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RESEARCH ARTICLE

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The 20th century and its new colours: Investigating the molecular structures of historical synthetic dyes using Raman spectroscopy

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Abstract

Characterising synthetic dyes on heritage textiles represents a relatively recent research frontier, which aims to obtain new information about the evolution of textile manufacturing and industrial chemistry. Whilst spectral enhancement or amplification methods are often considered a requirement for the Raman analysis of textile dyes, this work highlights the potential of standard Raman spectroscopy for the non-invasive analysis of synthetically dyed fibres. In this research, Raman spectroscopy was used for the chemical characterisation of early 20th century synthetic dyes, in both powder form and on dyed fibres. The dyes were produced by the Italian company Azienda Coloranti Nazionali e Affini (ACNA) and housed in the Sapienza University Museum of Chemistry. The investigation first employed literature research into the ACNA's commercial nomenclature. This information was used to hypothesise likely molecular structures of the dyes, pointing towards the azo dye class. The application of Raman spectroscopy confirmed these hypotheses and the high-quality spectra collected provided structural information about the dye molecules. Spectral features of azo-groups, aromatic moieties, and substituents were observable in spectra. Comparison with a Raman spectrum of wool allowed confident dye signal attribution, and some spectra displayed features linked to changes in the fibre during the dyeing process. Combining literature research and Raman vibrational information proved a powerful non-invasive approach for the characterisation of synthetic dyes, allowing molecular identification of some colorants and structural information for most. Standard Raman spectroscopy may provide a widely applicable, non-invasive method for acquiring information about synthetically dyed historical and artistic textiles in future research.

KEYWORDS

ACNA, azo, Raman spectroscopy, synthetic dyes, textiles

1 | INTRODUCTION

The fabric dyeing industry underwent a revolution in the mid-19th century after the discovery of the first synthetic dye, Mauveine, by William Henry Perkin in 1856.[1] The synthetic dye industry blossomed over the following century, with chemists discovering a full spectrum of new hues that reduced prices and lessened dependence on the finite abundance of natural sources.[2] Among the new synthetic dyes, the azo class is one of the largest and most chemically diverse of these groups.[3]

The first azo dyes were developed in the early 1860s.[3] They are defined by the inclusion of an azo bond (N=N) in their molecular structures and are typically—but not always—associated with red, yellow, and orange hues.[4] The earliest uses of azo dyes were on wool fibres, but modern developments diversified their applications to other textiles substrates and into other sectors such as food, cosmetics, and inks.[3] In the last 50 years, studies reporting links between the ingestion of certain azo dyes and the occurrence of some cancers have been published.[5] Nonetheless, azo dyes have persisted as an important and ubiquitous dye class due to their relatively simple syntheses and good fastness to light and moisture. For this reason, azo dyes are very well-represented within heritage collections.[3]

To answer conservation, curatorial, and historical questions about dyed heritage objects, it is necessary to understand the chemical identities of the colourants. Scientific identification is now an important practice for ancient textiles dyed with natural dyes.[6–9] However, more modern synthetically dyed objects are less well-studied. Interest in the identification of synthetic dyes is growing significantly as early synthetically dyed objects are re-categorised from contemporary to historical,[10,11] authentication questions arise,[12] and conservation issues begin to require attention.[13]

Traditionally and most commonly, textile dyes on fibres are analysed by extraction and separation of components using chromatography with either mass spectrometry[14–18] and/or photodiode array detection.[19,20] Whilst these techniques are still the gold-standard for confident identification,[7,9,21] they require sampling and are destructive. The irreplaceable nature of historical objects means that where possible, information should be obtained through non-destructive methodologies[7,22]—but this is complex for textile dye analysis. On a general level, non-destructive methodologies are intrinsically 'whole-sample' techniques—meaning that the signals from the dyes must compete with signals from the fibre, any fixatives, and any contaminants. This can result in high-complexity spectra which are difficult to interpret. The 'whole-sample' issue impacts all non-destructive methods, but is particularly problematic in infrared spectroscopy, which is strongly influenced by signals from the fibre.[7,23] Furthermore, elemental analysis techniques such as X-ray fluorescence spectroscopy are not indicative for organic molecule identification. Among the spectroscopic approaches, fibre optics reflectance spectroscopy (FORS) represents a useful analytical tool for the identification of dyes. FORS is totally non-destructive, it has been used with some success as part of a multi-technical approach, and it usually allows the identification of the molecular class of the dye. However, it is usually used as a preliminary screening method because it is limited by poor spatial resolution, overlapping of broad bands in mixed samples, limited distinguishing ability for similar compounds, and a strong substrate dependence.[24] These factors could play a major role in the analysis of aged and degraded samples.

These limitations of FORS and other non-destructive techniques mean that, in heritage science, Raman spectroscopy is the most promising for textile dye analysis research. The promise and ubiquity of Raman spectroscopy in heritage analysis lies in the following: its versatility, applicable to a wide range of materials; the quality of information it can provide, indicating specific structural features and offering quantitative analysis in some cases; and its non-destructive nature.[25] However, despite its potential, Raman spectroscopy presents several challenges of its own. For organic materials, the most significant limitation is the intense fluorescence effects induced by ultraviolet or visible Raman lasers,[25,26] which can mask the weak Raman scattering signals from the molecule under analysis. This is particularly problematic for dyes, which are usually applied in low concentrations to colour the substrate,[26] and it is particularly pronounced for the natural dyes, as the variability of the natural matrix generally means that hues are composed of a mixture of several compounds, each with very low concentration.

Several technological and methodological developments have sought to address this issue. The introduction of low-energy red and near-infrared lasers (e.g., 633 nm or 785 nm) to standard Raman systems[27]—which reduce the probability of fluorescence in organic materials—is the most simple strategy. However, this is not generally sufficient for natural dyes, whose identification generally requires more significant alterations to improve the quality of the Raman spectra. For example, most recent research utilises surface enhanced Raman spectroscopy (SERS), where the sample is treated with metal nanoparticles to amplify Raman signal strength and displace dye molecules from fibres.[28–32] FT-Raman, utilising a different detector system and a very long wavelength (1064 nm) laser to strongly reduce fluorescence, has also

been used in previous research.[33] Occasionally, the two techniques have been combined in FT-SERS.[34] These techniques have been successfully used for the identification of both natural and synthetic dyes in several cases and are extremely valuable tools in the dye analyst toolbox.[35–37] For instance, anthraquinones, flavonoids, and other natural dyes were detected in several ancient textiles through several SERS approaches, from the direct contact of noble metal nanoparticle colloids with the extract from archaeological and historical samples,[29,38–40] to the on-site deposition and formation of metal clusters on the fibre,[31,41,42] to the application of hydrogel for consequent SERS analysis.[30,43,44] In the literature, the application of SERS to the identification of synthetic dyes on textiles is reported,[32] while, analogously, FT-Raman was applied for the characterisation of dyes in historical matrices, as, for instance, indigo on pre-Columbian textiles[45] or indigo and brazilwood in traditional Swedish textiles of the 18th and 19th centuries.[46]

However, whilst these modified Raman approaches are frequently used for dye analysis in textiles, both SERS and FT-Raman come with some drawbacks. SERS utilises invasive sample pre-treatment, induces uneven amplification of signals, and has poor reproducibility,[47,48] requiring more specialised knowledge for data interpretation. FT-Raman usually requires long acquisition times and high laser intensities,[49] due to the intrinsic lower cross-section of Raman scattering in comparison to lower wavelength lasers (around one order of magnitude in comparison to most of the visible light lasers). FT-Raman spectrometers are usually less widely available than standard Raman spectrometers, making them less accessible for many analysts. Moreover, these two approaches are not applicable for on-site analyses.

Previous Raman studies of synthetic dyes have usually followed the same aforementioned methodologies used for natural dye identifications,[10,50,51] but their chemical situations are quite different. The molecular uniformity of a single dye created in a controlled laboratory environment is likely to be much greater than one, which depends on the natural matrix.[52] As such, this increases the potential of acquiring a good quality Raman spectrum for a synthetic dye with standard Raman spectroscopy. On the other hand, identification requires comparison with spectra of known molecules,[53] which is more complex for synthetic than natural dyes. Whilst a single synthetic dye sample is likely to have greater molecular uniformity, the structural diversity on a market scale is much greater for synthetic dyes as chemists were able to alter experimental designs in order to make small changes to molecular structures. The relative novelty of synthetic dye studies in heritage science combined with their chemical diversity make reference spectra difficult to obtain for comparison and literature data are increasing but still limited.

This research presents high-quality spectra of several synthetic azo dyes (both in powder form and on dyed wool fibres) acquired through the use of standard Raman spectroscopy equipped with a low-energy 633 nm red laser. This is one of only a small number of studies to successfully use standard Raman spectroscopy for the analysis of synthetic textile dyes on fibres and illustrates its potential for acquisition of informative spectra for the synthetic dyes. The dye samples analysed were from the Italian chemical company *Azienda Colouranti Nazionale e Affini* (ACNA) (*National Dyes Company and Affiliates* in English).[54,55] The specimens are part of the dye collection held by the Sapienza University Museum of Chemistry. These objects, obtained directly from ACNA, are unique in that they contain dyes produced by the company, some of which may not have been commercially available. No details or descriptions were available in the Museum archive about the investigated dyes, except for the names reported in the labels on the jar or on the cards, where they were collected. Information about the chemical identities of these dyes has the potential to contribute to a modern understanding of the manufacturing behaviours of the company during this period—in particular, providing information about the reliability of nomenclature.[56] Raman spectroscopy was paired with preliminary research into the commercial nomenclature of the samples, which suggested that they were most likely azo dyes. In this article, the Raman results of the investigation are shown. This represented the only non-invasive spectroscopic analysis applied to the samples from ACNA, which acts as part of a three-step protocol involving the above-mentioned preliminary nomenclature research and confirmatory liquid chromatography[57] as a final micro-destructive method. The aim is to illustrate the potential of standard Raman spectroscopy for non-destructive analysis of modern synthetic textile dyes through the successful identification of many of the investigated historical samples in this case study. Moreover, a preliminary database of early azo-dyes is provided, helpful for further studies.

2 | MATERIALS AND METHODS

2.1 | Dye samples

The samples analysed constituted 11 dyed fibres selected from a single sample card and four powder samples obtained from glass jars (Figure 1). Samples were acquired from the Sapienza University Museum of Chemistry's synthetic dye collection, which represents a

FIGURE 1 The collection of ACNA dyes stored in the Museum of Chemistry of Sapienza University of Rome.

precious source for the study of colorants, as highlighted in a recent study.[58] The spectroscopic analysis was focused on 15 samples, which were chosen based on their names, which appeared to suggest links with the azo class. The selection of these samples was based on the names reported on the jar and on the catalogue cards, with reference to the investigated literature.

The ACNA was an Italian chemicals manufacturer operational from 1882. It was involved in colourant manufacture since 1925 until 1999. The samples in the collection are likely to date from the 1930s—which is the period immediately following the company's change in direction from explosive production and is therefore an interesting period in their history.[55] Within the broader picture of European dye manufacture, it is important to highlight that the ACNA represented a fairly minor player in international dye production. This status means that it is not often mentioned in historical literature from the period, which made investigations into company nomenclature challenging. Literature research included online investigations into the names from the collection, some of which were linked to known dye molecules in historical patents.[59,60] This information was then consolidated and expanded upon by consulting the second edition of the Colour Index.[61] As with wider literature, ACNA dyes are under-discussed in the Colour Index, so particular attention was also paid to dyes from other companies with similar 'sounding' names.

This study is a first step towards understanding the full collection of synthetic dyes in the Sapienza University Museum of Chemistry and offers insight into the naming conventions and behaviours of the ACNA during this period.

2.2 | Raman spectroscopy

Acquisitions were performed using a Horiba Jobin-Yvon HR-Evolution micro-Raman spectrometer equipped with a 633 nm excitation laser and dry objectives. Acquisition over a 200–2000 cm^{-1} range was obtained by combining two spectra for each point analysed centred at 650 cm^{-1} and 1600 cm^{-1}, respectively. Three points on each sample were selected for acquisition using a motorised mapping stage equipped with a video camera. Spectra were then averaged, combined, backgrounds subtracted, and smoothed using Origin Pro 9.0 and LabSpec6. Specific acquisition settings were chosen for each sample depending on degradation sensitivities and fluorescence, and parameters were optimised for every spectrum; magnifications were 50× (numerical aperture: 0.50) or 100× (numerical aperture: 0.80); maximum laser power at the source: 15 mW; accumulation time between 3 s and 40 s; and number of scans was between 10 and 240 (for the specific parameters, see figure captions). Powder samples were placed directly on a microscope slide for analysis,

while fibres were stabilised on a slide with a small quantity of reversible adhesive putty. Background subtraction was performed on the Labspec6 software after fitting with a polynomial function (fit parameters: degree 9; max points 57; noise points 10). Smoothing was applied to only a small number of samples, where it was performed using the software Origin Pro 9.0 with the Adjacent Averaging method (for the samples and the parameters, see figure captions). Raman bands and acquired spectra were attributed by comparison to Raman spectra of standards, when they were available, and to data reported in literature.[62–68] When a strong similarity with the reference spectra was observed, chromatographic analysis with mass spectrometry detection was followed, which provided further data. These results will be only mentioned, and they are the object of another paper.[57] The whole set of nomenclature and Raman data, including spectra, is provided for all the standards and sample in Supporting Information.

3 | RESULTS AND DISCUSSION

Literature describes the characteristic Raman signals of azo compounds as one or two bands of variable intensity in the range between 1530 and 1640 cm^{-1}, attributable to the benzene quadrant stretch.[67–69] These signals were observed in all the acquired spectra, varying in spectral shape, intensity, and Raman shift between samples, but in most cases, the most intense peak is centred between 1590 and 1615 cm^{-1}. Additionally, all the acquired spectra contain a medium intensity band with a broadened shape between 1480 and 1520 cm^{-1}, which was attributed to an azobenzene ring vibration (Figure 2A). Literature reports that the main N=N stretching signal should be present between 1380 and 1470 cm^{-1}.[64,67,68] However, in some fibre samples, overlap with broad signals at 1317 and 1450 cm^{-1} from the wool (attributable to CH_2 modes) made this difficult to observe, so it is essential to consider the effects of the wool substrate during interpretation. For the investigated set of samples, overlap between dye and fibre signals is significantly more evident for yellow samples, while it is barely appreciable for red samples.

Comparison between the Raman spectra of the dyed samples and the spectrum of the wool highlights some interesting spectral changes which are likely to be related to the dyeing process (Figure 2B). In particular, the wool broad band at around 510 cm^{-1}[70–73] (S-S stretching of keratin disulfide bridges) disappears in all the Raman spectra of the dyed samples, with only three exceptions. This change suggests that there is breakage of S-S bonds, likely related to the dyeing process. Along with this

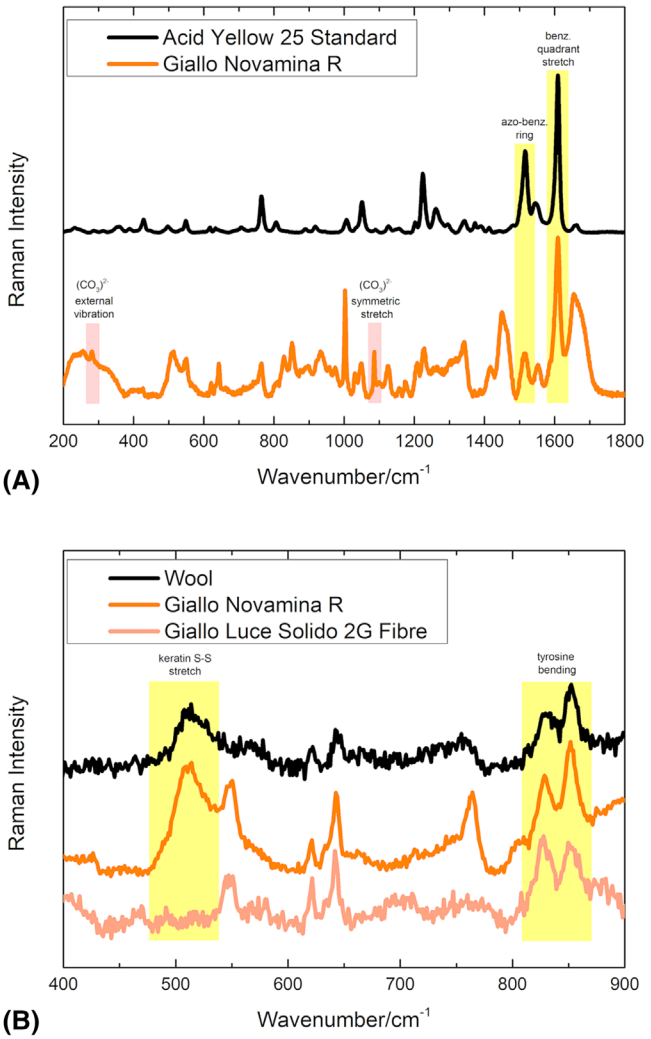

FIGURE 2 (A) Comparison of the spectra of an azo-dye standard (Acid Yellow 25) and of a historical sample (Giallo Novamina R), where characteristic signals of azo-dyes (yellow rectangles) and calcium carbonate (pink rectangles) are highlighted; (B) comparison of the spectra of wool and two historical samples in the range 400–900 cm^{-1}, where the bands related to the dye–fibre interactions in the dyeing and commented in the text are highlighted.

phenomenon, it is interesting to note that the relative intensities of the two tyrosine peaks at 827 and 853 cm^{-1} appear to inverted in intensity in most of the dyed samples when compared with the wool. This variation reflects the burying of the tyrosine side-chain, and it is generally attributed to the dyeing process.[71,72] Moreover, the only samples that are not affected by this intensity ratio inversion are those which do not present the cleavage of cysteine bonds. Finally, in all the dyed fibre spectra, three signals at 282, 713, and 1087 cm^{-1} are related to the presence of $CaCO_3$, likely used in the dyeing process to obtain specific shades through pH effects, or to

improve the fixation of the dye to the fibre as a mordant source (Figure 2A).

After the analysis of common spectral pattern, specific features of the different samples were investigated in order to obtain further information about the individual chemical structures of dyes, which are discussed below (Supporting Information):

- Rosso amidonaftolo 2G:

In the analysed collection, two samples—one a powder and the other a dyed wool fibre—were labelled with the commercial name *Rosso Amidonaftolo 2G*. Nomenclature research tentatively linked this commercial name to the azo dye Red 2G (C.I. Acid Red 1, 18050). The Raman spectra of these two samples were very similar, with the spectra of the dyed fibre showing little interference from the Raman spectrum of the wool. Several functional groups characteristic of Red 2G were observed in the Raman spectra of the *Rosso Amidonaftolo 2G* samples. In particular, both spectra contain an intense peak at 1279 cm^{-1}, likely indicative of an amide III band, and a shoulder at around 1625 cm^{-1}, representative of amide I. A doublet of signals at 1565 and 1597 cm^{-1}, clearly visible in the powder sample spectrum and partially obscured by an overlapping wool signal in the dyed fibre sample spectrum, along with a medium-strong peak at 1361 cm^{-1}, are indicative of naphthalene ring stretching. The peak observed at around 1171 cm^{-1} was attributed to the SO_2 symmetric stretching anche, consequently, to the presence of an SO_3 group. Comparison with data from literature[35,62] and with a Raman spectrum acquired in-lab of a powdered analytical standard of Red 2G confirmed the hypothesised attribution; however, some differences among the three spectra (samples and standard) were observed (Figure 3). The signal at 1171 cm^{-1}, which is intense in the dyed fibre sample, is barely visible in the powder sample and shifted to 1164 cm^{-1} and has a medium intensity in the spectrum of the standard. Moreover, a signal at 1492 cm^{-1}, attributed to azobenzene ring vibration, presents the same spectral shape and intensity in the spectra of the fibre sample and the analytical standard, but is split into two signals at 1470 and 1500 cm^{-1} in the spectrum of the powder sample. Finally, in the range between 400 and 600 cm^{-1}, some signals differ in intensity and shape across the different spectra. In particular, it is interesting to note that the doublet at 486 and 506 cm^{-1} observed in the spectrum of the powdered analytical standard are shifted to lower wavenumbers for both: the fibre sample, which is shifted 4 cm^{-1}, and the powder sample, which is shifted 11 cm^{-1}. Moreover, in the historical samples, the intensity of the second band decreases in comparison to the first. In the same range,

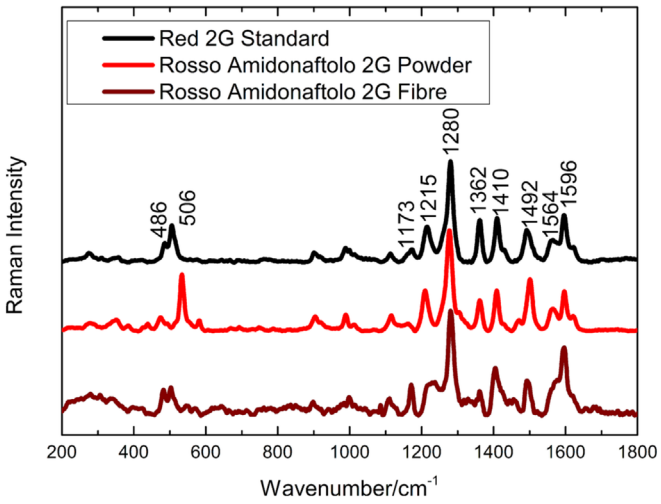

FIGURE 3 Comparison of Raman spectra obtained from the analytical standard of Red 2G (black line) and the historical samples of Rosso Amidonaftolo 2G in powder (red) and on fibre (burgundy); the characteristic wavenumbers for main peaks are highlighted.

an intense peak at 534 cm^{-1} is observable only in the historic powder sample. The identification to Red 2G was confirmed for both the samples by chromatographic analyses.

- Rosso Novamina 2G:

Preliminary research on the nomenclature of *Rosso Novamina 2G* mentioned four azo acid dye species—however, a historical document[59] and the Colour Index[61] strongly indicated that *Rosso Novamina 2G* is related to Acid Orange 19 (C.I. 14690). No Raman spectra were available in literature for Acid Orange 19 for spectral comparison, and an analytical standard could not be obtained. In addition, the Raman spectrum of *Rosso Novamina 2G* was very strongly affected by the signals from the wool in comparison to the other red dyes, meaning that only very few peaks were visible. However, if the intense band at 1605 cm^{-1} is generally indicative of the benzene quadrant stretch, its doublet with the peak at 1552 cm^{-1} is likely representative of naphthalene ring stretching. No signal attributable to sulfonic acid salts was observed around 1160 cm^{-1}, but the clear signal at 545 cm^{-1} could be indicative of an SO_2 wagging vibration in N-mono-substituted sulfonamide.

- Rosso Italana B and Rosso Italana R:

Extensive research into the use of these peculiarly spelled 'Italana' labelled dyes in the collection (which also considered the common spelling—'Italiana') found

no reference to them in any bibliographic resources. It is interesting to note that, in the Colour Index,[61] the only references to ACNA dyes labelled as 'Italian' (*Italian Berries*, *Italian Earth*, *Italian Pink*, *Italian Umber*) appear to refer to natural and mineral dyes. The only reference to 'Italana' in the Colour Index relates to a dye produced by ACNA as *Italanafuchsine*,[61] which corresponds (despite the common use of 'fuchsine' in reference to triarylmethane dyes) to a disulfonated azo dye, Acid Red 23 (C.I. 16130), the Raman spectrum of which is not available in literature. Another possible hypothesis is related to the eventual name of a company involved in the production or in the distribution of the textile dyes ('Italana' could be the crasis between 'Italia' and 'Lana', the Italian word for 'wool'), but no evidence was found in the investigated literature, which could confirm this.

The spectra acquired for *Rosso Italana B* and *Rosso Italana R* are remarkably similar. It is therefore likely that the chemical structures of both red *Italana* dyes are the same or at least very similar. Spectral comparisons with databases indicated possible correlations with structures similar to Acid Red 26 (C.I. 16150), which shares a common template with Acid Red 23, which was linked to 'Italana' by nomenclature.[35,62] Although comparison with reference spectra of Acid Red 26 does not offer a precise match, the presence of two signals at 1583 and 1606 cm^{-1} may suggest the presence of a naphthalene group. With reference to literature, the presence of the band at 1372 cm^{-1} would indicate that this naphthalene group is likely to be di-substituted. A medium-weak signal at around 1178 cm^{-1} is likely indicative of an SO_3 group, along with another peak at around 1044 cm^{-1} (barely visible in both the spectra).

- Rosso Luce Solido BL:

Nomenclature research into *Rosso Luce Solido BL* indicated only that the name was likely linked to a naphthol dye.[74] The Raman spectrum obtained for the dyed fibre has several similarities with the Raman spectra reported in literature for azo-pigments and dyes belonging to the Naphthol AS class. In particular, the highest intensity peak in the *Rosso Luce Solido BL* spectrum is at 1353 cm^{-1}, which is in agreement with the typical Raman shift observed for the highest intensity peak in the Naphthol AS class. Furthermore, the presence of lower intensity signals at 1419 (azo group stretch) and 1595 cm^{-1} (benzene quadrant stretch) along with the very weak C-N signals at 1107 and 1167 cm^{-1} and the naphthalene group signals at 732 and 1562 cm^{-1} (shoulder) would confirm this assignment, according to the protocol published by Vandenabeele et al.[67] Finally, a very weak, broad signal at 1650 cm^{-1} could be attributed to to Amide I, in which case the sharp peak at 1280 cm^{-1} is likely indicative of Amide III. This reinforces the hypothesis that *Rosso Luce Solido BL* is a Naphtol AS dye.

- Giallo Luce Solido 2G:

Two samples within the collection—a powder and a dyed wool fibre—were both labelled under the commercial name *Giallo Luce Solido 2G*. Literature research into the nomenclature linked this commercial name principally to Acid Yellow 11 (C.I. 18820), but also to Food Yellow 5 (C.I. 18965), Acid Yellow 46 (C.I. N/A), and Acid Yellow 12 (C.I. 18830).[61] It is important to highlight that Acid Yellow 11, Food Yellow 5, and Acid Yellow 12 share a common template structure.

Interestingly, the Raman spectra of the two identically named samples (fibre and powder, Figure 4) displayed many differences when compared. The Raman spectrum for the *Giallo Luce Solido 2G* powder presented signals which matched those reported in literature for Acid Yellow 11. The signal at 1436 cm^{-1} was tentatively assigned to the N=N stretch for a general mono-azo pigment, and the intense signal at 1600 cm^{-1} was assigned to a benzene quadrant stretch. A low intensity band around 1655 cm^{-1} was likely to be indicative of the presence of a pyrazole group, while the peaks at 1054 and 1169 cm^{-1} are indicative of the presence of an SO_3 group. Interpretation of the spectrum of the dyed wool sample was more complex, partly because the signals from the Raman spectra of the wool fibre overlapped strongly with the dye signals, making confident individuation of the main signals of the dye difficult. However, while some characteristic and intense peaks of Acid Yellow 11 are

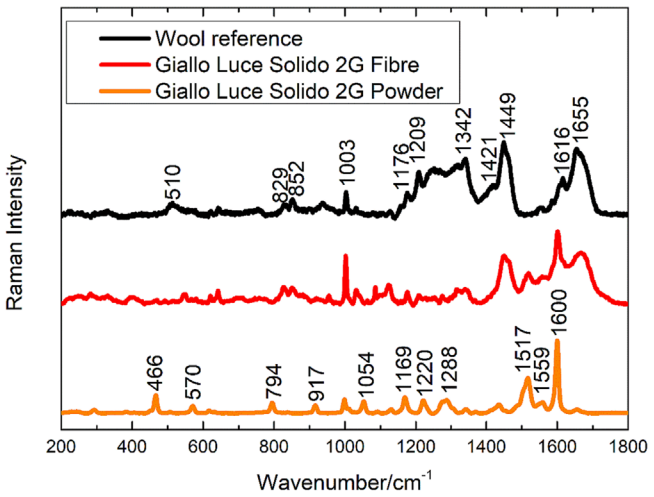

FIGURE 4 Comparison of Raman spectra obtained from the standard of wool (black line) and the historical samples of Giallo Luce Solido 2G on fibre (red) and in powder (orange).

present in the spectrum of the dyed fibre (those at 1517 and 1600 cm^{-1}), other expected peaks at 466, 570, and 795 cm^{-1} are not visible even in areas where there is little spectral contribution from the wool. These spectral differences could be due to the dyeing process and the interaction with the fibre, or alternatively may be indicative of the presence of a dye with a different molecular structure. Interestingly, the chromatographic analyses highlighted the presence of Acid Yellow 11 in the powder sample, while no evidence of the same dyes resulted for the fibre sample, reinforcing the second hypothesis.

- Giallo Novamina R:

Literature research into the commercial name *Giallo Novamina R* identified connections to three possible dyes: Acid Yellow 25 (C.I. 18835), Acid Yellow 39 (C.I. N/A), and Acid Yellow 61 (C.I. 18968).[61] Acid Yellow 25 and Acid Yellow 61 have very similar chemical structures based on the presence of sulfonyl, sulfonic, and pyrazolone groups. The presence of these common features is confirmed by some of the Raman peaks in the spectrum of the dyed fibre. Two medium-strong bands at 515 and 549 cm^{-1} were attributed to the sulfone scissoring vibrations, while the peak at 1049 cm^{-1} is likely indicative of the sulfonic substituent. The intense peak at 1516 cm^{-1} could be indicative of the pyrazole group along with a signal at 974 cm^{-1}, attributable to ring deformation. The presence of Acid Yellow 25 was eventually confirmed by comparison between the Raman spectrum of the dyed fibre and the spectrum of an analytical standard acquired using the same equipment, which were in good agreement. This was confirmed by chromatography.

- Tartrazina J:

The most plausible hypothesis for attribution of the *Tartrazina J* dyed fibre based on nomenclature corresponded to Tartrazine (C.I. Acid Yellow 23, 19140)[61]—a very well-known and ubiquitous azo dye. However, the Raman spectrum obtained for the sample showed differences in comparison to the Raman spectra of Tartrazine reported in literature.[51,75,76] This was confirmed by in-lab acquisition of a Raman spectrum of a Tartrazine analytical standard (Figure 5). While the general pattern of the spectrum does possess some similarities with the spectrum of the standard, some significant differences in Raman shift cannot be ignored. For instance, in the spectra of both standard and sample, intense peaks at 1502 and 1599 cm^{-1} attributable to the quadrant stretch of the benzene rings were observed. A further common signal at around 1175 cm^{-1} corresponds to the symmetric SO_2 stretch in sulfonic groups. On the other hand, the

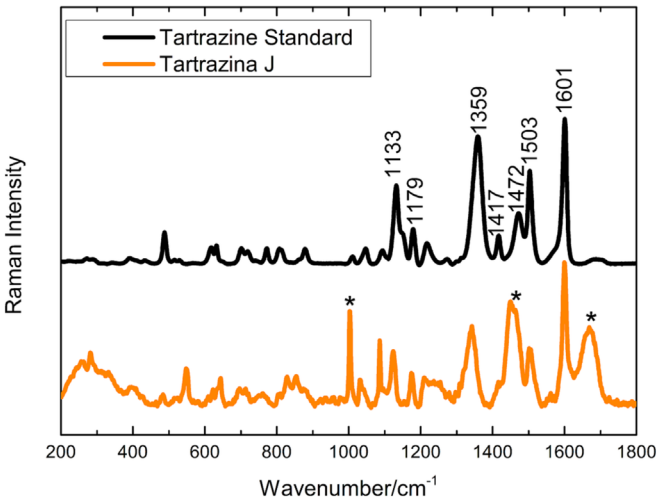

FIGURE 5 Comparison of Raman spectra obtained from the analytical standard of Tartrazine (black line) and the historical samples of Tartrazina J on fibre (orange); the characteristic wavenumbers for main peaks are highlighted, while the interference peaks from wool are evidenced by an asterisk.

Tartrazina J dyed fibre spectrum exhibits a broad peak at 1342 cm^{-1}, while in the spectrum of the standard, a corresponding but higher intensity signal is shifted to 1359 cm^{-1}. A sharp peak is present at 1124 cm^{-1} in the spectrum of the ACNA fibre, while the Tartrazine standard spectrum presents a similar peak shifted to 1134 cm^{-1}. In the lower wavenumber range, the differences are more evident: The signal at 548 cm^{-1} present in the spectrum of the historical sample is not observable in that of the analytical standard. Furthermore, a triplet of peaks at 609, 623, and 644 cm^{-1} in the spectrum of *Tartrazina J* dyed fibre is replaced by a doublet at 618 and 632 cm^{-1} in the analytical standard. These features observed in the spectra of the sample and in the reference spectra of Tartrazine, Acid Yellow 11, and Acid Yellow 17 (which are dyes of similar structure) suggest that the molecule present in the dyed fibre belongs to the same class. It is therefore likely to contain a pyrazole substituent, along with sulfonic groups.

- Giallo Eliaminia RL:

The commercial nomenclature of the dye powder sample labelled *Giallo Eliaminia RL* raised several connections with literature. The English translation—*Yellow Eliaminia*—was listed on several chemical databases as synonymous with a variety of different dyes: Direct Yellow 29, Direct Yellow 44, Direct Yellow 49, and Direct Yellow 50.[61] Whilst a wide range of molecules, the dyes connected to the nomenclature share some chemical features. Specifically, they are diazo structures with the

presence of a central carbamide group. The existence of such a carbamide group was confirmed by the presence of some signals in the spectrum of the *Giallo Eliaminia RL* powder. In particular, the weak bands at 1514 and 1572 cm^{-1} were considered indicative of N-H deformation vibrations in N,N′-dialkyl substituted ureas. The peak expected between 1300 and 1360 cm^{-1} for N-C-N asymmetric stretching in a carbamide group is somewhat obscured by an intense peak at 1339 cm^{-1}. It was however possible to tentatively assign a shoulder peak present in this intense signal at 1320 cm^{-1} to this N-C-N stretching. If this assignment is accurate, the intense peak could be attributed to an NO_2 substituent. This attribution is in agreement with a signal at 824 cm^{-1} attributed to nitro-group scissoring modes. A moderate strength signal at 1176 cm^{-1} may be indicative of N-C-N symmetric stretching in carbamides, but it is fundamental to mention that this signal could also be indicative of the same mode in the azo group.

- Giallo Italana 2G and Arancio Luce G:

Little information was available in literature regarding the nomenclature of the dyed fibre labelled *Giallo Italana 2G* (see *Rosso Italana B* and *Rosso Italana R*). However, the Colour Index links *Arancio Luce G* to Acid Orange 10 and Food Orange 4, which have the same chemical structure (C.I. 16230).[61] The Raman spectra of both samples show significant interference from the wool signals but present a remarkable similarity to each other. Specifically, both the spectra display a characteristic doublet of peaks at 257 and 282 cm^{-1}, while other peaks at 395, 472, 511, 550, 638, 712, and 1087 cm^{-1} are also observable in both spectra.[68,77] At higher wavenumbers, differences between the spectra of the two dyes were evident despite both still maintaining similar spectral patterns. The Raman spectrum of *Arancio Luce G* has an intense peak at 1235 cm^{-1}; in the spectrum for *Giallo Italana 2G*, this signal is weaker and shifted to 1228 cm^{-1}. The peaks at 1495 and 1597 cm^{-1}, attributed to azobenzene ring vibration and benzene quadrant stretch, respectively, in the spectrum of *Arancio Luce G*, are shifted to 1519 and 1604 cm^{-1} in the spectrum of *Giallo Italana 2G*. Additionally, a peak at 1372 cm^{-1} in the spectrum of *Arancio Luce G* is not observable in that of *Giallo Italana 2G*. It is interesting to note that the spectrum of *Arancio Luce G* also presents a remarkable similarity with the spectrum of the aforementioned analytical standard of Red 2G and with the spectrum reported in literature for Acid Yellow 10; however, these are not perfect matches. In particular, Red 2G displays similar Raman peaks—slightly shifted—at 1493 and 1595 cm^{-1}. Furthermore, an intense peak at 1235 cm^{-1} in *Arancio Luce G* shifts to 1282 cm^{-1} in the spectrum of Red 2G. Based on this data, it is possible to hypothesise that *Giallo Italana 2G* and *Arancio Luce G* share the same template structure of Red 2G and Acid Yellow 10—a phenylazonaphtalene. Moreover, the two dyes appear to contain a substituent chlorine atom, but they may have different substituents on the aromatic moieties, which would explain the differences in Raman shifts related to azobenzene vibrations.

- Rosso Naftolo SJ and SEII Pag

For two samples in the collection, strong fluorescence effects meant that spectra could not be acquired. One sample, *Rosso Naftolo SJ*, was a dyed fibre sample linked by nomenclature to the naphthol group. The second sample was labelled only with a handwritten label, unlike the other typed labels in the collection, and was denoted *SEII Pag*, which may have been an internal company name or code.

These results show that Raman spectroscopy has a potential for the characterisation of synthetic dyes of historical and artistic interest, particularly when combined with literature research. Standard Raman spectroscopy is non-destructive, widely accessible, and fairly rapid. Currently, the resolution and stability of the bench-top Raman spectrometer is likely required for this analysis, but the success of standard Raman spectroscopy opens for use of high-resolution portable Raman spectrometers for on-site analysis of textiles. From a diagnostic point of view, it is interesting to note that beyond the possibility of identifying the general features of azo-dyes, in some samples standard Raman had the potential to reveal the specific molecular structure of the dye. In these cases, comparison with reference spectra (hypothesised on the base of the nomenclature or literature) was fundamental. In most the cases, the precise identification was not possible—especially when the wool spectral pattern interference is observable—but acquired spectra provided information related to the presence of specific functional groups and consequent speculations about molecular structures. This information is precious if combined with other non-destructive techniques (e.g., FORS) and if considered preliminary for addressing further analyses. A multi-technical approach (for instance with chromatography) is mandatory when unambiguous identification of exact molecular structures is the goal of the study.

Raman spectroscopy also extends the amount of information beyond the molecular structure of the dye. For example, the Raman spectra in this study offered some information about the impact of the dyeing process on the exposed surface of the proteinaceous fibres, evidencing of S-S bonds breaking and tyrosine burying

for most of the samples. Moreover, in some spectra the use of inorganic compounds for fibre dyeing, such as calcium carbonate, was detected. A further question to investigate is represented by the identification of eventual mordants present on the fibre. If the use of other techniques (e.g., XRF) is necessary for the characterisation of these species, Raman spectroscopy could provide further information related to the interaction of the dye on the fibre through or without the mordant. Combining the identification of inorganic species with the evaluation of the mechanisms of dyeing through its effect on the fibre secondary structure interaction, it has the potential for providing a more informative characterisation of textile production and manufacturing. This information could then be brought into wider context by conducting similar investigations on other historical azo dye subclasses.

As pointed above, the development of reference spectral databases appears to hold the key to the successful use of standard Raman for dye identification, but this task is complex. For example, it is important to define that whilst many Raman spectra of azo-pigments used in painting are present in online databases, these cannot always be directly compared with dyed textile samples; even if the discrimination between dyes and pigments is more faint for synthetic compounds than for natural ones, it is clear from the case of Rosso amidonaftolo 2G that spectral differences could arise between the dye in powder and on fibre. Therefore, further research involving Raman spectroscopy for the development of databases is necessary to transform the investigative potential into real diagnostics for textiles of the 19th, 20th, and 21st centuries. In the case of the investigated ACNA dyes, it was unclear whether they were commercially available or the result of internal synthetic research routes, never distributed due to some issues. Some dyes, connected by literature without a corresponding C.I. number (e.g., Acid Yellow 39), were likely little used, if at all commercially available. It is therefore not possible to dismiss the chance that the dyes in the samples may not be well-documented dyes synthesised by other producers or available on the market. In these cases, even if extensive databases were available, finding reference spectra may not be possible.

4 | CONCLUSIONS

This work combined literature research with the use of Raman spectroscopy to non-destructively obtain information about the chemistries and identities of unknown synthetic azo dyes in both powder form and on dyed fibres. Literature research into the commercial dye names was an excellent tool for informing early hypotheses about chemical identities and proved essential in reinforcing confident identifications. Raman spectra of different samples were varyingly informative. For example, unwanted Raman signals from fibrous matrices impacted the spectra of yellow and orange dyes more strongly than for reds. Nonetheless, the combination of commercial nomenclature and Raman spectroscopy provided information about likely functional groups and molecular characteristics for most analysed samples. Furthermore, in some specific cases (e.g., *Rosso Amidonaftolo 2G*) commercial nomenclature, Raman spectroscopy, and comparison with known reference materials allowed fairly confident molecular identification. Therefore, depending on the sample and research question, this approach could provide sufficient information about the chemical identities of synthetically dyed samples without use of destructive chromatography or modified Raman methods. For example, this investigation was able to confirm that all of the dyes successfully analysed are likely to belong to the azo class. For more detailed research questions, where reference spectra are not available for comparison, or in cases where literature information contradicts Raman findings, further analysis with micro-destructive methods such as SERS or chromatography may be required. In these cases, standard Raman spectroscopy may still offer preliminary or complimentary information, which may help to guide sampling locations and reinforce or contradict identification hypotheses.

The use of standard Raman spectroscopy for the analysis of dyed textiles is a relatively new approach, as most previous research has relied on modified Raman techniques such as spectral enhancement through SERS, or fluorescence reduction by FT-Raman—each of which have significant drawbacks. Whilst dye identification on naturally dyed textiles will generally require these modifications due to their low dye concentrations and intrinsic molecular variability, this research shows that high-quality, informative spectra can be acquired using standard Raman spectroscopy for some synthetic dyes. Standard Raman spectroscopy is simpler to perform than modified techniques, making it generally more accessible across the varied heritage sector. This potential of standard Raman spectroscopy for non-destructive analysis of synthetic dyes in situ is therefore extremely valuable for dye analysts. To fully understand and access the scope of this potential, further investigations across different synthetic dye classes must be carried out. This work and further investigations will also contribute to improving reference spectrum availability, which in turn will contextualise and inform interpretation of future Raman analyses of synthetic dyes.

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