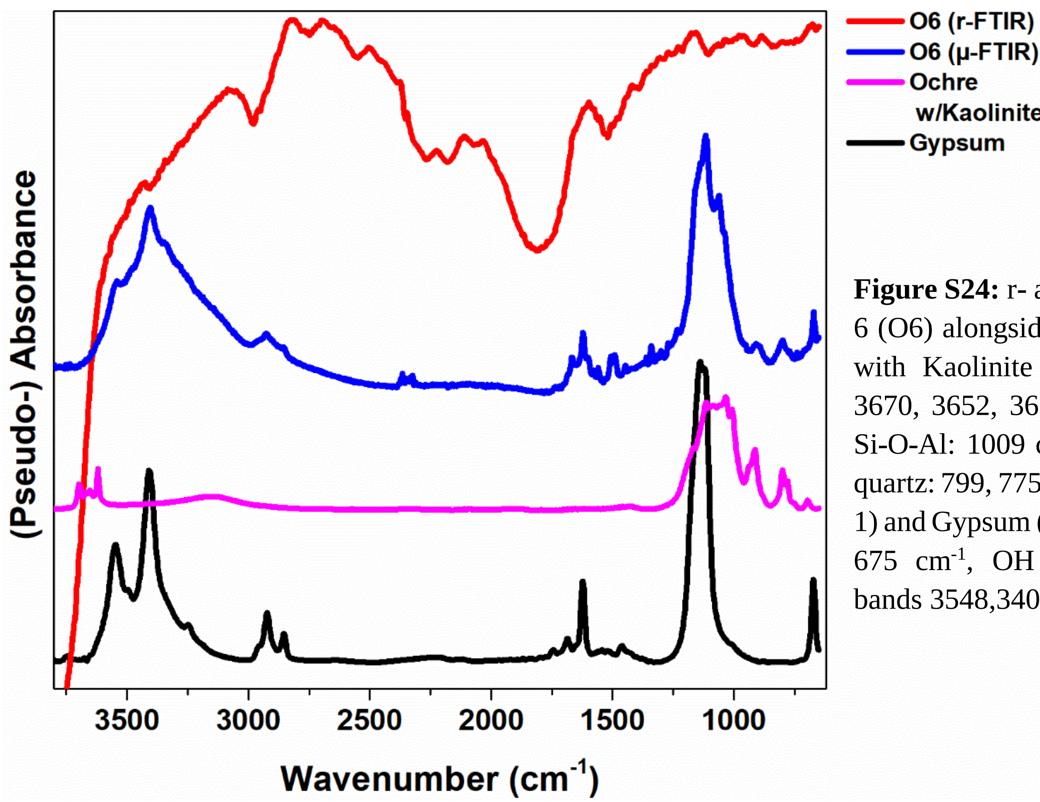

Figure S24: r- and μ-FTIR spectra of Orange 6 (O6) alongside reference spectra for Ochre with Kaolinite (outer hydroxyl ions 3696, 3670, 3652, 3620 cm^{-1}, Si-O-Si: 1027 cm^{-1}; Si-O-Al: 1009 cm^{-1}; Al-O-H: 936, 914 cm^{-1}, quartz: 799, 775 cm^{-1}; haematite: 540, 469 cm-1) and Gypsum (sulfate vibration bands; 1112, 675 cm^{-1}, OH stretching and deformation bands 3548,3408, 1676,1619 cm^{-1}).

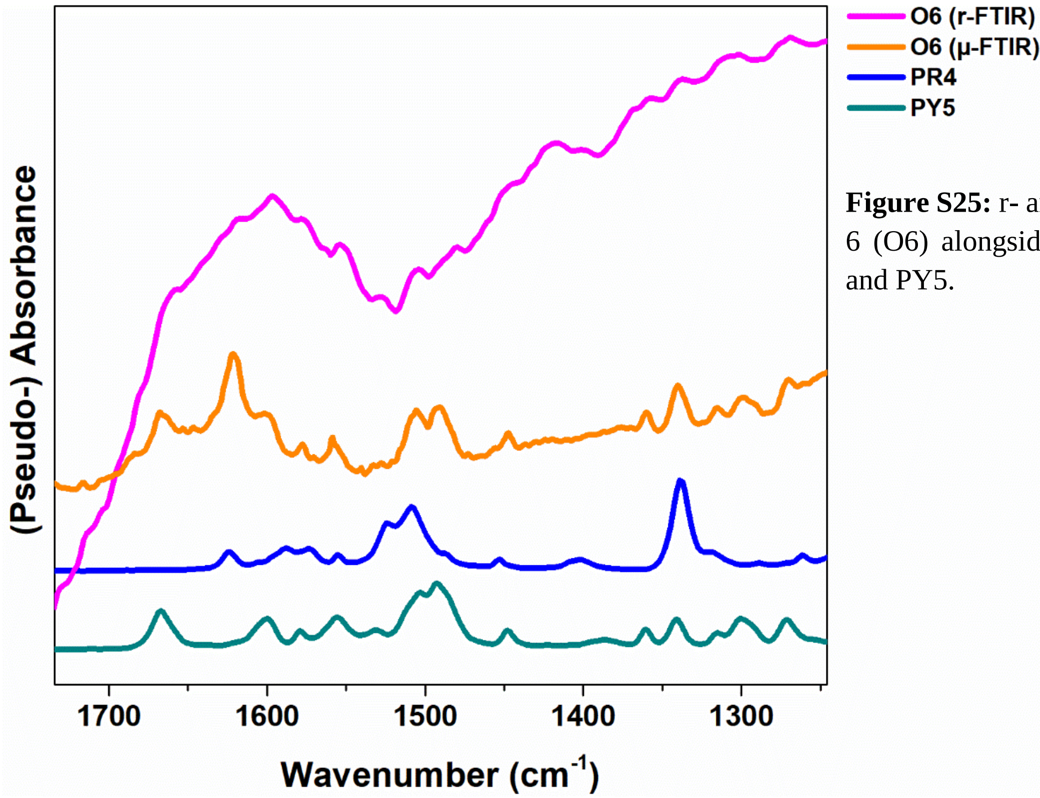

Figure S25: r- and µ-FTIR spectra of Orange 6 (O6) alongside reference spectra for PR4 and PY5.

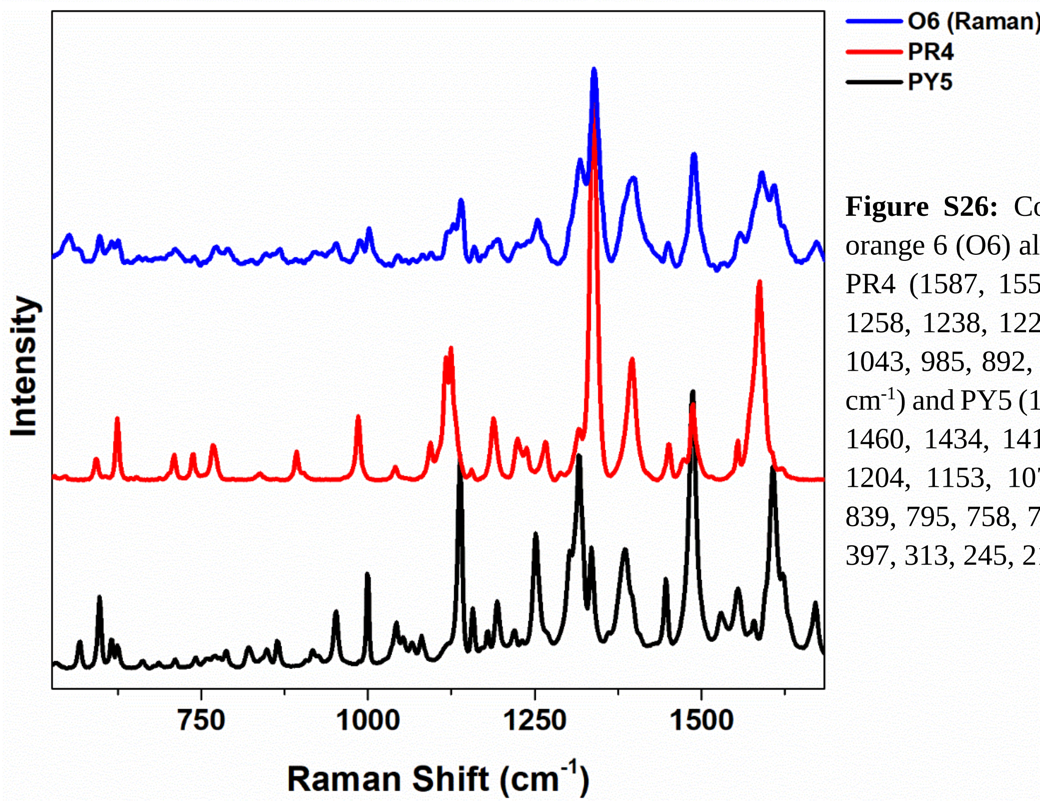

Figure S26: Confocal Raman spectrum of orange 6 (O6) alongside reference spectra for PR4 (1587, 1556, 1485, 1450, 1395, 1337, 1258, 1238, 1225 , 1189, 1124, 1117, 1092, 1043, 985, 892, 767, 738, 709, 624, and 593 cm^{-1}) and PY5 (1667, 1598, 1575, 1532, 1500, 1460, 1434, 1411, 1368, 1338, 1302, 1243, 1204, 1153, 1079, 1050, 1030, 1001, 893, 839, 795, 758, 715, 674, 626, 583, 457, 443, 397, 313, 245, 213, and 112 cm^{-1}).

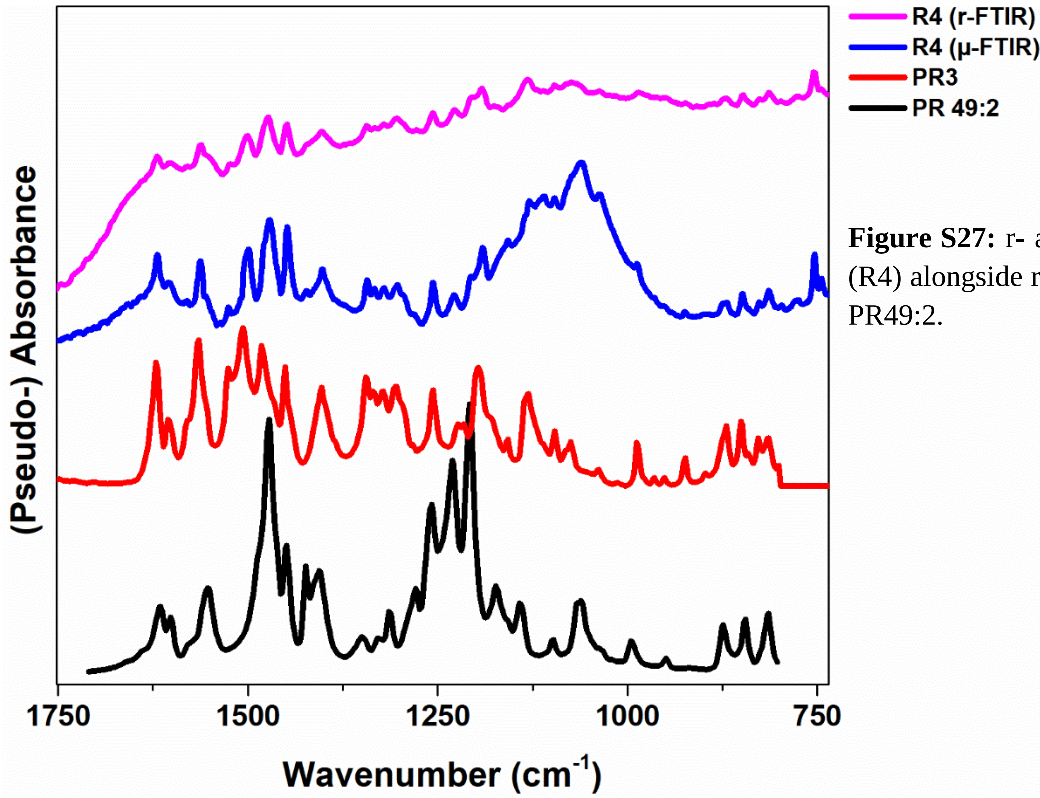

Figure S27: r- and μ-FTIR spectra of Red 4 (R4) alongside reference spectra for PR3 and PR49:2.

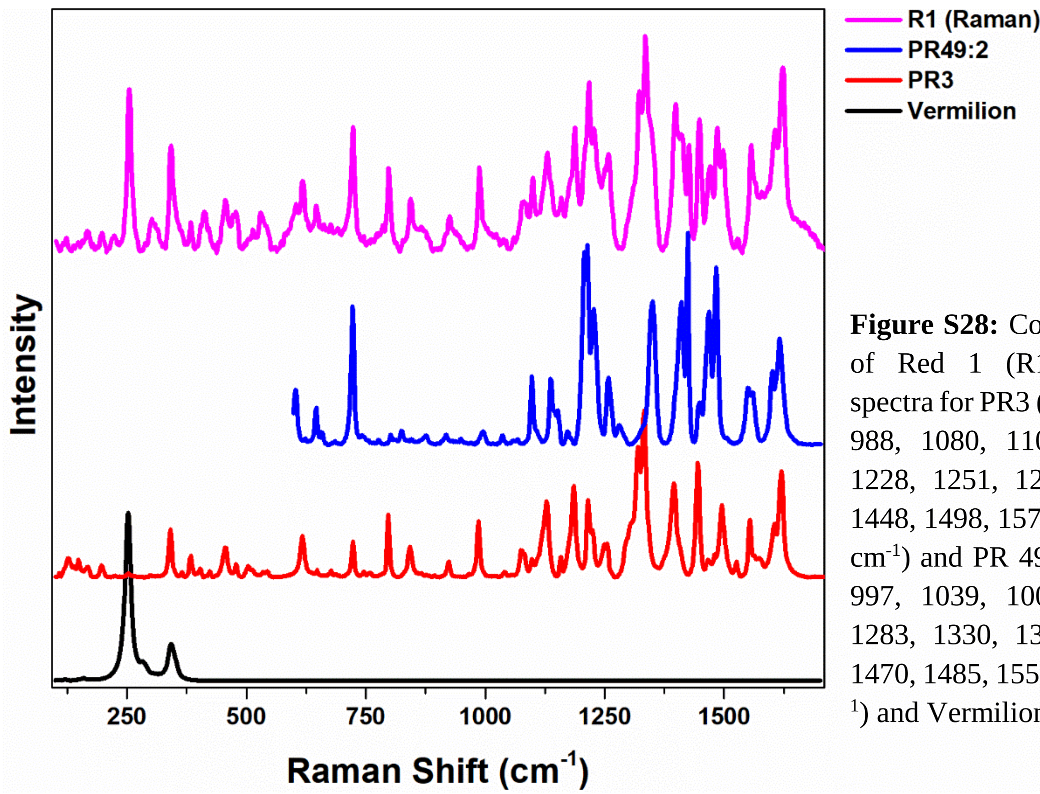

Figure S28: Confocal Raman spectrum of Red 1 (R1) alongside reference spectra for PR3 (617, 722, 798, 843, 925, 988, 1080, 1100, 1160, 1187, 1217, 1228, 1251, 1258, 1322, 1335, 1398, 1448, 1498, 1572, 1557, 1607, and 1623 cm^{-1}) and PR 49:2 (602, 648, 655, 723, 997, 1039, 1000, 1140, 1155, 1260, 1283, 1330, 1351, 1412, 1426, 1452, 1470, 1485, 1554, 1560, 1603, 1619 cm^{-1}) and Vermilion (255 and 342 cm^{-1}).

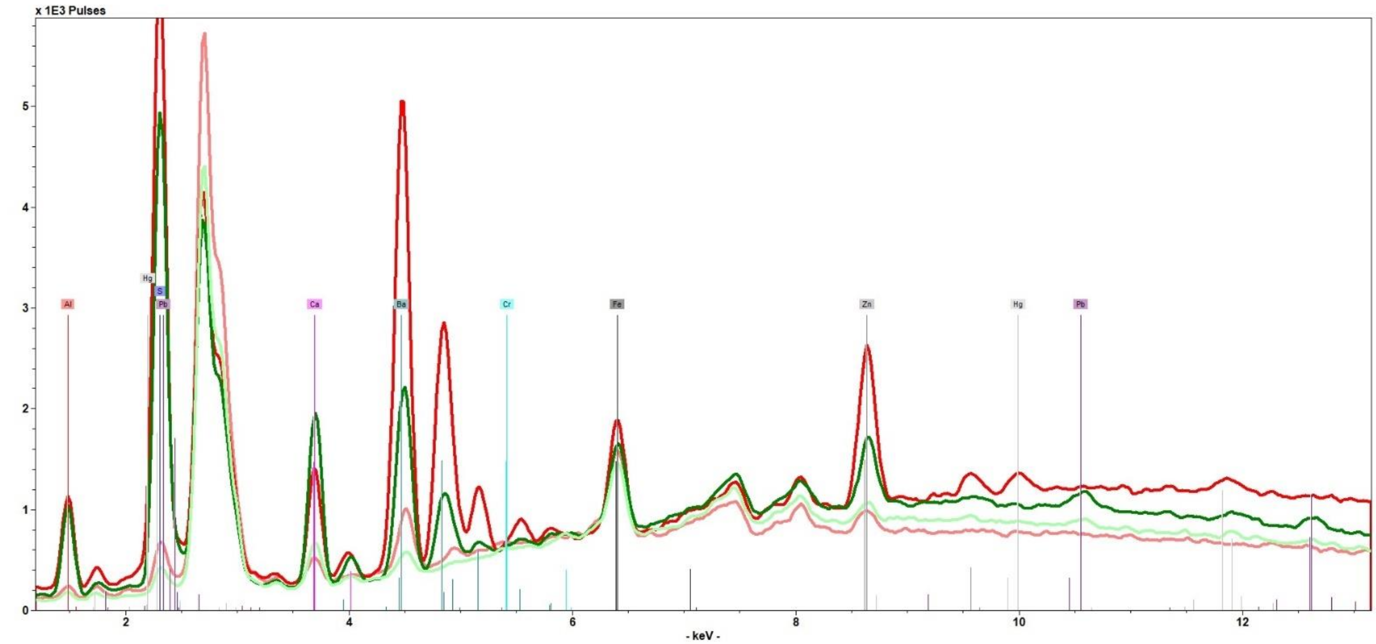

Figure S29: p-XRF spectrum for the red gouaches: (red and light red) R1 and paper support (plate P1) and (green and light green) R2 (plate P4). Elements present in the gouaches: Al, S, Ca, Cr, Zn, Ba, Hg and Pb.

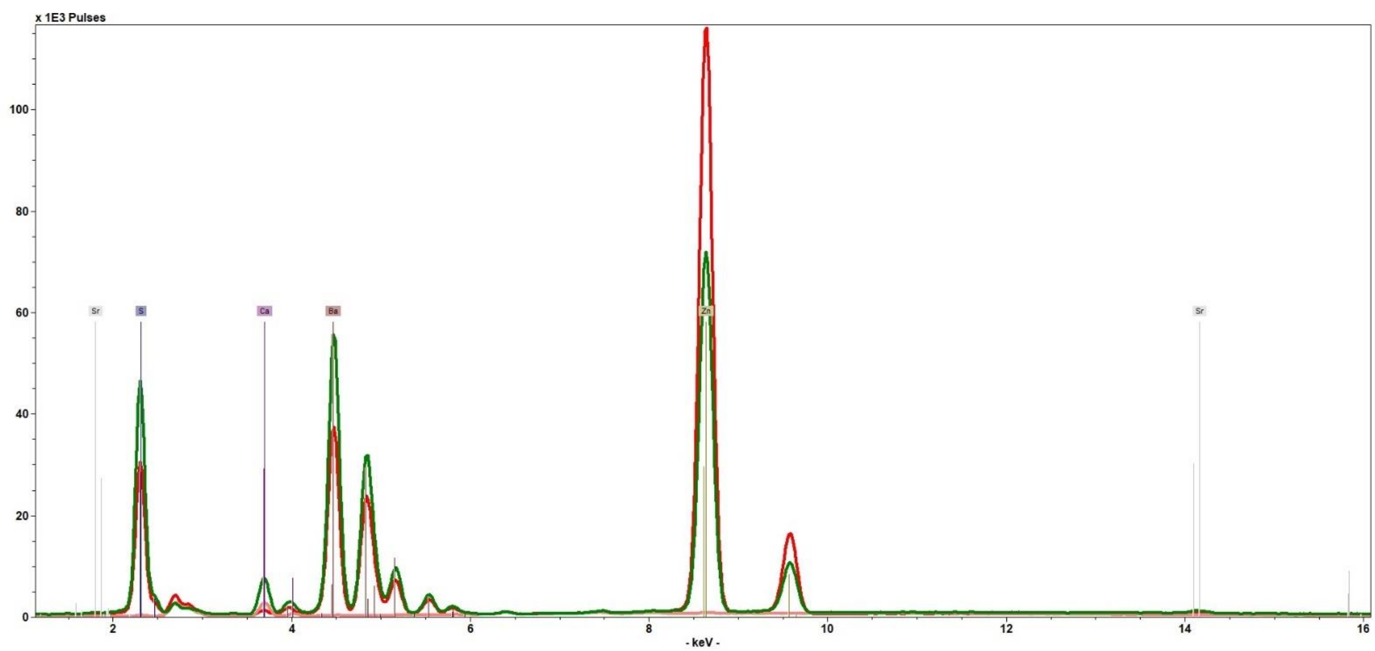

Figure S30: p-XRF spectrum for the white gouaches: (red and light red) W1 and paper support (plate P12) and (green and light green) W2 (plate P17). Elements present in the gouaches: S, Ca, Zn, Sr, Ba.

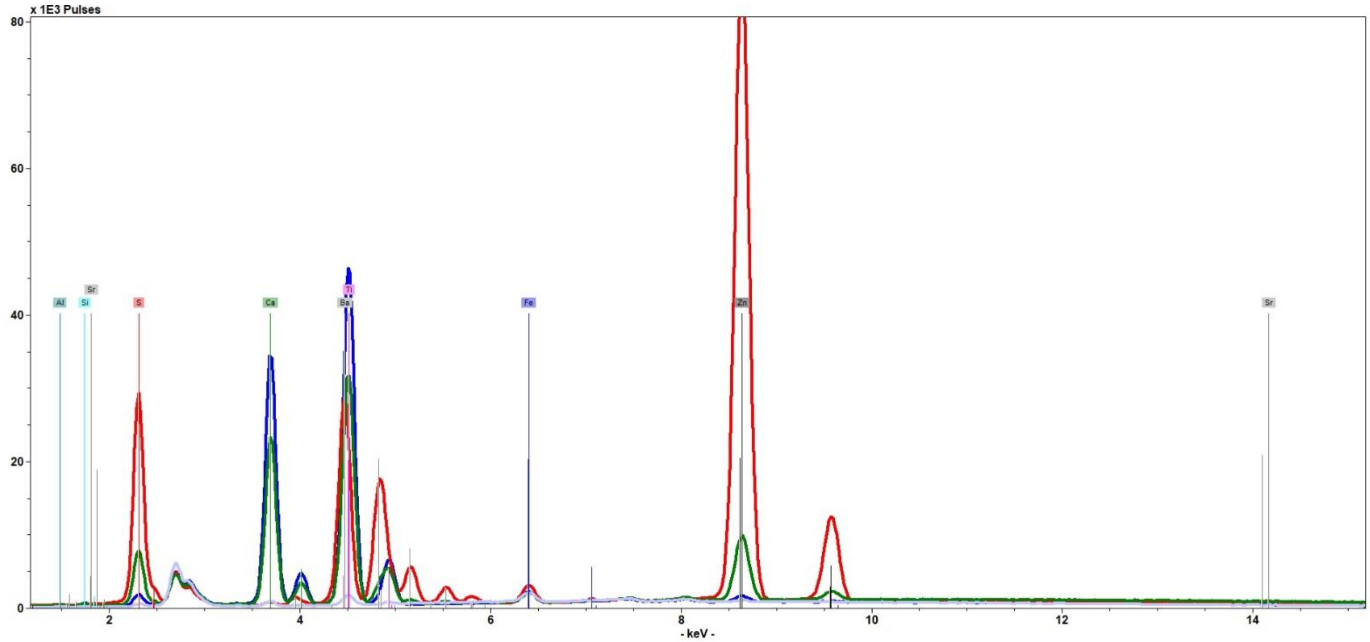

Figure S31: p-XRF spectrum for the gray gouaches: (red) Gy1 (plate P18), (green) Gy2 (plate P7) and (blue and light blue) Gy3 and paper support (plate P9). Elements present in the gouaches: Al, Si, S, Ca, Ti, Fe, Zn, Sr, Ba.

Synthetic procedure for obtaining silver nanoparticles (AgNP) via the Lee-Miesel method, in addition to acid-pretreatment considerations for SERS analysis.

AgNPs for SERS measurements were synthesized using the Lee-Meisel method. Two mL of a boiling 1% w/w solution sodium citrate were added to a 100 mL boiling solution of $1x10^{-3}$ M $AgNO_3$ under agitation and left to simmer under reflux for approximately an hour. Colloids were concentrated 5 times over by centrifugation. SERS spectra were obtained before and after sample acid-based treatments that hydrolyze the pigments or dye into the colloid solution and, as a result, in greater contact with silver nanoparticles. Spectra were obtained of the same sample successively following each treatment. The first spectra were obtained by dropping 2 µL of AgNPs onto the sample followed by 0.8 µL of KNO_3 to induce aggregation of the AgNPs. Second, after the colloidal solution was allowed to evaporate, 1 µL of 1% HNO_3 was dropped directly onto the sample before adding 2 µL of AgNPs— here HNO_3 to act as an aggregating agent. Third, after the solution was allowed to evaporate again, the sample was exposed to HF vapor. After 10 min of exposure, 2 µL of AgNPs followed by 0.8 µL of KNO_3 were added for the final SERS spectra.