

Early synthetic textile dyes of the late 19th century from the “Primo Levi” Chemistry Museum (Rome): A multi-technique analytical investigation



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ABSTRACT

In the present work a historical collection of early synthetic dyes, stored at the “Primo Levi” Chemistry Museum of the Università La Sapienza di Roma, the so-called *coloreria*, was investigated through different analytical techniques: Fourier-transform Infrared (FTIR), UV-visible, Raman and surface-enhanced Raman (SERS) spectroscopies, CHN elemental analysis, electron-spray ionization mass spectrometry (ESI-MS) and X-ray diffraction (XRD). The aim was to characterise five dyes of unknown composition, produced by one of the main dye manufacturers of the 19th century, the Leopold Cassella & Co. The combination of the different methods led to the identification of the five colourants as Chrysoïdine G, Amaranth, Direct Scarlet B, Acid Fuchsin and Nile Blue, and extensive bibliographic research confirmed the reliability of the hypotheses formulated on the basis of the analytical data.

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1. Introduction

Since 1856, when William Perkin discovered the first synthetic dye, mauveine, more than 400 new colourants have been developed. The early synthetic dyes were industrially manufactured from organic molecules, and soon replaced those obtained from natural sources, such as flowers, wood, berries, roots or insects and shellfish. The analysis of early synthetic dyestuffs is still a somewhat unexplored area when it comes to historical or artistic objects [1]. Some of them have been studied by spectroscopic methods, such as FTIR [2–4], UV-visible [5] Raman [6–9] and fluorescence [1] spectroscopies, or by thin-layer (TLC) and liquid (HPLC) chromatographic techniques [1,2,10–13], similarly to the analysis of natural dyes. Likewise, SERS spectroscopy has also been widely applied for the characterization of some of these synthetic substances belonging to certain chemical classes, both in the fields of conservation and forensic sciences [14–17]. In addition, a consistent group of early synthetic dyes was examined by mass spectrometry with matrix assisted laser desorption ionization (MALDI) [18].

However, the lack of reference materials is also a major challenge. Most of the early synthetic dyes invented in the 19th century, in fact, are no longer available on the market because the production process was not convenient or the properties of the dye

were unsatisfactory, and therefore those dyes were progressively replaced by more advanced and suitable materials. For this reason, the analysis of synthetic dyes dating back to the second half of the 19th, or the beginning of the 20th, century can represent an interesting study from the point of view of future research in the field of diagnostics of cultural heritage, laying the basis for their identification in historical and artistic objects.

In this work, some of the early synthetic dyes from the collection stored at the “Primo Levi” chemistry museum of the Università La Sapienza di Roma, the so-called *coloreria*, were investigated. This collection includes numerous samples of pigments and dyes, natural, artificial and synthetic, coming from the natural world and from the main manufactures that have made the history of the dyeing industry, in Italy and beyond, from the second half of the 19th century to the whole of the 20th century [19].

However, part of the dyes belonging to the *coloreria* are of unknown composition: the only information available about some dye bottles are, in fact, labels carrying a series of numbers and, sometimes, a partially illegible name. In this scenario, the identification of these colourants represented a topic of interest for the conservation and valorisation of the collection, as well as for orienting subsequent diagnostics studies on real artefacts. Many of these dyes, in fact, were soon replaced due to their poor fastness to light and washing, an aspect that make their identification even more important in order to preserve historical artefacts dyed with them over time.

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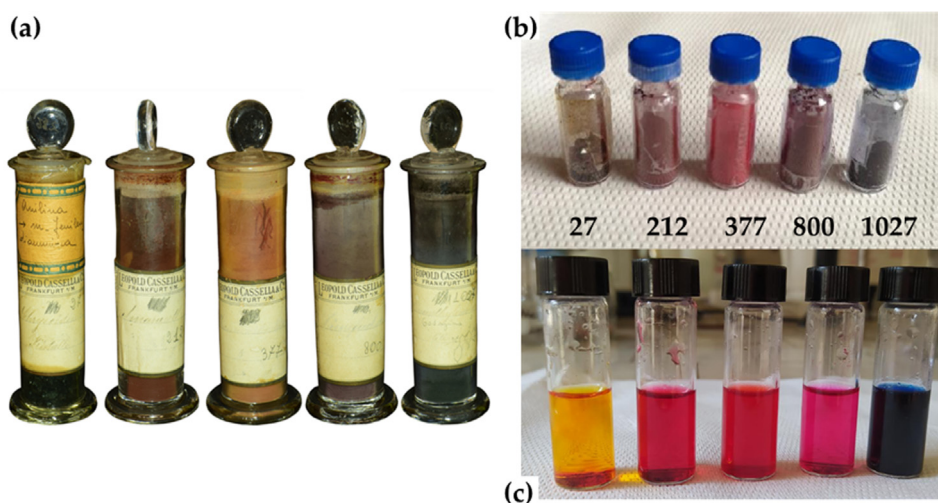


Fig. 1. The dyes under investigation: (a) the original containers; (b) as powders and (c) in aqueous solution.

2. Aim of the work

The present work focuses on the identification of five dyes of unknown composition belonging to the above-described *coloreria* of the “Primo Levi” chemistry museum of Università La Sapienza di Roma. To investigate the chemical nature of these colouring substances, different analytical techniques were applied: Fourier-transform infrared (FT-IR), UV-visible, Raman and surface-enhanced Raman (SERS) spectroscopy, CHN analysis, X-ray diffraction (XRD) and electrospray ionization mass spectrometry (ESI-MS). Furthermore, an extensive literature search was carried out in order to verify whether the dyes recognised on the basis of the analytical results were historically consistent. In particular, the main bibliographic sources were the manuals of Leopold Cassella & Co. [20,21], where the different dyes produced by the company are listed together with their physical properties (i.e. fastness to light and washing), the hues they take on fabrics and the dyeing methods. However, as a drawback, the formulas and chemical structures of the dyes listed are not reported in these manuals.

3. Materials and methods

3.1. Reference materials

The samples under investigation (Fig. 1) were taken from the original containers of some synthetic dyes from the collection of the Leopold Cassella & Co. company, dating back to 1885 (about thirty years after Perkin’s discovery). Leopold Cassella & Co. was a chemical and pharmaceutical company, founded in 1798 in Germany, in Frankfurt am Main, by Leopold Cassella together with his half-brother Reiss, and operating as an independent company until 1995. The main production was represented by dyes, drugs and cosmetics.

The dyes were identified by a number and in three cases by only partially legible labels. Some solubility tests were carried out and all dyes demonstrated to be water-soluble, with the exception of dye 27, which dissolves only slightly in this solvent. Due to the impossibility of preparing solutions of known concentration, as the molecular weights of the dyes were not known at the beginning, for subsequent analyses a small amount of each sample, ranging from 1 to 2 mg, was dissolved in 4 mL of water. A brief description of the samples is given in Table 1.

2.2. Analytical methodologies

FT-IR analyses were performed by a Jasco FTIR-620 spectrophotometer. All the samples were previously ground and dispersed in KBr to obtain pellets. The spectra were recorded as a sum of 16 scans with a 4 cm^{-1} resolution.

Raman analyses were performed directly on the powder dye. A Bruker BRAVO handheld spectrometer was used for the measurements. This instrument is based on the patented SSE™ (Sequentially Shifted Excitation) technology, which provides for the excitation of spectra by means of two diode lasers operating at different temperatures and emitting respectively at 785 and 850 nm. A suitable algorithm, therefore, allows to extract the final Raman spectral data. The spectra are collected in two sequential steps, from 300 cm^{-1} to 2000 cm^{-1} and from 2000 cm^{-1} to 3200 cm^{-1} . The average spectral resolution is approximately 11 cm^{-1} and the applied laser power is always less than 100 mW for both lasers. The acquisition time varies from 250 to 500 ms and the number of accumulations from 1 to 5 (these parameters are automatically set by the instrument).

UV-visible spectra were acquired in the spectral range 400–750 nm using a JASCO UV/VIS/NIR V-570 spectrometer. The analyses were performed on the dyes in the initially prepared aqueous solutions, diluting them 1:2 and using a cell having a 1-cm optical path.

SERS analyses were performed on the reference dyes in aqueous solution as initially prepared. 200 μL of silver nanostar colloid, prepared according to the procedure reported in [22], was stirred on a magnetic plate, then 5 μL of sodium perchlorate aqueous solution (1.8 M) and 10 μL of the dye solution was added. Although the activation by aggregation is not required for these nanoparticles due to the large enhancement provided by their special morphology, it was found that more intense SERS spectra are obtained if a small amount of sodium perchlorate is added to the nanoparticles prior to the analyte. A micro-drop of the final suspension was deposited on a glass slide and SERS analyses were performed using a JASCO RMP 100 portable Raman micro-probe. The micro-probe is equipped with a notch filter and an Olympus 50 \times microscope objective and is connected through fibre optics to a compact Lot Oriol MS125 spectrometer with a 1800 lines/mm grating and a Peltier-cooled CCD detector. A Nd:YAG laser delivered the exciting radiation at 532 nm, with an output laser power of approximately 100 mW. The spectral resolution is 8 cm^{-1} . All SERS spectra were

Table 1
Summary table of the investigated dyes: number, writings on label (if legible) and sample description.

Inventory number	Legible writings	Description
27	<i>Aniline - m. phenylenediamine</i>	Small dark crystals, yellow-orange in aqueous solution (slightly soluble)
212	<i>Amaranth</i>	Dark red-brownish powder, brilliant red in aqueous solution.
377	-	Dark red powder, red in aqueous solution.
800	... <i>fuchsin</i>	Dark red-brownish powder, reddish-violet in aqueous solution.
1027	-	Black powder, blue in aqueous solution.

recorded between 2000 and 200 cm^{-1} as a sum of 30 scans with an exposure time of 2 s.

For CHN analysis, a CHNS/O PerkinElmer 2400 Series II Elemental analyzer was used, capable of determining the concentration of carbon, hydrogen and nitrogen in the sample. Acetanilide was used as a calibration standard.

ESI-MS analyses were performed by a Thermo Fisher LCQ Fleet ion trap mass spectrometer on the aqueous solution of the dyes. The instrumental conditions were: capillary voltage 50 V, source voltage 4 kV, source temperature 45 °C, capillary temperature 275 °C, tube lens voltage 85 V, shift gas flow rate 20 arbitrary units, auxiliary gas flow rate 10 arbitrary units. Mass spectra were acquired from m/z 50 to 2000 in positive and negative modes. The sample was introduced into the ESI source by a syringe pump at a flow rate of 20 $\mu\text{l}/\text{min}$.

XRD analyses were performed by means of a Philips PW 1820 diffractometer with vertical scan. The instrument was equipped with collimator plates (Soller's slits), a single crystal graphite monochromator and a Na(Tl) scintillation counter with impulse height amplification. The incident radiation corresponded to Cu K α (1.5418 Å) (settings HV: 40 kV and 40 mA) and the acquisition was run at room temperature in the range 5°–65°

4. Results and discussion

The analytical results leading to the identification of each dye will be discussed and presented in detail below and are summarized in Table 2. The reliability of the hypotheses put forward on the basis of such results was confirmed by comparison with historical data from the literature.

Sample 27 – This dye was identified as Basic Orange 2, also known as Chrysoidine G. Considering the results and the reference data for FT-IR (Fig. 2a and [23]), Raman (Fig. 3a and [8]) and UV-visible (Fig. S1a Supporting Information and [24]) analyses, it can be seen that the sample corresponds to the dye Chrysoidine G, with formula $\text{C}_{12}\text{H}_{13}\text{ClN}_4$ and molecular mass 248.71 u. Furthermore, the SERS spectrum (Fig. 4a) of the unknown sample showed a high degree of correspondence with the spectroscopic results reported in [25] for the same dye as forbidden cancerogenic additive in food. The SERS spectral pattern resembles that observed in the Raman spectrum, except for some minor changes. In particular, bands due to in-plane vibrations such as those at 1291, 1271 and 1173 cm^{-1} decrease slightly in intensity, while some signals attributable to out-of-plane vibrations of the aromatic rings, at 960, 895, 805, 750 and 490 cm^{-1} , become evident (Table S1 Supporting Information, [26,27]). Furthermore, the band at 1407 cm^{-1} assigned to the N=N stretching vibration is more evident in the SERS spectrum, possibly due to a pre-resonance effect with the π - π^* transition of that bond associated with the use of the 532-nm exciting radiation [16].

In light of the information supplied by the vibrational spectra, the results of the CHN analysis and mass spectrometry were interpreted. From CHN analysis, the percentage of hydrogen is slightly higher than that of the Chrysoidine G dye, and that of carbon and nitrogen lower, but the C/N ratio is as expected for that dye (Table S2 Supporting Information). On the other hand, considering the

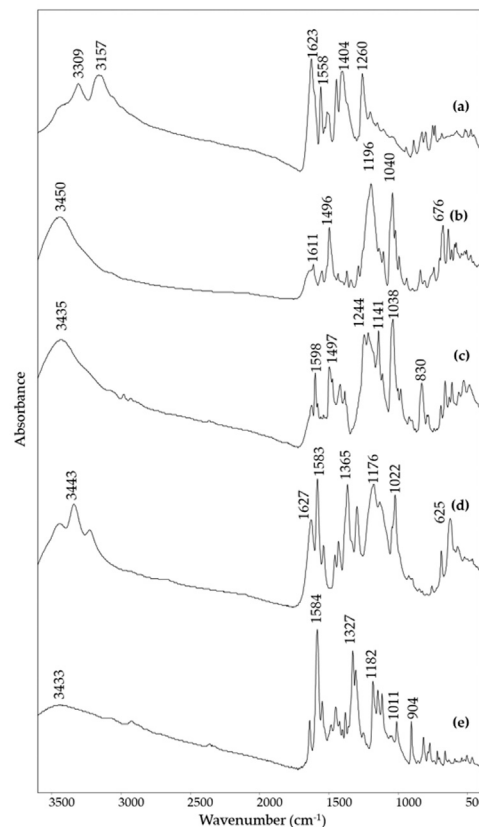


Fig. 2. FT-IR spectra of the investigated dyes in KBr pellets: (a) 27, (b) 212, (c) 377, (d) 800 and (e) 1027.

molecular mass of the Chrysoidine dye ($M = 248.71$), the peak at m/z 213 in the ESI (+) mass spectrum (Table 2) may correspond to $[\text{M}-\text{Cl}]^+$. Little information was found about this dye: it was introduced in 1876 after its discovery by Otto N. Witt and it was used to dye wool and silk in neutral baths as well as cotton. It is fast to light, air and washing [28]. In reference [28], *A Dictionary of Coal Tar Colours* dated to 1892, this dye is named Chrysoidine R, but currently the use of the letter “R” refers to a dye with a similar structure but with an additional methyl group on the diaminobenzene ring. Finally, this colourant is mentioned in *The Printing of Cotton Fabrics* by L. Cassella [21] as “Chrysoidine”. The writing on the label (*Aniline - m. phenylenediamine*) clearly refers to the molecular structure.

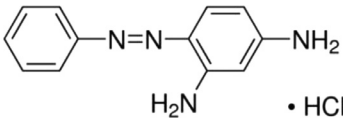
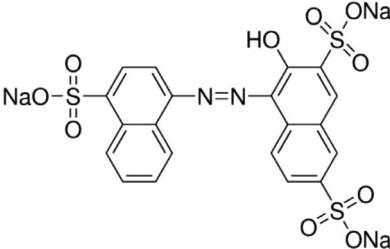
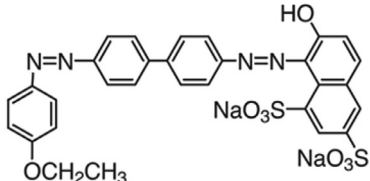
Sample 212 – This dye was identified as Acid Red 27 ($\text{C}_{20}\text{H}_{11}\text{N}_2\text{Na}_3\text{O}_{10}\text{S}_3$). In agreement with the original label, this dye is also known as Amaranth. An almost perfect match was found between the FT-IR spectra of the unknown sample (Fig. 2b) and the Amaranth dye [29], and a similar result was obtained for Raman (Fig. 3b) and UV-vis (Fig. S1b Supporting Information) spectra, respectively compared with the spectroscopic data reported in [9,30] and [31,32]. Furthermore, SERS analyses were performed, and a spectrum dominated by intense and well-defined signals was

obtained (Fig. 3b). The spectral pattern has a rather good correspondence with the reference data reported in [9], although some variations in the relative intensity and position of the signals were found, due to the experimental conditions (a different excitation wavelength and a different colloid were used in the two experiments). The pattern of the normal Raman spectrum is similar to that expected for the keto tautomer of a 1-phenylazo-2-naphthol dye [Table S1, 14]. The SERS spectrum seems to correspond mainly to the same form, although the contribution of the hydro tautomer cannot be ruled out. Indeed, an enhancement is observed for bands due to the C=O stretching mode (1646 cm^{-1}) and the in-plane

OH/NH bending modes (1555 and 1377 cm^{-1}), while some signals due to out-of-plane vibrations (938 and 771 cm^{-1}) are not present in the SERS spectrum. These observations suggest that there is a perpendicular orientation of the molecule with respect to the silver nanostars, within the limits of its planarity, in accordance with what is reported in [14] for the similar molecule of Acid Red 18, and that the oxygen and nitrogen atoms involved in the tautomerism are those that interact with the metal.

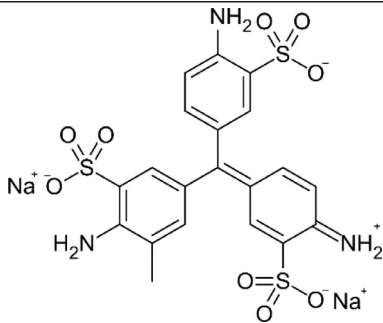
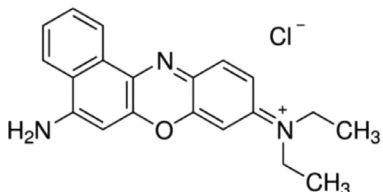
The CHN analysis shows a percentage of hydrogen higher than that of Amaranth (Table S2 Supporting Information); this may be due to the presence of a greater quantity of H_2O in the sample,

Table 2
Summary table of the analytical results obtained on the examined dyes.

	Molecular structure	FTIR bands (cm^{-1})	Raman bands (cm^{-1})	SERS bands (cm^{-1})	Absorption maximum (nm)	Main m/z peaks	Proposed identification
27		33309br, 3158br, 1626 vs, 1558s, 1510 m, 1445s, 1403s, 1258s, 1201s, 1151 w, 1106 w, 1054 w, 943 w, 888 m, 828 m, 801 m, 750 m, 735 m, 577 w, 518 w, 472 w.	1594s, 1567 w, 1500 w, 1597s, 1495 w, 1374s, 1291s, 1271s, 1202 w, 1170 m, 996 w, 520 m, 462 m.	1620sh, 1597s, 1532 m, 1501 w, 1491 w, 1377 vs, 1287sh, 1271s, 1180mw, 1152mw, 1000 w, 965 w, 587vw, 520sh, 490 w.	445 sh	213.27 (+)	Chrysoidine G (C.I.: Basic Orange 2, 11,270)
212		3435br, 1634sh, 1611 w, 1550 w, 1496 m, 1434 w, 1370 w, 1341 w, 1287 w, 1195 vs, 1138 w, 1106 m, 1040 vs, 1020 m, 993 w, 939 w, 840 w, 811 w, 742 m, 676 m, 638 m, 613 w, 593 w, 582 w, 541 w, 519 w, 504 w, 472 w, 406 w.	1571 vs, 1550 w, 1512s, 1479 m, 1456 w, 1435 m, 1399 w, 1364s, 1348s, 1286 w, 1232 m, 1177 m, 1137 w, 1112 w, 1060 m, 988 w, 938 m, 741 m, 701 w, 502 m, 400 w.	1646 m, 1590 w, 1561 vs, 1521sh, 1377s, 1277 w, 1246 m, 1176 w, 1126 w, 830 m, 812 m, 767 w, 695 w, 620 s.	512	581.54 (-) 604.49 (-)	Amaranth (C.I.: Acid Red 27, 16,185)
377		3434br, 2980 w, 2928 w, 1598 m, 1581 w, 1557 w, 1538vw, 1497 m, 1474 w, 1418 m, 1384 m, 1244s, 1216s, 1141s, 1114 w, 1038 vs, 1002 w, 982 w, 920 w, 900 w, 830 m, 792 w, 782 w, 740vw, 690 w, 657 m, 660 w, 612 m, 560 w, 522 m, 482 w.	1595s, 1491 w, 1450 w, 1414 m, 1402 m, 1377 w, 1281 m, 1247 w, 1181 m, 1140s.	1600 vs, 1490 m, 1455 w, 1377 m, 1288 w, 1245 m, 1118 m, 695vw, 492vw, 287vw.	504	699.41 (+) 653.86 (-)	Direct Scarlet B (C.I.: Direct Red 37, 22,240)

(continued on next page)

Table 2 (continued)

Molecular structure	FTIR bands (cm ⁻¹)	Raman bands (cm ⁻¹)	SERS bands (cm ⁻¹)	Absorption maximum (nm)	Main m/z peaks	Proposed identification
	3444br, 3338br, 3225br, 1627s, 1583 vs, 1538 m, 1456 w, 1430 w, 1365 vs, 1298s, 1176 vs, 1132s, 1021s, 924 w, 898 w, 826 w, 796 w, 758 w, 688 m, 625 m, 571 w, 520 w, 500 w, 435 w.	1581s, 1538 w, 1360s, 1302 w, 1295 m, 1130 w, 1020s, 991 w, 927 w, 759 w, 687 w, 627 w, 622 w, 571 w, 462 w, 386 w.	1617s, 1590s, 1555s, 1522 vs, 1434 w, 1372s, 1335 w, 1281 w, 1184s, 1143 w, 1010 w, 965 m, 914 m, 827 m, 769 w, 653 w, 614 m, 529 w, 448 w, 356 m, 280 m, 232 m, 174vw.	494sh + 546	590.97 (-)	Acid Fuchsin (C.I.: Acid Violet 19, 42,685)
	3433br, 3072 w, 2923 w, 2361 w, 1637 m, 1584 vs, 1548 m, 1484 w, 1449 m, 1422 w, 1402 w, 1327s, 1306s, 1251 w, 1181 m, 1147 m, 116 m, 1046 w, 1011 m, 904 m, 772 w, 817 w, 717 w, 703 w, 661 w, 634 w, 591 w, 542 w, 504 w, 467 w.	1637s, 1614 w, 1528 w, 1523 w, 1500 m, 1494 m, 1430 w, 1405 m, 1143 m, 902 w, 759 w, 716 w, 687 w, 622 w, 591 s, 571 w, 539 m, 508 w, 462 w.	1645 vs, 1537 m, 1493 m, 1452 w, 1403 m, 1384 m, 1184 w, 1143 w, 908 w, 859 w, 807 w, 745 w, 722 w, 665 w, 593 vs, 545 w, 517 w, 446 w, 315br.	608 + 646	318.39 (+)	Nile Blue (C.I.: Basic Blue 12, 51,180)

Abbreviations: s = strong; m = medium; w = weak; vs = very strong; vw = very weak.

which may also explain the higher intensity of the signals at 3500–3300 cm⁻¹ in the IR spectrum of dye 212, with respect to the comparison spectrum [29]. The lower quantities of carbon and nitrogen is also due to the presence of inorganic additives (see below the results of XRD analysis). Acid Red 27 has a molecular mass of 604.47 u and this information was used to interpret ESI-MS experimental data. The main peak in the ESI (-) mass spectrum (Table 2) is at m/z 604, corresponding to the molecular mass of the Ama-

ranth dye (M = 604.47). A second peak at m/z 581 corresponds to [M-Na]⁻.

Amaranth, whose name derives from amaranth grain, a plant characterised by its red colour, is an anionic dye. It usually comes in the form of a trisodium salt and can be applied to both natural and synthetic fibres. Like all azo dyes, at the middle of the 19th century, Amaranth was obtained from coal tar and only later its main source became petroleum by-products [33]. It was discovered

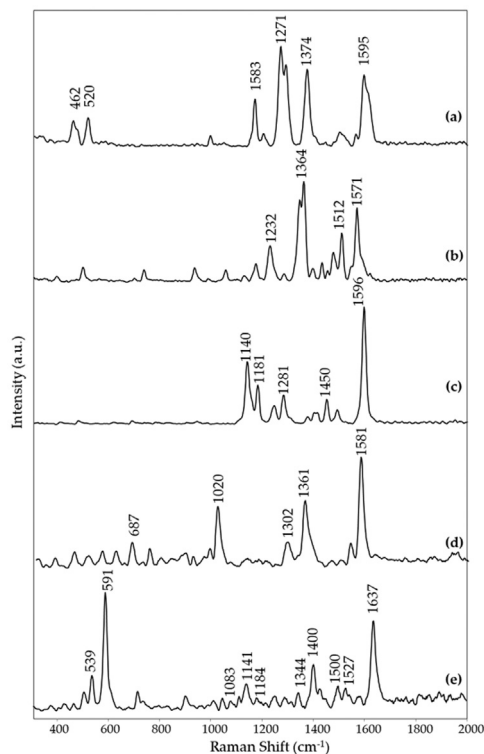


Fig. 3. SSE Raman spectra of the investigated dyes in solid form: (a) 27, (b) 212, (c) 377, (d) 800 and (e) 1027.

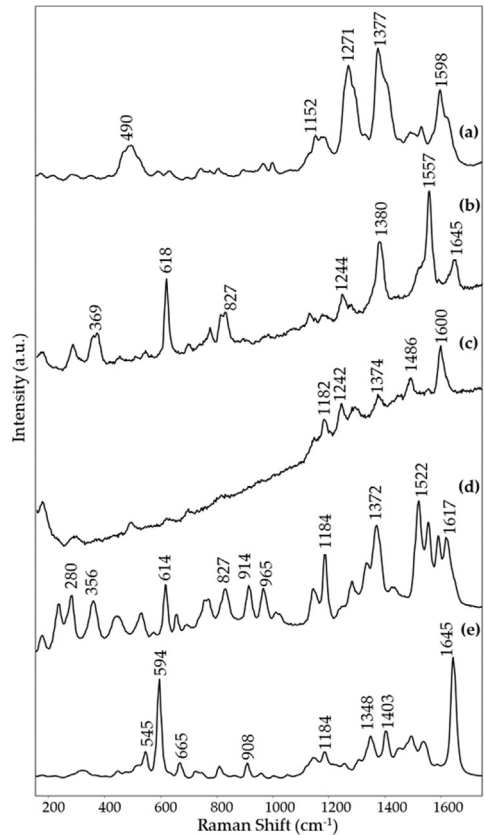


Fig. 4. SERS spectra ($\lambda_{exc} = 532$ nm) of the investigated dyes in aqueous solution: (a) 27, (b) 212, (c) 377, (d) 800 and (e) 1027.

in 1878 [28] and, as a further confirmation of the proposed identification, the name of this dye is reported in *The Dyeing of Wool* by L. Cassella [20]. In addition to dyeing, as it is one of the fastest colours known [28], this synthetic colourant has found application in cosmetics and as a food additive, however since 1976 it has been banned in the United States as a suspected carcinogen and in the early 1980s it was replaced by the dye Allura red [34]. As for Europe, Italian legislation has prohibited the use of Amaranth in most food and beverages, with the exception of caviar, while its use is still permitted in other countries where this dye continues to be used as a food colouring in sweets and drinks [35].

Sample 377 - Starting from the IR spectrum (Fig. 2c), the sample corresponds to the Diphenyl Red BS dye [36], also known as Direct Scarlet B or Direct Red 37, whose molecular formula and mass are respectively $C_{30}H_{22}N_4Na_2O_8S_2$ and 676.63 u. On the other hand, Raman, SERS and absorption spectra were not found, to the best of our knowledge, to be taken into account for comparison and they are reported here (Figs. 3c, 4c and S1c Supporting Information respectively) for the first time. A tentative assignment of Raman bands for this dye is proposed in Table S1, based on those reported in the literature for two other 1-phenylazo-2-naphthol dyes, Acid Red 26 and the aforementioned Acid Red 18 [14]. In the SERS spectrum an enhancement is observed for bands at 1590 and 1490 cm^{-1} , involving the C=C and C=O stretching modes of the keto tautomer, and at 1373 cm^{-1} , possibly assigned to the OH bending of the hydro tautomer, while the band at 1140 cm^{-1} , due to the CH in-plane bending and SO_3 stretching modes, becomes less intense. In the light of the hypothesized assignments, an interaction between the dye molecule and the silver particles through the oxygen atom of the -OH group can be supposed, thus also explaining the intensity loss of the signal due to sulfonate groups that in this situation should be further away from the metal surface.

Referring to the CHN analysis, a higher percentage of hydrogen (Table S2 Supporting Information) was found than that of the reference dye, Diphenyl Red BS, which also affects the intensity of signals at 3500–3300 cm^{-1} in the IR spectrum. For the lower percentages of carbon and nitrogen the same considerations already advanced for sample 212 can be applied. In any case, the C/N ratio is in agreement with what expected for this dye. Furthermore, taking into account the molecular mass of the Diphenyl Red BS dye ($M = 676.63$), in the mass spectrum ESI (+) the peak at m/z 699 corresponds to the $[M + Na]^+$ ion and in the mass spectrum ESI (-) the one at m/z 653.86 corresponds to $[M - Na]^-$ (Table 2). Diphenyl Red BS, also known as Direct Scarlet B or Diamine Scarlet B, was introduced in 1890 and is the product of diazotization of benzidine on both sides, followed by coupling with β -naphthol disulfonic acid and *p*-ethoxybenzene [13]. The use of this colourant, as sodium salt, for dyeing fabrics (especially cotton) was limited as it has proved to be poorly lightfast and reddens in an alkaline environment, although it is stable in acid conditions [28]. However, its name is documented again among Leopold Cassella's dyes in *The Dyeing of Wool* [20].

Sample 800 - For this sample spectroscopic analyses suggested that it corresponds to Acid Fuchsin (also known as Acid Violet 19 or Acid Magenta). The reference FT-IR [37], Raman [38] and UV-visible [39] spectra have, in fact, a high degree of similarity with those obtained from the unknown sample (Figs. 2d, 3d and S1d Supporting Information respectively). Moreover, the high-quality SERS spectrum (Fig. 4d) obtained from an aqueous solution of this dye showed correspondence with literature data referring to colourants belonging to the same family of fuchsin dyes [40]. The main signals, attributable to the skeleton of the molecules, are in fact well recognisable. To the best of our knowledge, the SERS spectrum of Acid Fuchsin is presented here for the first time. Compared to the normal Raman spectrum, the enhancement of several bands associated with the conjugated double bond system, and

in particular with the aromatic rings, is observed, and especially at the lower wavenumbers such bands can be assigned to out-of-plane vibrational modes (Table S1, [4,40]). These observations suggest a parallel orientation of the dye molecule with respect to the silver surface, with an interaction taking place mainly through the π electron system.

Again, similarly to the previous dyes, a greater amount of water in the sample was suggested by the relative intensity of the IR signals in the range $3500\text{--}3300\text{ cm}^{-1}$ and this is also confirmed by the higher percentage of hydrogen detected by the CHN analysis (Table S2 Supporting Information). For the lower percentages of carbon and nitrogen the same considerations already advanced for sample 212 can be applied. However, Acid Fuchsin has formula $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$ and atomic mass 585.54 u. Instead, the present sample showed a higher C/N ratio (Table S2 Supporting Information), suggesting that three methyl groups are present in the examined dye, one for each aromatic ring, rather than a single one. This hypothesis is supported by the ESI-MS (-) spectrum, which is dominated by the signal at m/z 591 attributable to $[\text{M}-\text{Na}]^-$ and also presents a weaker peak at m/z 612 corresponding to $[\text{M}-\text{H}]^-$. Therefore, $\text{C}_{22}\text{H}_{21}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$ can be taken as the formula of the unknown dye, giving a molecular mass of 613 u. In fact, in the literature it is reported that Acid Fuchsin can derive as a sulfonated form from basic fuchsin or from the single dyes (rosaniline, pararosaniline and new fuchsin) of which the latter is a mixture [41]. Of the three individual dyes, the trimethylated form is new fuchsin, also known as Magenta III.

Fuchsin was discovered in 1858 when August Wilhelm von Hofmann studied the action of CCl_4 on aniline and described a "carbtriphenyltriamine" formed by the condensation of three molecules of aniline with the carbon atom of CCl_4 and corresponding to a red dye. In the following years, several processes were developed for large-scale production and the dye was marketed under various trade names, e.g. Fuchsin, Magenta, Anilinrot, Rosein [42]. New fuchsin was mentioned for the first time in 1899 [43]. The acid dye (Acid Fuchsin or Acid Magenta) was obtained from fuchsin dyes by treating the starting molecules with fuming sulphuric acid [28]. This dye still has widespread use in histology as a biological stain today. In Cassella's manuals Acid Magenta is mentioned for dyeing wool [20], even if it is poorly fast to light and washing [28].

Sample 1027 - Identifying this dye proved to be the most challenging. Indeed, referring to FT-IR analysis, a perfect match with reference dyes was not found, at least as far as we know. However, the FT-IR spectrum of the unknown dye (Fig. 2e) was comparable to that of 5,9-bis-dimethylamino-benzo[a]phenoxazinyl-7-ium chloride, which has the same chemical formula ($\text{C}_{20}\text{H}_{20}\text{ClN}_3\text{O}$) [44] and a molecular structure very similar to that of the dye Nile Blue cation (Fig. S2 Supporting Information), with four methyl instead of two ethyl groups. Comparing the Raman bands observed for this sample and those reported in the literature for Nile Blue, only a partial correspondence is found with the FT-Raman spectrum of the historical reference sample discussed in [8], while a more complete similarity is detected with the modern sample examined in [45]. In this scenario, interesting results were provided by SERS analysis: the main peaks in the spectrum (Fig. 4e), in fact, correspond to those reported for Nile Blue A (Basic Blue 12), which is often used as a SERS probe [46–48]. The recognised dye belongs to the oxazine family, the earliest member of which was Meldola's Blue, obtained from the reaction between nitrosodimethylaniline hydrochloride and β -naphthol. The dyes belonging to this small series are generally not simple colourants, but rather a mixture of several colouring molecules that have not been completely separated from each other [28]. This information may explain the slight difference between the spectra of the historical sample examined in the present study and the one reported in [8]. The normal Ra-

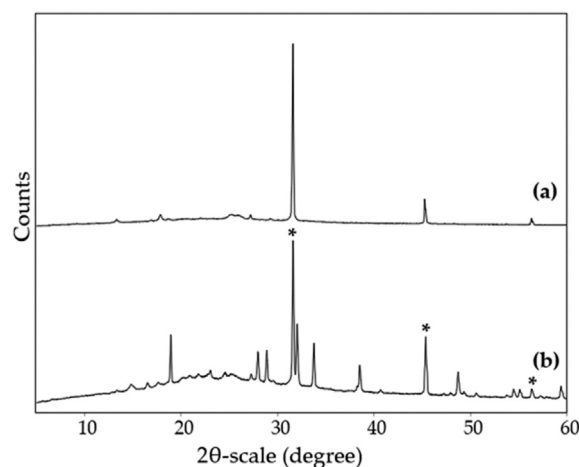


Fig. 5. XRD patterns of (a) halite in sample 212 and (b) thenardite and halite (*) in sample 800.

man and SERS spectra are quite similar, suggesting that the entire aromatic system is interacting with the metal particles, as most bands are assigned to its ring vibrations (Table S1).

As a further characterisation, CHN and ESI-MS analyses were considered. The elemental analysis revealed a higher proportion of hydrogen and carbon than Nile Blue stoichiometry (Table S2 Supporting Information). In any case, the molecular mass of the dye is 353.85 u and in the positive-ion ESI mass spectrum of the sample a peak referable to $[\text{M}-\text{Cl}]^+$ is observed at m/z 318. In the case of this dye, no correspondence was found in Cassella's manuals, but the introduction of this blue substance dates back to 1879 and is therefore contemporary with the industrial production of the Leopold Cassella company [28]. Nile Blue was used to dye both wool and silk, although the results in neutral or faintly acid baths was not so good; dealing with cotton, a mordanting with tannins leads to a very fast colour [28].

As a final characterisation, XRD analyses were performed on all samples. It is well known that, in the case of dyes, this technique can be helpful for their identification if they are in crystalline form, or provide indications on the presence of inorganic additive and fillers. In particular, referring to the dye samples, it was found that the peaks are most likely related to the presence of sodium salts, rather than to a possible crystalline structure of the dyes themselves [49]. In samples 212, 377 and 1027 the characteristic peaks (Fig. 5a) of the mineral halite (NaCl) are detected [50], while in sample 800 the peaks observed are attributable to both halite and thenardite (Na_2SO_4) (Fig. 5b) [51]. For sample 27, only broad peaks were observed, which cannot be assigned. However, the presence of the aforesaid salts justifies the reduced percentage of carbon and nitrogen detected by CHN analysis, compared to that of the reference compounds.

5. Conclusion

In this work, five early synthetic dyes of unknown composition from an Italian museum collection were analysed using different techniques (FT-IR, Raman, SERS and UV-vis spectroscopies, ESI-MS and CHN) in order to understand their chemical composition. In addition, the reliability of the identification was verified by an extensive bibliographic search of the corresponding dye in books and manuals of the corresponding period (second half 19th century). The combination of this information and the analytical results confirmed the successful identification of the five dyes, namely two basic ones, Chrysoidine and Nile Blue, and three acid ones, Amaranth, Acid Fuchsin and Direct Scarlet B. Besides summarising the

spectroscopic data that characterize each dye, SERS spectra for Diamine Scarlet B and Acid Fuchsin were reported for the first time in the present work.

Furthermore, shedding light on the nature of these unknown historic dyes belonging to the museum contributed to their valorisation. Moreover, as a future prospect, the investigation here described can disclose the possibility of identifying these colourants in artistic objects. This is a fundamental aspect in the field of conservation and restoration, even more so if we consider the poor resistance to light of some of these substances, which makes them susceptible to decay relatively quickly.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2022.11.013.

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