

SUPPLEMENTARY INFORMATION

Shedding light on the composition and degradation mechanism of dyes in historical ink's collection (19th-20th century)

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S1 Experimental details

S1.1 Reagents and solvents

The solvents and reagents used for the sample pre-treatments were: ethylenediaminetetraacetic acid disodium salt (EDTA, Fluka, USA), dimethylformamide (DMF; 99.8% purity, J.T. Baker, USA), ethanol (Sigma Aldrich, Italy), acetone (99.8% purity; Sigma Aldrich, USA) and MilliQ water. The eluents used for TLC were: acetone, isopropyl alcohol (HPLC grade; 99.8% purity; Sigma Aldrich, Italy) and ammonium hydroxide solution (ACS reagent, 28.0–30.0% NH₃ basis). The reagents used for the synthesis of silver nanoparticles were: silver nitrate (AgNO₃; 99.8% purity; Merck, Germany) and sodium citrate tribasic dehydrate (ACS reagent; 99.0% purity; Sigma Aldrich, Milan). The eluents used for HPLC-DAD and HPLC-ESI-Q-ToF were: water and acetonitrile, both HPLC grade (Sigma Aldrich, USA) for HPLC-DAD analysis and both LC-MS grade (Sigma Aldrich, USA) for HPLC-ESI-Q-ToF analysis. All eluents were added with 0.1% v/v of formic acid (FA; J.T. Baker, USA). PTFE filters (4mm thickness and 0.45 µm pore diameter) were used for the purification prior to HPLC injection.

The standards and reference materials used for the identification of the different dyes were:

Rhodamine 6G	Sigma Aldrich (Milan)
Rhodamine B	Sigma Aldrich (Milan)
Eosin Y	Sigma Aldrich (USA)
Eosin B	Carl Roth GmbH+Co.KG (Germany)
Erythrosine	Reference material from the collection of Cultural Heritage Agency of the Netherlands (Amsterdam)
Cotton Scarlet	Sigma Aldrich (USA)
Fuchsin	Kremer pigmente (Germany)

S1.2 Preparation of Ag nanoparticles

The synthesis of the silver nanoparticles (AgNPs) was performed according to Lee & Meisel procedure [1]. 27 mg of AgNO₃ were dissolved in 150 mL of deionized water and brought to boiling. A solution of 1% trisodium citrate (3 mL) was added. The solution was kept on boiling for 1 hour at dark (reflux, magnetic stirring). Silver nanoparticles were concentrated and partially separated from surfactant by centrifugation at 6000 rpm for 15 min. The supernatant was removed and the solid was redispersed in deionized water to obtain a 10-fold

preconcentration. Nanoparticles were characterized by UV-Vis spectroscopy (Perkin Elmer Lambda 25 double beam spectrophotometer, scans from 300 to 600 nm, scan rate 240 nm/min, 1 nm slits). Briefly, a UV-Vis measurement was performed on AgNPs dispersion (1:10 dilution). The values of maximum absorbance and the corresponding wavelength were registered and used to roughly estimate the dimensions of the NPs (Supplementary Information, Table S.1) [2], using tabulated values and Lambert-Beer's law.

S1.3 Surface Enhanced Raman Scattering (SERS)

SERS measurements were made on a Renishaw InVia instrument coupled with an optical Leica DLML microscope, equipped with a NPLAN objective 20× and 50×. The spectrometer consists of a single grating monochromator (1800 lines mm⁻¹), coupled with a CCD detector, a RenCam 578 × 400 pixels (22 μm × 22 μm) cooled by a Peltier-element. The excitation wavelength was obtained by a Nd:YAG laser at 532 nm. Typical measurements conditions were 10 s acquisition time and 2 accumulations with a laser power at the sample lower than 0.3 mW. All SERS spectra were recorded between 350-2200 cm⁻¹, where the main Raman and SERS signals of dyes are located. The spectral intensities were normalized by scaling their values between 0 and 1. The spectral calibration of the instrument was performed on the 520.5 cm⁻¹ band of a pure silicon crystal.

S1.4 Thin Layer Chromatography- Surface Enhanced Raman Scattering (TLC-SERS)

The components of historical inks were separated by a silica gel plate (TLC Silica gel 60 plates; aluminium sheets; Supelco) as stationary phase and a 11:1:2 isopropyl alcohol:acetone:ammonia solution as eluent. 1-2 mg of ink's powder was suspended in 50 μL of acetone. A small amount (~2 μL) of the extract was deposited onto the TLC plate by means of a glass capillary and eluted in a glass-developing chamber. The separated spots were visualized under a UV lamp at 254 and 365 nm. The separated components were analysed directly on the TLC plate by placing 1 μL of AgNPs on top of each spot.

S1.5 High Performance Liquid Chromatography (HPLC-DAD-MS²)

The HPLC-DAD system consists of a PU-2089 quaternary pump (Jasco International Co., Japan) equipped with a degasser, an AS-950 autosampler (Jasco International Co., Japan), an MD-2010 spectrophotometric diode array detector (DAD) (Jasco International Co., Japan). ChromNav software was used to carry out data acquisition and data analysis. The DAD detector operated with spectra acquisition in the range of 200–650 nm every 0.2 s with 4 nm resolution.

For HPLC-ESI-Q-ToF analysis, an HPLC 1200 Infinity, coupled to a Jet Stream ESI-Q-ToF 6530 Infinity detector and equipped with an Agilent Infinity autosampler (Agilent Technologies, Palo Alto, CA, USA) was used. MassHunter® Workstation Software (B.04.00) was used to carry out mass spectrometer control, data acquisition, and data analysis. The mass spectrometer operated in ESI ionization, both in negative and positive mode, and the working conditions were: drying gas N₂ (purity>98%) temperature 350 °C and 10 L/min flow; capillary voltage 4.5 KV; nebulizer gas pressure 35 psig; sheath gas temperature 375 °C and 11

L/min flow; fragmentor voltage 175 V. High resolution MS and MS/MS spectra were acquired both in negative and positive mode in the range 100-1700 m/z at a scan rate of 1.04 spectra/sec (CID voltage 30 V, collision gas N₂, purity 99.999%). Auto-calibration was performed daily using Agilent tuning mix HP0321 (Agilent Technologies) prepared in acetonitrile.

The chromatographic separation was performed in both systems on an analytical reversed-phase column Poroshell 120 EC-C18 (3.0 x 75 mm, particle size 2.7 µm,) with a pre-column Zorbax (4.6 x 12.5 mm, particle size 5 µm) both Agilent Technologies (Palo Alto, CA, USA). The eluents were A: formic acid (FA 0.1% v/v) in LC-MS grade water and B: formic acid (FA 0.1% v/v) in LC-MS grade acetonitrile. The flow rate was 0.4 mL/min and the program was 15% B for 2.6 min, then to 50% B in 13.0 min, to 70% B in 5.2 min, to 100% B in 0.5 min and then hold for 6.7 min; re-equilibration took 11 min. During the separation, in both systems, the column was thermostated at 30 °C. The injection volume was 10 µL and 1 µL for the HPLC-DAD and HPLC-MS/MS analysis, respectively.

Prior to HPLC analysis, 100-200 µg of ink's powder were suspended in 300-400 µL of 0.1% EDTA aqueous solution/DMF (EDTA-DMF, 1:1, v/v), and sonicated for 1 h at 60 °C. The supernatant was purified with PTFE syringe filters (4 mm thickness and 0.45 µm pore diameter, Agilent), and then injected in the chromatographic system.

S1.6 Pyrolysis coupled to gas chromatography-mass spectrometry (Py-GC/MS)

Py-GC/MS analysis was performed using a multi-shot pyrolyzer EGA/PY-3030D (Frontier Lab, Japan) coupled to a 8890 gas chromatograph, combined with a 5977B mass selective single quadrupole mass spectrometer detector (Agilent Technologies, USA). For the mass spectrometer unit (MS), the following parameters were applied: electron impact ionization (EI 70 eV) in positive mode; ion source temperature set at 230 °C; scan range of 35-600 m/z; interface temperature set at 280 °C. To characterize the ink's binder, pyrolysis with in-situ silylation using hexamethyldisilazane (HMDS) as derivatizing agents was carried out. The furnace was set at 550 °C. 150 µg of ink's powder were directly weighted in a deactivated stainless-steel cup. Prior to Py-GC/MS analysis, 4 µL of HMDS were added to the sample, and inserted in the furnace. The pyrolysis products were separated with an HP-5MS capillary column (95% dimethyl-5% diphenyl-polysiloxane; 30 m x 0.25 mm, film thickness 0.25 µm; Agilent Technologies, USA). The GC injector was operated in split mode at 280 °C and with a 20:1 ratio. The GC oven temperature program was: 36 °C for 10 min, 10 °C/min up to 310 °C for 20 min. Helium (He, purity 99.9995%) was used as gas carrier, with a constant flow of 1.2 mL/min.

Table S. 1: Characterization of silver nanoparticles. For the estimation of the diameter, ref. [1] was used.

	λ_{\max} (nm)	d (nm)
Lee & Meisel AgNPs	408.5	34

Table S. 2: SERS typical wavenumbers (cm⁻¹) for rhodamine 6G, rhodamine B, eosin Y, eosin B, erythrosine, fuchsine and cotton scarlet (AR73) (w= weak, m=medium, s=strong) (laser at 532 nm).

Rhodamine 6G	Rhodamine B	Eosin Y	Eosin B	Erythrosine	Fuchsine	Cotton scarlet
1649m	1647s	1620s	1626s	1608s	1617s	1597s
1572w	1529m	1560w	1567m	1499s	1589s	1502s
1510s	1507s	1505s	1510s	1471s	1552m	1466s
1310s	1432w	1478m	1462m	1441w	1518s	1446w
1182m	1358s	1444m	1404w	1302s	1436m	1421s
1125m	1279m	1352w	1336s	1269s	1373m	1377m
1088w	1198m	1310w	1283s	1154w	1281w	1240s
772m	1077w	1271m	1177m	943s	1185m	1144s
659w	933w	959w	1095w	765w	1153w	-
633w	734m	759m	958w	608m	912w	-
610s	622s	638s	704m	556m	832w	-
-	-	329w	477w	-	-	-
-	-	383w	-	-	-	-

Table S. 3: SERS typical wavenumbers (cm⁻¹) obtained with SERS and TLC-SERS analysis of French inks.

French Ink	Dyes	Wavenumber (cm⁻¹)
1	Cotton scarlet	1594, 1499, 1464, 1391, 1307, 1230, 1184, 1136, 723, 641, 413
	Methyl Violet/Crystal Violet	1620, 1588, 1431, 1377, 1296, 1175, 1140, 913, 805, 586, 477, 438, 416
2	Eosine Y	1620, 1585, 1559, 1507, 1455, 1384, 1334, 1279, 1243, 1178, 1029, 943, 640, 472, 363
4	Rhodamine 6G	1649, 1570, 1510, 1361, 1310, 1181, 1126, 1086, 770, 610, 567, 403, 356, 310
	Rhodamine B	1646, 1528, 1506, 1357, 1278, 1200, 619, 354
5	Rhodamine B	1646, 1527, 1507, 1431, 1357, 1278, 1196, 1077, 931, 735, 619, 487, 355
6	Methyl Violet/Crystal Violet	1617, 1587, 1510, 1389, 1365, 1289, 1215, 1172, 912, 801, 758, 730, 525, 439, 417
7	Eosine Y	1624, 1596, 1541, 1502, 1319, 1174, 1125, 1125, 1061, 1029, 765, 647, 595, 552, 496, 460
9	Acid Red 73	1595, 1498, 1463, 1440, 1417, 1375, 1307, 1237, 1185, 1138, 999, 647, 529, 469
	Methyl Violet/Crystal Violet	1618, 1588, 1296, 1179, 913, 806, 757, 437, 419
10	Eosine Y	1619, 1559, 1509, 1457, 1371, 1330, 1176, 1030, 957, 911, 810, 787, 768, 708, 640, 612, 500, 471, 414
	Rhodamine 6G	1648, 1596, 1572, 1508, 1361, 1309, 1181, 1125, 1086, 1008, 929, 771, 658, 635, 611, 567, 522, 449, 401, 356
	Rhodamine B	1646, 1594, 1527, 1507, 1431, 1357, 1279, 1192, 1075, 932, 787, 734, 619, 550, 521, 354
11	Eosine Y	1620, 1559, 1498, 1461, 1322, 1294, 1246, 1176, 1030, 1005, 812, 711, 639, 570, 540
12	Rose Bengale	1611, 1543, 1505, 1454, 1325, 1271, 1239, 1185, 690, 607, 498, 438, 392
13	Eosine Y	1619, 1554, 1503, 1454, 1328, 1178, 1093, 942, 761, 709, 671, 641, 570, 541, 471, 423
	Rose Bengale	1613, 1546, 1496, 1453, 1323, 1242, 1168, 1007, 954, 690, 612, 568, 532, 487, 436
14	Cotton scarlet	1632, 1593, 1561, 1500, 1464, 1441, 1419, 1376, 1326, 1239, 1185, 1141, 928, 672
15	Eosine Y	1621, 1560, 1510, 1457, 1325, 1187, 955, 695, 615, 582, 489, 438
16	Rhodamine B	1645, 1595, 1564, 1506, 1432, 1359, 1279, 1193, 1074, 763, 620, 432, 352

Table S. 4: TLC-SERS retention factors for the standards and French inks. Spots associated with eosin Y are marked in purple; those associated with Rose Bengal are marked in orange; those associated with Acid Red 73/Cotton Scarlet are highlighted in red; those associated with Rhodamine B are marked in gold; those with Rhodamine 6G are marked in yellow. Gray-labelled spots were not assigned.

R _f	C01	C02	C04	C05	C06	C07	C09	C10	C11	C12	C13	C14	C15	C16
0.1	Gray		Gray		Gray									
0.2	Gray	Purple	Gold			Gray		Purple			Purple		Gray	
0.3		Purple					Red	Purple	Purple		Purple	Red	Purple	Gold
0.4						Purple		Yellow	Purple	Orange	Purple		Purple	
0.5		Purple	Gold	Gold		Purple		Gold	Purple	Orange	Purple		Purple	Gold
0.6		Purple	Yellow			Purple		Yellow	Purple	Orange	Purple			Gold
0.7										Orange	Orange			Gold
0.8		Purple	Gray			Purple		Purple	Purple				Gray	Gray
0.9	Red						Red					Red		Gray

Table S.5: List of compounds detected by HPLC-DAD-MS². For each compound, the following information are reported: molecular markers, retention time (t_R , min), absorbance wavelength (λ_{max} , nm), pseudo-molecular ion, and tandem mass fragmentations (MS²). The most intense product ions are highlighted in bold.

Commercial name	Molecular markers	t_R (min)	λ_{max} (nm)	Molecular ion	MS ²
Amido naphthol red G	AR1	8.4	315, 507, 536	464.021 [M-H] ⁻	464.021, 358.979 , 343.957
Fast acid magenta B	AR33	7.2	315, 536	422.010 [M-H] ⁻	422.010, 248.996 , 185.033
Cotton scarlet	AR73	14.3	347, 511	511.044 [M-H] ⁻	301.959
Methyl violet	Hexa MP	20.7	-	372.243 [M] ⁺	372.243 , 356.211, 340.171, 328.191
	Penta MP	19.5	-	358.228 [M] ⁺	358.228 , 342.195, 326.166, 314.177
	Tetra MP I	18.2	-	344.213 [M] ⁺	344.213 , 328.180, 313.159, 300.159
	Tetra MP II	17.7	-	344.213 [M] ⁺	344.213 , 328.180, 300.159
	Tri MP I	16.9	-	330.196 [M] ⁺	330.196 , 314.163, 299.144, 237.134
	Tri MP II	16.4	-	330.196 [M] ⁺	330.196 , 315.172, 300.155, 287.158
Methylene blue	BB9	11.8	-	284.123 [M] ⁺	284.123, 268.091 , 240.072
	BB9-Me	11.1	-	270.108 [M] ⁺	270.107 , 254.076 , 228.072
Eosin Y	pseudo Eo Y	-	-	716.736 [M-H] ⁻	659.716 , 579.797, 522.765
	2DBEo	18.5	-	488.869 [M-H] ⁻	445.879, 364.961 , 335.962
	DBEo	20.2	467	566.779 [M-H] ⁻	442.863 , 415.858, 334.953
	Eo	21.7	495, 531	646.688 [M-H] ⁻	602.609, 522.772 , 442.861
Rose Bengale	2DCRB	24.4	-	902.568	824.588, 734.661, 607.766 , 126.900
	DCRB	25.0	-	936.531	-
	DIRB	24.7	-	846.589	768.608, 676.690, 550.789 , 126.904
	RB	25.4	523, 563	972.501 [M-H] ⁻	972.501, 894.525, 804.588, 678.687 , 126.904
Orange II	AO7	14.6	310, 491	327.045 [M-H] ⁻	327.045, 170.996 , 155.985
Orange 2R	AO8	15.4	-	341.051 [M-H] ⁻	341.051, 185.012 , 170.002
Rhodamine B	Rh	11.5	-	331.111 [M] ⁺	331.111 , 313.100, 287.117, 270.098
	TrisDERhB	13.7	-	359.143 [M] ⁺	359.143 , 343.104, 330.098, 315.088
	BisDERhB I	15.9	527	387.174 [M] ⁺	387.174 , 357.126, 343.109, 329.105
	BisDERhB II	16.2	532	387.174 [M] ⁺	387.174 , 357.126, 343.109, 329.105

	DERhB	18.2	539	415.206 [M] ⁺	415.206 , 385.157, 371.142
	RhB	19.9	518, 556	443.234 [M] ⁺	443.234 , 399.169, 355.105
	pseudo RhB	20.8	-	729.452 [M] ⁺	729.452 , 443.235, 399.169
Rhodamine 6G	TrisDERh6G	13.5	-	359.143 [M] ⁺	359.143 , 315.148
	BisDERh6G	15.5	-	387.174 [M] ⁺	387.174 , 371.138, 358.135, 343.109, 313.135
	DERh6G	17.9	520	415.206 [M] ⁺	415.206, 387.174 , 358.134, 313.136
	Rh6G	20.4	494, 527	443.234 [M] ⁺	443.234, 415.200 , 386.160
Shellac resin	Shellolic acid	4.8	-	295.110 [M-H] ⁻	251.121, 175.109, 119.045
	Epishellolic acid	5.9	-	295.110 [M-H] ⁻	277.106, 233.111, 147.041, 103.051
	Oxidised shellolic acid	8.6	-	293.096 [M-H] ⁻	228.074, 175.112, 119.040, 107.044
	Oxidised epishellolic acid	9.0	-	293.096 [M-H] ⁻	249.103, 205.113, 175.112, 109.068
	Jalaric acid	10.8	-	279.118 [M-H] ⁻	261.105, 217.117, 189.123, 147.042
	Laccishellolic acid	11.9	-	279.118 [M-H] ⁻	279.118, 217.117, 147.041, 119.046
	Jalaric acid isomer	12.3	-	279.118 [M-H] ⁻	261.105, 217.117, 189.123, 147.042
	Aleuritic acid	12.6	-	303.211 [M-H] ⁻	303.211 , 285.202, 267.196, 201.112, 171.098, 127.117
	Unknown ester III	13.7	-	553.327 [M-H] ⁻	303.211 , 267.115, 249.104, 203.103
	Shellolic-aleuritic	14.7	-	581.322 [M-H] ⁻	303.211, 277.101 , 251.123, 233.112
	Aleuritic-Llak	15.3	-	551.312 [M-H] ⁻	303.211 , 285.198, 265.100, 247.088, 191.102
	9,10-dihydroxyhexadecenoic acid	16.9	-	285.200 [M-H] ⁻	285.200
	Butolic acid	21.9	-	243.191 [M-H] ⁻	243.191, 197.193 , 141.130
6-oxotetradecanoic acid	23.0	-	241.174 [M-H] ⁻	223.172 , 197.191, 157.125, 139.112	

Table S.6: List of compounds detected by Py(HMDS)-GC/MS. For each compound, the following information are reported: pyrolytic markers, retention time (t_R , min), molecular weight, MS fragmentations, and label used in Figure S.1. The most intense product ions are highlighted in bold.

Compounds	Pyrolytic markers	t_R (min)	MW	MS (m/z)	Label
Eosin Y	Benzoic acid TMS	23.6	179	179 , 105, 135	
	β -naphthol TMS	28.1	216	73 , 201, 216	
Orange II	β -naphthol TMS isomer	28.3	216	73 , 201, 216	
	Aniline	18.4	93	93 , 66, 73	
Amido naphthol red G	Hydroxyquinoline	25.7	145	145 , 117, 89	
	N-phenyl acetamide	25.9	135	93 , 135, 66	
	Hydroxyquinoline TMS	27.9	202	202 , 172, 94	
	Unknown	33.5	135	93 , 135, 66	
	Acetophenone	20.2	120	105 , 77, 120	
Cotton scarlet	β -naphthol TMS	28.1	216	73 , 201, 216	
	β -naphthol TMS isomer	28.3	216	73 , 201, 216	
	Azobenzene	29.1	182	77 , 51, 182	
	Benzenamine, N-(phenylmethylene)-	29.7	180	180 , 77, 51	
	Phenylazophenol TMS	33.2	270	165 , 73, 270	
	Phenyldiazenyl aniline	33.7	197	92 , 65, 197	
	3-(Diethylamino)phenol TMS	28.0	237	222 , 237, 73	
Rhodamine B	Unknown	30.1	355	133 , 355, 105	
	Unknown	30.3	353	131 , 353, 103	
	Unknown	32.3	290	205 , 275, 73, 290	
	Unknown	36.6	260	134 , 91, 47, 260	
	Unknown	37.9	314	237 , 314, 285	

Gum Arabic	Levoglucofan 3TMS	29.7	378	73, 204, 217	
	Octanoic acid TMS	24.0	216	73, 117, 201	
	Nonanoic acid TMS	25.4	230	73, 117, 215	
	Tetradecenoic acid TMS	31.0	298	73, 117, 283	
	Tetradecanoic acid TMS	31.2	300	73, 117, 285	
Shellac resin	Hexadecenoic acid TMS	32.9	326	73, 117,129, 311	
	Hexadecanoic acid TMS	33.0	328	73, 117,129, 313	
	Butolic acid TMS	33.1	388	73, 117,185, 215	
	Octadecenoic acid TMS	34.5	354	73, 117, 129, 339	
	Octadecanoic acid TMS	34.7	356	73, 117,129, 341	

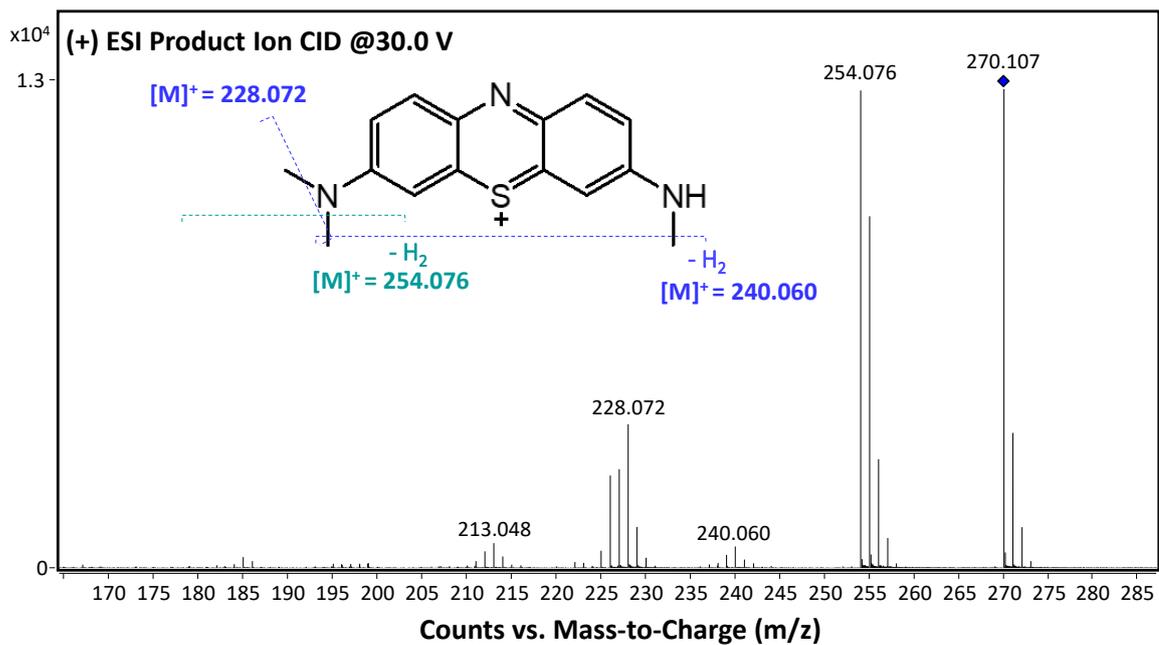


Figure S. 1: Tandem mass spectrum of BB9-Me ($t_R = 11.1$ min, C₁₅H₁₆N₃S⁺)

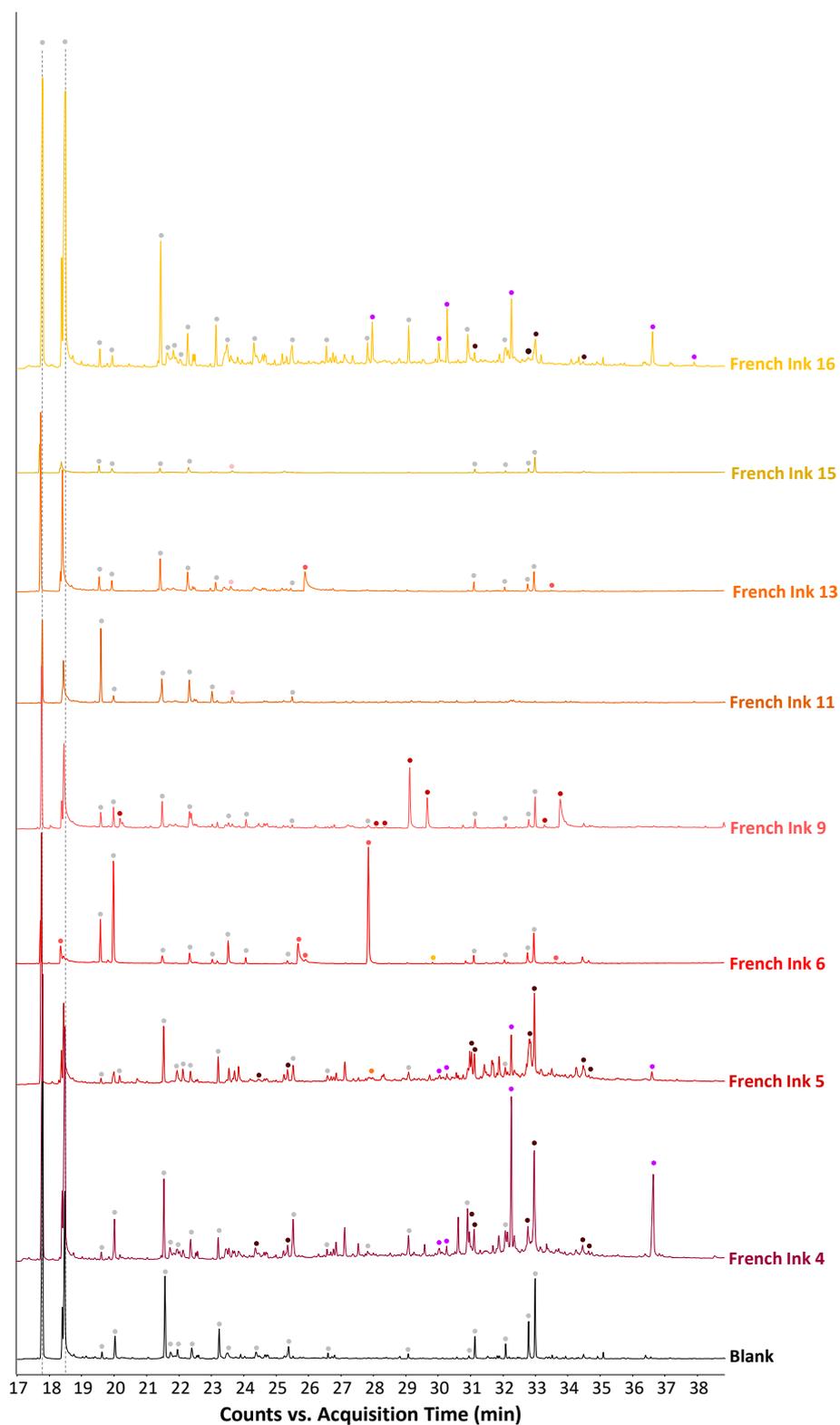


Figure S.2: Total Ion Chromatograms (TIC scan) obtained through Py(HMDS)-GC/MS. Blank (black pyrogram), French Ink 4 (violet pyrogram), French Ink 5 (dark red pyrogram), French Ink 6 (red pyrogram), French Ink 9 (light red pyrogram), French Ink 11 (dark orange pyrogram), French Ink 13 (orange pyrogram), French Ink 15 (dark yellow pyrogram), and French Ink 16 (yellow pyrogram). The peaks present in the blank are marked with a grey dot. The peaks associated to dyes, binder and additives are highlighted with a colored dot (legend is reported in Table S.2) All pyrograms are presented in the same scale and are stacked for purpose of clarity.

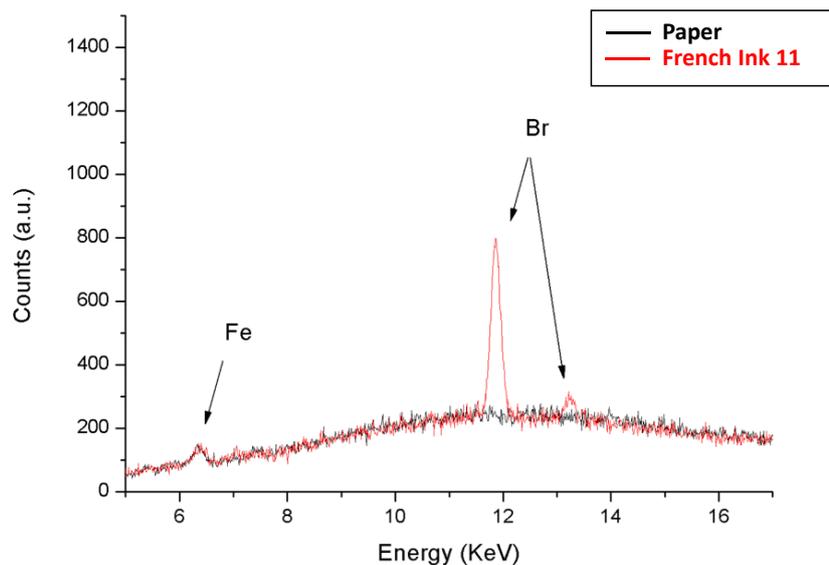


Figure S. 3: XRF spectra acquired for the paper support (Whatman filter paper) and for the French Ink 11 reference mock-up.

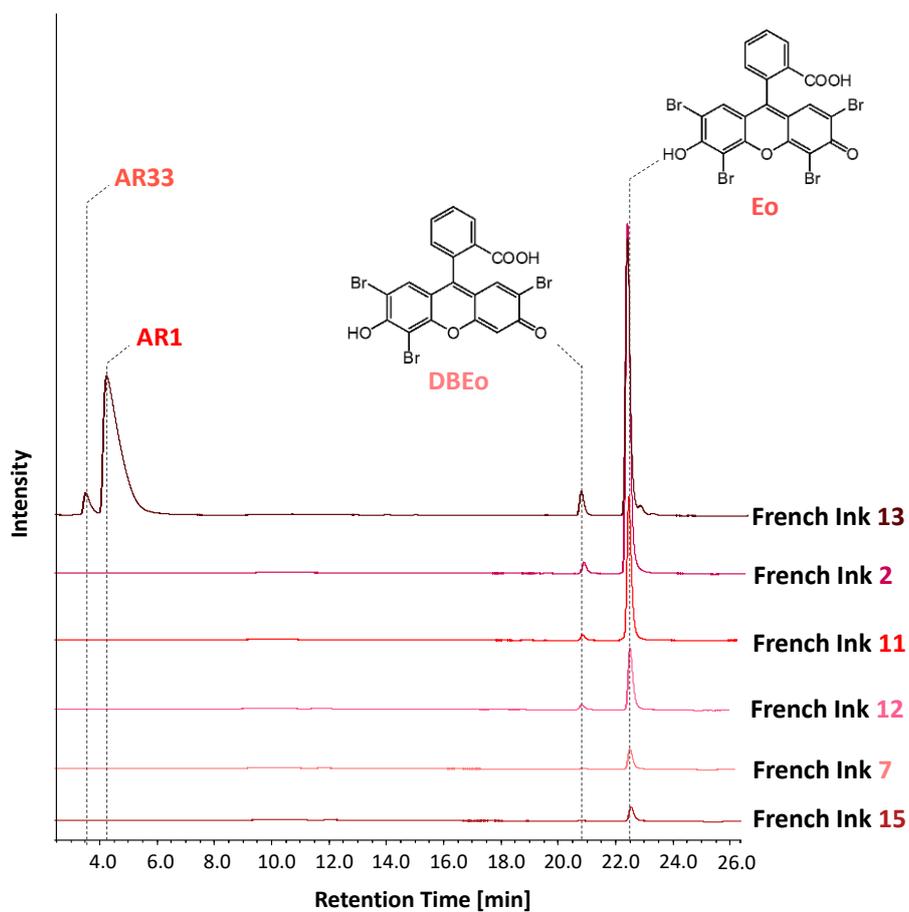


Figure S. 4: HPLC-DAD chromatograms (500-550 nm) of French Ink 15 (red brown profile), 7 (peach profile), 12 (pink profile), 11 (red profile), 2 (raspberry profile) and 13 (brown profile). All chromatograms are presented in the same scale and are stacked for purpose of clarity.

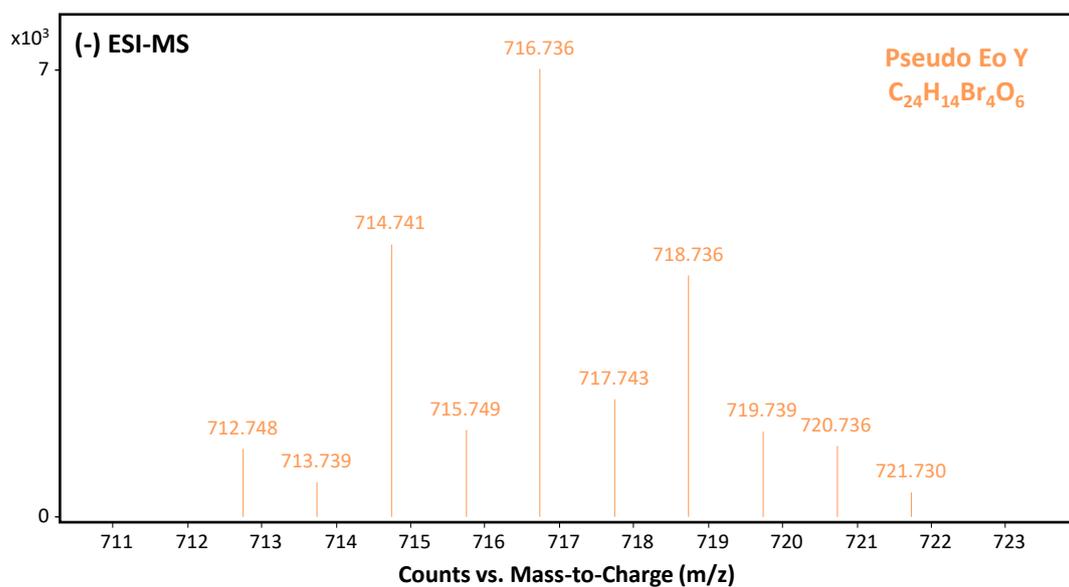


Figure S. 5: Mass spectrum of pseudo Eo Y. Negative ionisation mode. The mass spectrum is zoomed in a proper m/z range allowing the visualization of the isotopic cluster.

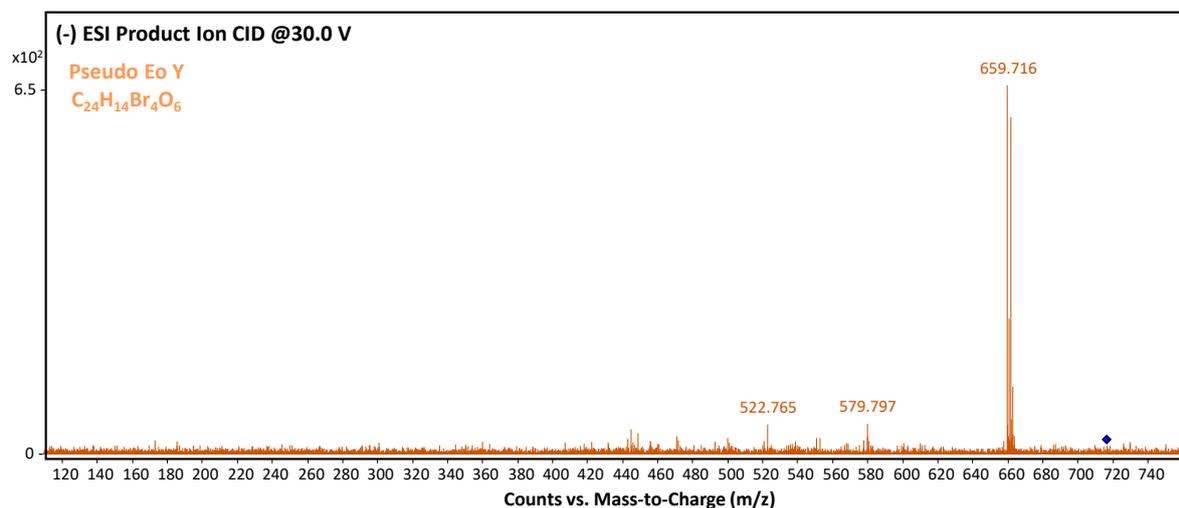


Figure S. 6: Tandem mass spectrum of pseudo Eo Y. Negative ionisation mode.

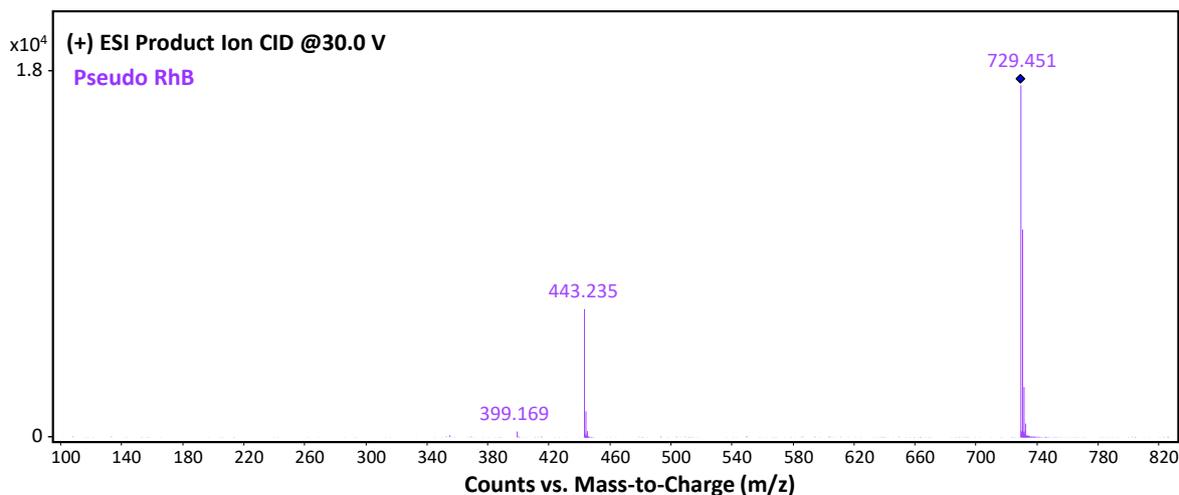


Figure S. 7: Tandem mass spectrum of pseudo RhB. Positive ionisation mode.

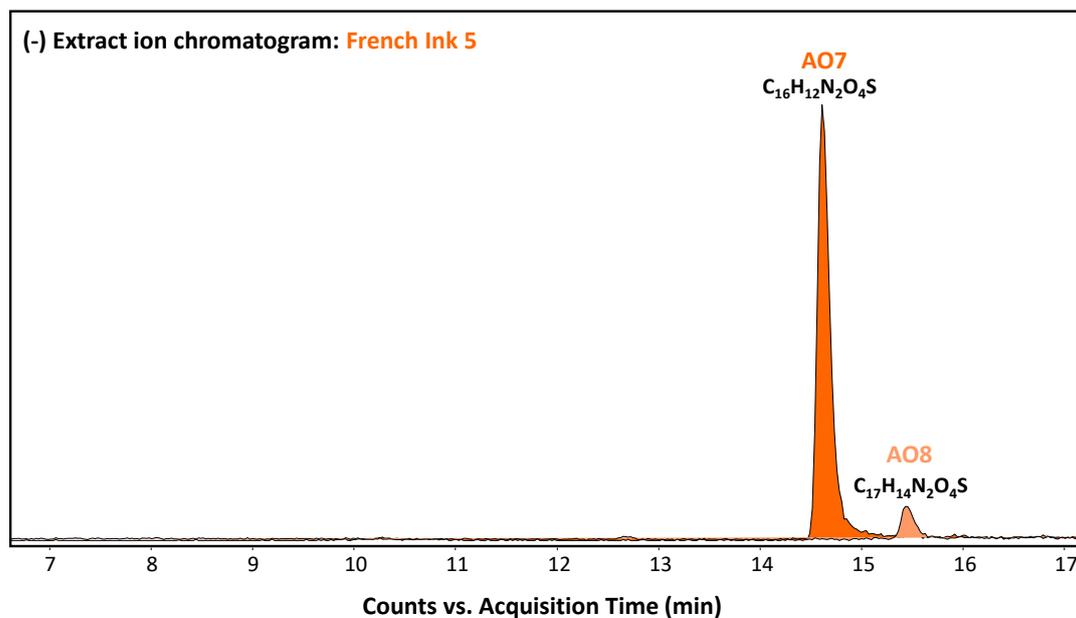


Figure S. 8: HPLC-ESI-Q-ToF Extract Ion Chromatograms (EIC) obtained by plotting the counts in function of time of the ions corresponding to the molecular ions of the single species detected in the EDTA-DMF extracts of the French Ink 5. The detected species, highlighted in the chromatograms, are orange II (AO7, C₁₆H₁₂N₂O₄S), and orange 2R (AO8, C₁₇H₁₄N₂O₄S). Negative ionisation mode.

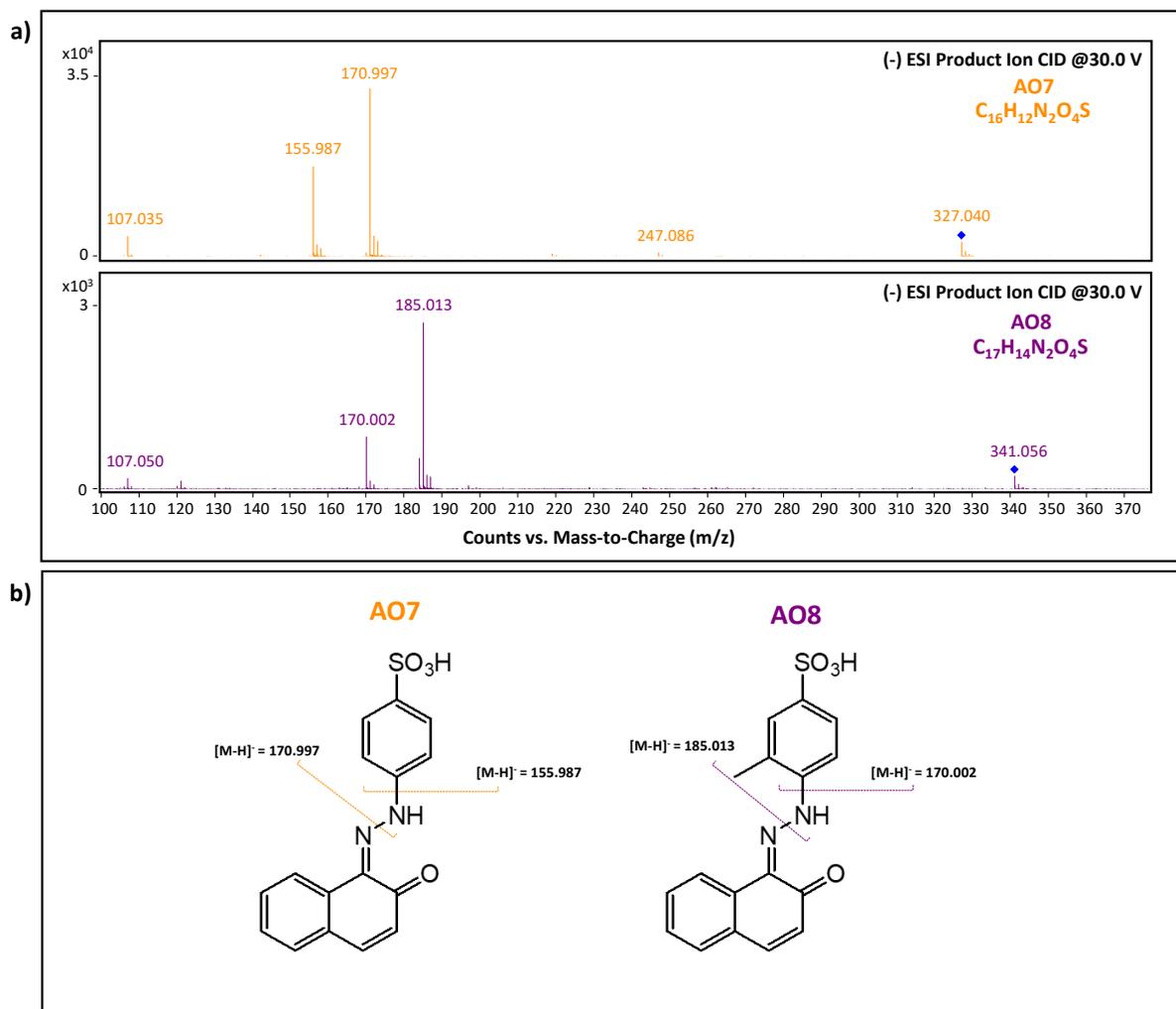


Figure S. 9: Tandem mass spectra acquired for AO7 and AO8. Negative ionisation mode. a) Tandem mass spectrum of AO7 (orange) and AO8 (violet); b) Hypothesized fragmentation pathway.

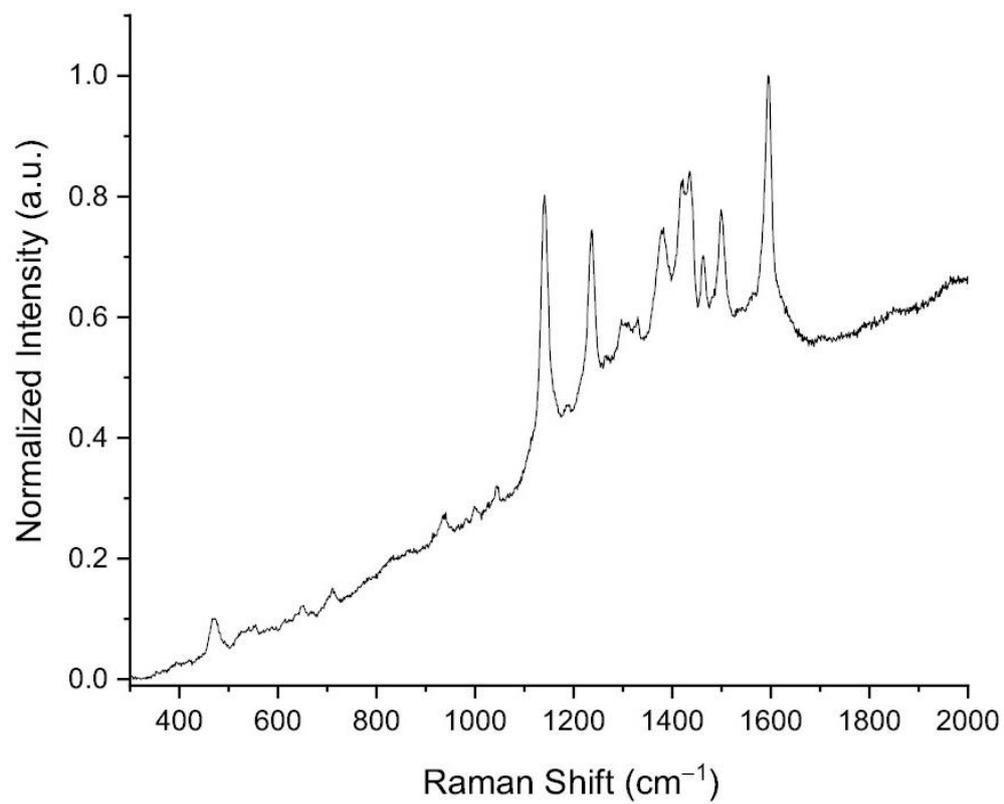


Figure S. 9: Raman SERS spectrum of AR73 after TLC separation of the extract of French Ink 1.

References

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