



Coupling of electron and vibrational spectroscopy with false colour imaging for the investigation of natural dyes in historical fabrics (15th–18th centuries)

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Received: 14 September 2022 / Accepted: 1 July 2023
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Abstract A series of historical textile fragments belonging to the Guggenheim collection had been previously studied by FORS and IRR imaging. The need for further analysis emerged in order to get a better understanding of the applied dyes. Under this perspective, SERS measurements and false colour images (UVFC and IRFC) were acquired on selected samples dated back between the fifteenth and the eighteenth centuries and constituted by velvets, embossed velvets, brocades, brocatelles, damasks, lampasses, satins, gros and taffetas of Italian manufacture. The cross-checking of spectroscopic data allowed for confirming some of the results previously obtained, but in the majority of cases much more complex situations were found. On many occasions, SERS and FORS demonstrated their complementarity allowing for discovering the use of mixtures instead of single dye as previously assumed. In addition to indigotin, cochineal and tannins, already identified in the previous investigation, new data allowed for determining the presence of orcein, annatto, luteolin, quercetin and saffron. The FC images supported the obtained results but evidenced the need for the generation of a complete database of historical dyes employed with different dyeing procedures, substrates, mordants and as mixtures with different proportions. The multi-technique approach, involving both non-invasive and micro-invasive methods, also allowed for checking the compatibility of compounds with both the declared historical period and the origin of the investigated textile fragments.

1 Introduction

A set of historical textile fragments from the Guggenheim collection was characterised for the first time in 2018 through FORS in the mere VIS spectral range. For some compounds, a more detailed study involving the acquisition of micro-sized samples was proved to be necessary and only recently allowed. Some criticalities emerged during the investigation, especially in the identification of yellow dyestuffs, both alone and in mixtures. For this reason, a more detailed study on the whole range of colours exhibited by selected fragments of the collection was performed by SERS (Table 1). The chosen subset of textiles is constituted by velvets, embossed velvets, brocades, brocatelles, damasks, lampasses, satins, gros and taffetas, mostly from Venice and other Italian manufacturers, and dating back between the fifteenth and the eighteenth centuries. Even though no specific analysis has been performed, it may be assumed that the majority of fragments has been realised using protein-based fibres, specifically silk and occasionally wool. In a few cases, cellulose-based fibres seem to be present, probably cotton.

The FORS technique has been widely exploited in the field of cultural heritage in the last decades. This technique demonstrated its usefulness in the study of natural dyes in historical textiles in a totally non-invasive way due to features related to the electronic transitions of dyeing molecules [for example] [1–4]. However, the technique also presents a series of drawbacks, first and foremost the broadness of absorption bands making the unambiguous identification of compounds not always possible. For this reason, FORS is normally coupled with other analytical techniques integrating the results or used on mockups to determine the influence of several variables on the spectra such as the type of fibre, mordant and ageing [5]. Some of these variables were taken into consideration for the series of mockups created to build the online database of IFAC-CNR [6, 7].

Some of the most recent studies on historical textiles coupled FORS with multiband imaging, SEM–EDX (Scanning Electron Microscopy–Energy-Dispersive X-Ray analysis) and HPLC–MS (High-Performance Liquid Chromatography–Mass Spectrometry) [8] in order to determine the colouring agents and to integrate the information obtained through reflectance spectroscopy. This is

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Table 1 List of the selected samples

Sample	Colour	FORS	SERS
C1T2a	Red	Cochineal	Carminic acid
C1T2b	Yellow/gold	Flavonoids	/
C1T3	Green	Indigotin + turmeric	Luteolin
C1T4	Purple	indigotin + cochineal	Orcein
C1T4	Blue	Indigotin	Indigotin + Orcein
C1T5	Red	Cochineal	Carminic acid
C2T1	Purple	Anthraquinones (madder) + alum	Carminic acid
C2T2	Red	Cochineal	Carminic acid
C2T3	Green	Indigotin	Saffron
C2T3	Yellow	Flavonoids	Saffron
C2T3	Brown/orange	/	Annatto
C2T4	Blue	Indigotin	Indigotin
C2T5	Blue	Indigotin	Orcein
C2T5	Grey	Indigotin	Orcein
C2T6	Blue	Indigotin	Indigotin + Orcein
C2T6	Brown/orange	/	Annatto
C2T7	Dark red	Cochineal	Carminic acid
C2T8	Red	Cochineal	Carminic acid
C2T9	Red	Cochineal	Carminic acid
C3T1a	Blue	Indigotin	Indigotin
C3T1b	Green	Indigotin	Luteolin
C3T2	Red	Cochineal	Carminic acid
C3T4	Brown	Tannins	Quercetin + Tannin + Annatto
C3T6a	Green	Indigotin	Indigotin
C3T6b	Green	Indigotin + turmeric	Indigotin
C3T7	Blue	Indigotin	Indigotin + orcein
C3T9	Dark pink	Anthraquinone	Orcein + annatto
C3T9	Light pink	Anthraquinone	Orcein
C3T12	Brown	Tannins	Annatto + luteolin
C3T12	Red	Anthraquinone	Annatto
C3T12	Dark brown	Tannins	Annatto

Colours indications and spectroscopic results

because HPLC is a separative method and is still the most used technique to investigate historical textiles, although micro-invasive. FORS results have been integrated with multiband imaging in the case of Chinese textiles from Dunhuang (seventh–tenth-century AD [2]), where this combination allowed for identifying dyes as protoberberine-based yellows, gromwell, indigo and tannins, as well as for mapping their distribution. However, once again the results were not considered definitive but helped in narrowing the number of samples for further micro-invasive HPLC–MS analysis. Similarly, also the study of nineteenth-century Central Asian ikat textiles foresaw the use of both FORS and HPLC, with the first exploited to have a preliminary understanding of the typology and distribution of some dyes, e.g. indigo, insect-based red dyes and synthetic dyes [9].

Surface-enhanced Raman scattering (SERS) spectroscopy has been widely applied to identify dyestuffs since it is known as one of the most effective analytical methods to this aim, with the advantage of requiring extremely small samples (approx. 20–100 μg) [10]. This is one of the main benefits of SERS in the field of cultural heritage, where sampling is rarely permitted, and only very small amounts of material can be collected for analysis. This, together with the enhancement of the Raman signals (up to 14 orders of magnitude) and the quenching of the fluorescence background [10–13], normally observed when analysing many organic compounds, makes SERS one of the most powerful techniques for the study of organic colourants [11, 12, 14, 15] in historical and archaeological textiles [11, 12, 16–20]. Additionally, recent works proposed attempts at quantitative studies for which the use of standard calibration solutions is essential [21, 22].

As known, the SERS effect takes place when organic molecules with π -electron systems or atoms carrying lone electron pairs are adsorbed onto the surface of nanometric metallic particles. To this aim, many nanosized supports with various shapes have been tested (spherical [12], stars [23], rods [24]), mainly using silver as a metal. In most cases, colloids were used, but also pastes [11] proved to be quite effective, with or without [11] pre-hydrolyzation with HF, as well as photo-reduced Ag nanoparticles directly generated on the dyed fibre from AgNO_3 solutions [25].

Among the huge variety of natural dyes, anthraquinones are the most frequently studied and many papers reported their SERS spectra [for example, 10, 19, 25, 26]. As all other dyes obtained by natural sources, extracts contain mixtures of various compounds. Minor components are often hardly distinguishable due to differences in their SERS cross-sections, leading to different signal enhancements [22]. This is the case of madder, where the relative proportion between purpurin and alizarin is generally ca. 1:1.5, while the optimal proportion able to allow collection of the purpurin spectrum would be around 10:1 [25]. In other cases, issues can derive from the steric hindrance, as due to the carboxylate group in carminic acid [25], or to the Br atoms in 6,6-dibromoindigotin [11].

SERS demonstrated its high potentiality in the identification of dyestuffs difficultly recognisable with non-invasive techniques such as flavonoids, despite a certain attitude of flavonols to degrade and form condensation products between the polyphenolic rings in the presence of Ag nanoparticles [25]. On the other hand, it has been reported that flavonols tend to dominate the spectrum of mixtures, hiding signals of other components, such as indigotin in green hues [1].

Eventually, for the investigation of the textile fragments from the Guggenheim collection, past analytical results were integrated also with false colour images acquired in both the IR and UV spectral ranges. This totally non-invasive technique is becoming more and more relevant in the field of cultural heritage and has been recently used also in studies focussing on historical textiles.

A wide study of Asian colourants [2] provided a reference database of materials and demonstrated the potentiality of multiband imaging techniques to distinguish some dyes displaying typical colours, such as Chinese sumac and madder (brownish), sappanwood and gromwell (green), saffron, cape jasmine, turmeric and Chinese goldthread (red). The FC imaging, coupled with other imaging techniques, was also used to provide a preliminary distribution of diverse dyeing materials used in Late Antique textiles from Egypt. This work showed the complementarity of different imaging methods and their usefulness to guide the successive analysis [8]. A slightly different approach was recently used by Colantonio et al., (2022) [27] in a study about two items from French Polynesia conserved at the museum of the Congregation of the Sacred Hearts of Jesus and Mary (Rome). The authors used Hypercolorimetric Multispectral Imaging (HMI) to obtain the FC images allowing the visualisation of dyes/pigments used in the decorations.

This study aimed to present new results obtained on a set of historical textile fragments belonging to the Michelangelo Guggenheim collection. A preliminary totally non-invasive work based on FORS data allowed identifying some of the compounds employed as dyestuff, without compromising the integrity of the objects. However, a new set of measurements was performed by means of the minimally invasive analytical technique SERS to disclose more detailed information about the used dyeing recipes. Both Raman spectroscopy and FORS have already demonstrated their complementarity in past studies carried out on diverse materials, such as wall and mobile paintings [3, 28]. Additionally, spectroscopic results have been further integrated with multispectral imaging and, to the best of the authors' knowledge, this is the first time that these three techniques are simultaneously applied to the study of historical textiles.

1.1 Textile art between the fifteenth and the eighteenth centuries

In the fifteenth century, Florence was the main production site of silk textiles and exported heavy velvets decorated with the “*a griccia*” and “*a cammino*” motives [29] and precious scarlet red textile embellished with gold and silver wires all over Italy, but also in Spain, France, Belgium, Great Britain and Turkey. The colour was given by brazilwood, kermes or by «*grana*», a cheaper dye derived from the insects belonging to the same superfamily as kermes, but imported usually from Majorca, via Genoa and Provence [29–32].

The Florentine and Venetian manufacturers remained relevant in the sixteenth century, but Genoa emerged as the most important production area for black velvets, until the eighteenth century. At the same time, clothes details (small slashes to show the contrasting colour of the vest/shirt) and decorative motifs (double pint oval often including the family coat of arms) changed together with a new clear distinction between dress and furniture fabrics. The former presented the new smaller decoration “*a mazze*”, while the latter maintained the large ovals, often joined by big crowns, amphorae and animals. However, the same typologies of fabrics were used, including heavy silk textiles like velvets, lampasses and damasks decorated with gold and silver wires and coloured with bright tints, often red. Later, the brocatelle (a cheaper variation in the lampasses) was introduced for furnishing, and satins, brocades and lampasses for the “*a mazze*” decoration [29, 30, 33–35].

During the seventeenth century, Genoa remained one of the main producers of silk textiles, and the furnishing “*giardino*” velvets (with large and realistic floral polychrome motifs) were among the most required goods in Europe, as well as the crimson damasks. In the seventeenth century, the difference between clothes and furnishing fabrics was extended to the textile typologies: velvets were used almost exclusively for furnishing, while lighter textiles like damasks, lampasses, satins, taffetas and brocades were preferred for clothes. Finally, the decorative motives became larger, more realistic, coloured, with increased use of gold and silver wires in garments.

From about 1680, Lyon began to produce “*a pizzo*” textiles, characterised by vertical decorations imitating the laces patterns [29, 36–39] and, in the following century, France became the principal centre of fashion and silk textiles production, with Lyon and Tours as the main production areas.

At the beginning of the eighteenth century, the new “*bizarre*” decoration (asymmetric placement of exotic Middle and Far East motifs and imaginaries elements) was introduced, becoming more naturalistic around 1720. It was also realised in Italy and Spain on damasks enriched with gold and silver wires or on polychrome silks.

Around 1730, Jean Revel (1684–1751), a Lyonnais painter and the most known French silk textiles designer, invented the so-called “Revel style”, a new decoration style for clothing fabrics quickly spread throughout Europe. He exploited the newborn “*berclé*” or “*point-rentre*”, allowing the creation of colour shades and realistic and naturalistic elements (such as flowers, leaves and fruits) freely arranged.

Due to commercial and cultural exchanges with China, the fashion of the “chinoiserie” spread in Europe since the end of the seventeenth century. It also affected fabric decorations and some “*bizarre*” and “*Revel style*” textiles started to show pagodas, umbrellas and scenes of Chinese life.

Around 1750, the so-called “*a meandri*” (parallel vertical waves of trunks, branches or lace ribbons with bunches of flowers, becoming smaller over time) decorative pattern was introduced, as well as the so-called “*a la Bérain*” (grotesques coupled with medallions, herms, wreaths, divinities, fauns, etc.) decoration for furnishing fabrics. This inspired by the work of the French architect, engraver and decorator Jean Bérain (1637–1711). In parallel, also the “*Pillement*” (reminiscent of the “*chinoiserie*”) style, inspired by the work of the Lyonnais painter and decorator Jean-Baptiste Pillement (1728–1808), became particularly famous. Finally, it is worthy of mention the “*Lasalle*” style for furnishing fabrics (large ovals arranged vertically with realistic birds, flowers, cupids, musical instruments, vases, wreaths and ribbons), created by the French designer and silk producer Philippe de Lasalle (1723–1805), in which chenille wires provided three dimensionality to the decorations [35–40].

2 Materials and methods

2.1 The samples

Single threads were carefully sampled from the borders of historical textile fragments belonging to the collection that Moisé Michelangelo Guggenheim (Venice, 17th November 1837–21st September 1914), donated to the Venetian School of Art applied to Industry (currently “Michelangelo Guggenheim” Art High School of Venice). Each sample was 2–5 mm long and was collected where it was possible to individuate a free end of the thread.

The proposed study did not focus on the identification of the textile fibres, and consequently, specific information is not available. However, it is possible to assume that most of the fragments were produced using silk fibres. In a few cases, a cellulose-based fibre, probably cotton, was used.

A list of the samples textiles is provided in Table S1, also reporting their production period, geographical origins and type of fabric (when available).

2.2 The analytical methods

Images of textile fragments were captured in UV-Reflected light (UVR) in the 320–380-nm range with a modified Samsung NX1100 digital camera with low-pass filter removed and by fitting a Bader-U (Baader Planetarium GmbH, Mammendorf, D) filter on Olympus Zuiko (Tokyo, Japan) 28-mm f/2.8 and a 50-mm Macro f/3.5 lenses. Near infra-red (NIR) images were collected in the 900–1150 nm spectral range with the same camera coupled with a Hoya (Kenko Tokina Ltd., Tokyo, Japan) RM90 IR pass filter. Textile samples were illuminated by an incandescent tungsten lamp.

The VIS images were collected with a Nikon D800e digital camera coupled with a Zeiss Makro-Planar 100mmf/2.8 lens on a macro-repro stand, at ISO100, f8 aperture and shutter speed between 1/2 and 1/16 s. Both white and colour calibrations have been performed for each picture by using a ColorChecker Passport panel and its proprietary X-Rite software (Grand Rapids, MI, USA).

The Adobe Lightroom software was employed to convert the original UVR and IR images (TIFF format) into B/W ones. All images were post-processed by means of Adobe Photoshop CS6 (San Jose, CA, USA) software to generate UV-FC and IR-FC images. For the firsts, after splitting the RGB channels of the VIS image, the red channel was replaced by the green one and the green one by the blue one. To generate IF-FC images, the green channel was replaced by the red one and the blue one by the green one.

The dyes were extracted from approx. 1 mg of textile sample suspended in 50 μL of 0.5 M oxalic acid/ methanol/ acetone/ water (1: 30: 40: 40 v/v/v/v) solution and ultrasonicated for 30 min at 60 °C. A citrate-reduced silver colloid was obtained according to Lee and Meisel [41]. For SERS analysis, 5 μL of the colloidal Ag solution was mixed with 1 μL of sample extract, a drop was then deposited on a microscope glass slide, and the measure was acquired immediately.

The SERS spectra were collected using a Renishaw InVia instrument coupled with an optical Leica DLML microscope, equipped with a NPLAN 20 \times objective. The laser source was a NdYAG laser with at 532 nm and a laser power output between 1 and 5 mW. The spectrometer consists of a single grating monochromator (1200 lines mm^{-1}) coupled with a CCD detector, a RenCam 578 \times 400 pixels (22 $\mu\text{m} \times$ 22 μm) cooled by a Peltier element. The spectral calibration of the instrument was performed on the 520.7 cm^{-1} band of a pure silicon crystal. All SERS spectra were recorded between 350 and 2000 cm^{-1} , where the main Raman and SERS signals of dyes are located, with 3 accumulations and exposure times of 10 s. The spectral intensities were normalised by scaling their values between 0 and 1 with no smoothing or baseline correction.

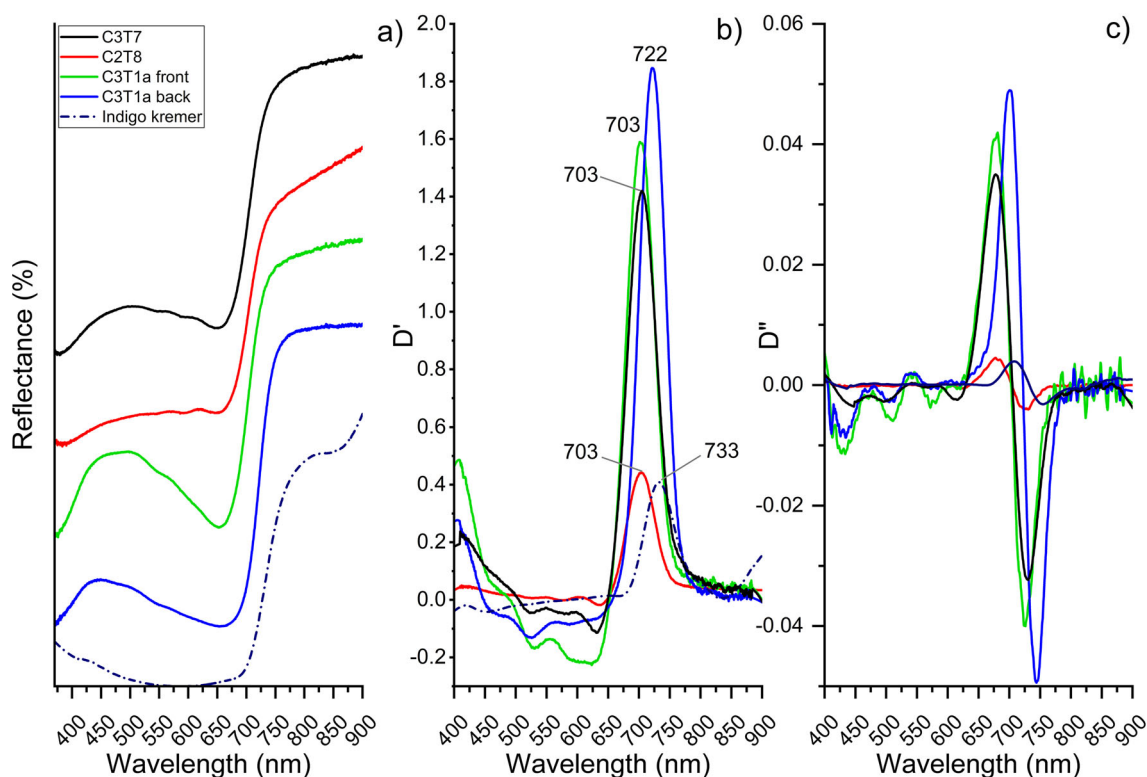


Fig. 1 **a** FORS normalised spectra of blue areas on C3T7, C2T8, C3T1 (front and back) and reference spectrum of indigo. Spectra were vertically shifted for a better comparison; **b** the first derivative of spectra in (a); **c** the second derivative of spectra in (a)

3 Discussion of the results

3.1 Blue dyes

In all selected textile fragments, FORS spectra revealed the use of indigo/woad as blue dye (Table 1). Spectra and derivatives reported in Fig. 1 match the typical profile of indigo/woad, with its main absorbance bands at about 470 (better visible in C3T12a), 545 and 655–660 nm, and the inflection point falling between 703 and 722 nm (Fig. 1b). In the specific case of sample C3T1a, some differences between the front and the backsides were imputable to the conservation state of this dye, with the back showing values closer to those of pure indigo (Fig. 1). The presence of a second compound could be observed in the spectra acquired on samples C2T5 and C3T7. In both cases, an additional structure appeared between 590 and 650 nm: the main absorption of indigo/woad resulted indeed slightly shifted towards lower wavelengths, and the minimum at approx. 590 nm could match with that of orcein [42]. However, the second typical absorption maximum of this dye, located at ~ 544 nm, fell in the same position as one of the indigo/woad diagnostic bands.

The presence of indigo/woad in the textiles of the Guggenheim collection was previously reported [3], and the acquisition of new data by SERS allowed for confirming the exclusive presence of this dye in only two samples, i.e. C2T4 and C3T1a (Fig. 2a, Table 1).

In other threads, sampled from C1T4, C2T5, C2T6 and C3T7 (Fig. 2e, Table 1), SERS spectra revealed the presence of the direct dye orcein or orchil (see Sect. 3.6) in combination with indigotin, except in C2T6 where Raman spectroscopy could only detect orchil. Obtaining different results with SERS and FORS confirms the complementarity of these two spectroscopic techniques, allowing for a better understanding of the complexity of the dyeing materials.

Orchil is known to be very sensitive to light and tends to fade easily: as previously mentioned [43], when indigotin and orchil were used together, the final hue should appear violet or violet blue, with the purplish component provided by orcein, fading over time [44].

The use of indigotin was further confirmed by UVFC and IRFC images showing a prevailing yellow-greenish and pink hues respectively in correspondence with the blue areas (Fig. 2c,d) [2]. The FC images can be challenging to interpret because the ageing of both fibres and dyes, and additional artefacts can arise from the presence of metal threads, the combination of different typologies of fabrics and the possible use of mixtures of dyestuffs applied to obtain the final hue. As shown in Fig. 2b-d, sample C3T1a was

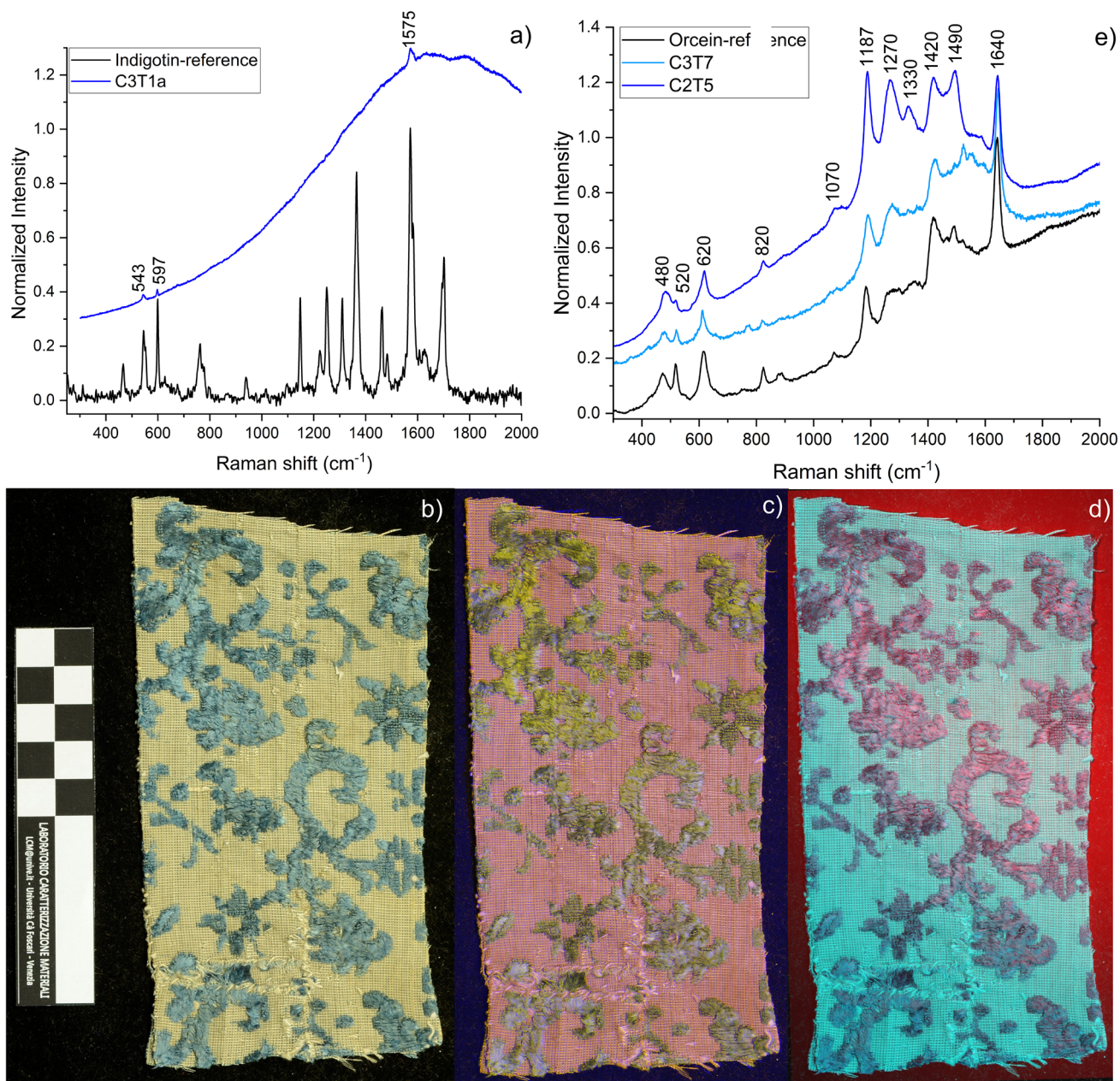


Fig. 2 **a** SERS spectra of C3T1a and the indigotin reference; **b** VIS image of C3T1a; **c** UVFC image of C3T1a; **d** IRFC image of C3T1a; **e** SERS spectra of C2T5, C3T7 and orcein reference. Raman spectra were normalised to 1 and vertically shifted for a better comparison, with no smoothing or baseline correction

in a bad conservation state, affecting both the background and the blue embroidery. In addition, the blue hue of some areas of the UVFC image was the result of a slight overexposure due to the preferred orientation of threads.

Additionally, the UVFC and IRFC images of samples containing both dyes (Fig. 7g,h) can be misleading if considered alone because of the prevalence of the false colours informing only about the presence of indigotin (not shown) [2]. How orcein and its degradation products affect the FC image is difficult to establish due to the lack of references in the literature. Both the UVFC and IRFC images of sample C2T6 are presented in Fig. 6e,f: while the first shows a certain consistency with the presence of indigotin, the latter does not allow for a clear interpretation about the presence of this dyestuff.

It is worth mentioning that the possible use of Indigotin in C3T12 was pointed out by the IRFC images in which the blue embroidered flowers appear pink (Fig. S1).

The combination of indigotin and orchil, whose use for textile dyeing restarted at the end of the thirteenth century, is already reported in the literature for textiles from Krakow churches dating back to the fifteenth–seventeenth centuries [45].

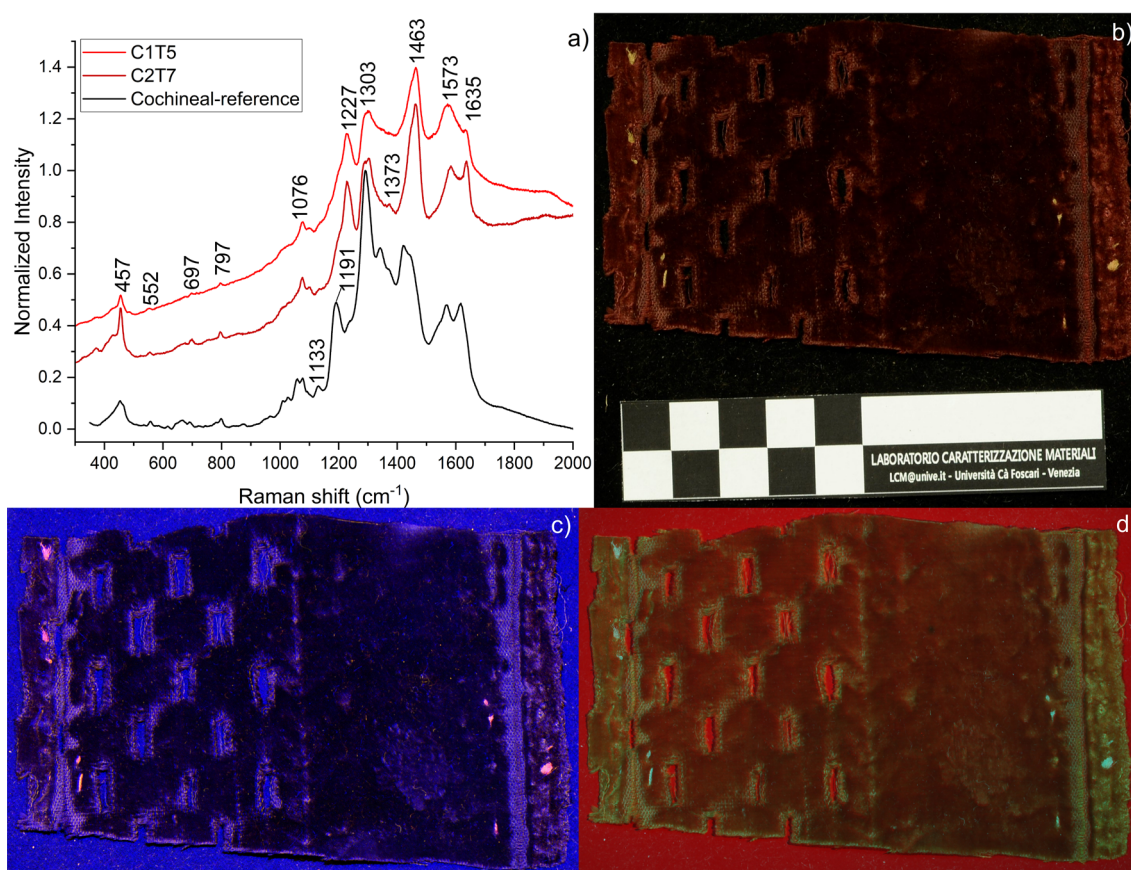


Fig. 3 SERS spectra of C1T5, C2T7 and cochineal reference. Spectra were normalised to 1 and vertically shifted for a better comparison, with no smoothing or baseline correction; **b** VIS image of C2T7; **c** UVFC image of C2T7; **d** IRFC image of C2T7

The only source of indigotin in Europe was woad (*Isatis tinctoria*) until the introduction of indigo (*Indigofera tinctoria*) in the sixteenth century and its definitive prevalence in the seventeenth century [44]. Currently, a certain date is available only for three of the cited textiles fragments: C1T4 and C3T1a dated back to the sixteenth and end of the sixteenth century, while C3T7 dated to the seventeenth century [3]. Therefore, the use of indigo was highly probable for the last two fragments, while both dye sources should be considered possible for C1T4. On the other hand, orcein was extracted by lichens such as *Rocella tinctoria* or *Rocella fuciformis*, both growing on rocky coasts of the Mediterranean Sea [46]. The lichen-deriving dyes have been known since antiquity (Egyptians and Romans among users) and rediscovered in 1330, when they were imported from Eastern countries by a Florentine merchant named Federigo [44]. Orchid was, in fact, used as a substitute for the precious Tyran purple, and it was also indicated as “false shellfish purple” [47]. The secret of dyeing with orchil was strictly protected by the Florentine textile industry for almost two centuries, determining part of its fortune. The recipes started to be available from the beginning of the sixteenth century, when Florence exported orchil to Flanders, England and Germany. This dye became particularly popular after 1703, when the *Rocella tinctoria* was discovered in the Canary Islands [44]. Depending on the pH of the dyeing bath and the presence of mordants, several hues, from bright red or orange to purple, could be obtained [48].

3.2 Red and pink hues

The results from SERS measurements carried out on red threads showed in most cases a good match with previously acquired FORS spectra [3] and confirmed the use of anthraquinones of animal origin (Table 1). Carminic acid was identified, pointing out the utilisation of cochineal as dyestuff (Fig. 3a). As evident from Fig. 3b–d, the cochineal-dyed sample C1T5 appeared dark in the UVFC image, and the same behaviour was found for all the samples in which SERS identified this insect-based dyestuff (Table 1). Despite these consistent results found on the studied textile fragments, the available literature reports about cochineal as being characterised by a dark-green hue [7, 49], but no information about the effect of the fibre and its conservation condition were found. However, the dark colour could be related to a particularly high concentration of the dye and further enhanced for velvets. On the other hand, the typical IRFC colour exhibited by cochineal should be golden yellow [7, 49], while sample C2T7 showed a dark red colour with green parts on the borders where the velvet is not present.

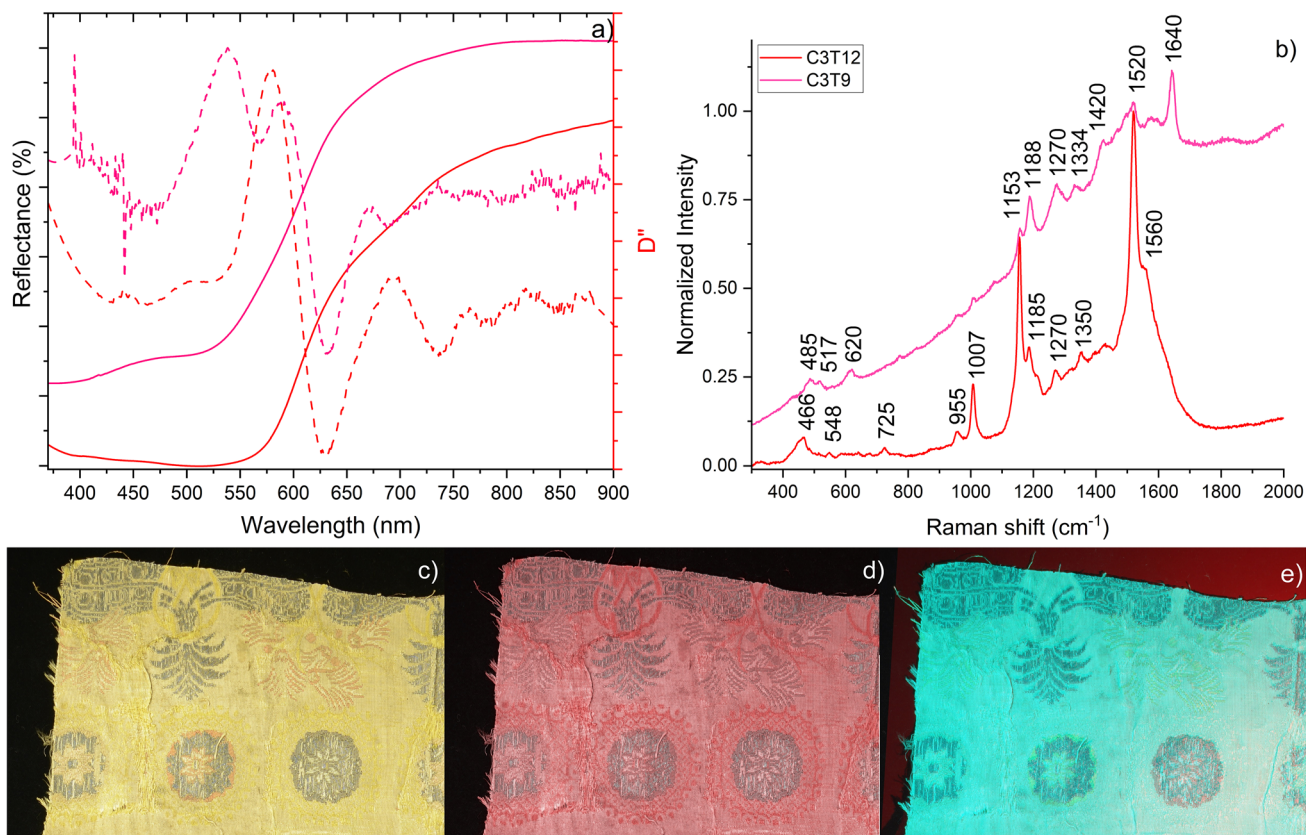


Fig. 4 **a** FORS normalised spectra and second derivatives of C3T12 (red) and C3T9 (pink); **b** SERS spectra of C3T12 (red) and C3T9 (pink). Spectra were normalised and vertically shifted for ease of comparison, with no smoothing or baseline correction. **c** VIS image of C3T9; **d** UVFC image of C3T9; **e** IRFC image of C3T9

Except for samples C2T8 and C2T9, for which a date could not be attributed, almost all cochineal-dyed fragments studied in this work were dated later than the sixteenth century [3]. The American cochineal was imported in Europe from 1518, shortly after the discovery of Mexico, and quickly replaced Polish and Armenian cochineal, as well as kermes [50]. Indeed, the American cochineal could be considered the most probable source for the investigated samples [44]. An exception is represented by the oldest red fragment, C2T2, dated between the fifteenth and sixteenth centuries.

In one of the examined cases, the SERS result differed from what previously found: ref [3] reported the use of brazilwood for the red areas in C3T12, and a mixture of brazilwood and tannins for C1T1b. Such attributions seemed not correct since the pure brazilwood spectrum was collected on the orange embroidery of C1T1b. Brazilwood was a cheaper dye also used to obtain orangish hues, as attested in the literature [51, 52]. On the other hand, the FORS spectrum collected on C3T12 was not very specific (Fig. 4a, Table 1) but resembling instead those reported for highly concentrated anthraquinones, exhibiting an additional weak and broad absorbance band between 700 and 725 nm.

The SERS spectrum collected on C3T12 (Fig. 4b, Table 1) highlighted the presence of annatto (*Bixa Orellana L.*) due to the presence of its three main peaks located at about 1520, 1153 and 1007 cm^{-1} , and attributed to C = C stretching, C–C stretching and in-plane rocking of CH_3 + C–C stretching vibrations, respectively [17]. Normally, annatto provides a yellow-orange hue deriving from the main colouring agents, i.e. bixin in liposoluble preparations, and norbixin in hydro soluble ones (carotenoids) [53, 54].

However, this dyestuff was also used to obtain red hues, depending on the employed mordant, not essential to the dyeing process, and on the substrate. For example, when applied to silk, it generates red hues, and the embroidery detail on C3T12 exhibited a bright red colour. Annatto is a direct dye, able to bind itself to the fibres without a fixer [55], and mordants could be deliberately added to impart a different colour, varying from yellow lemon in presence of tin, to orange when mixed with aluminium [44]. In addition, Dutch recipes from the seventeenth and eighteenth centuries reported the use of annatto as an after treatment used to brighten the cochineal red colour [44]. Annatto was also often added to adulterate and improve the colour of batches of the much more expensive cochineal, sometimes intentionally diluted with colourless compounds used as fillers [56]. This dye started to be imported from Central America in the sixteenth century and became particularly popular in the Spanish productions of the eighteenth century due to the brightness of obtained colours on silk, despite its instability and tendency to degrade [53]. This piece of information is compatible with sample C3T12, dating back to the last quarter of the eighteenth century [3], but not with the hypothesised location.

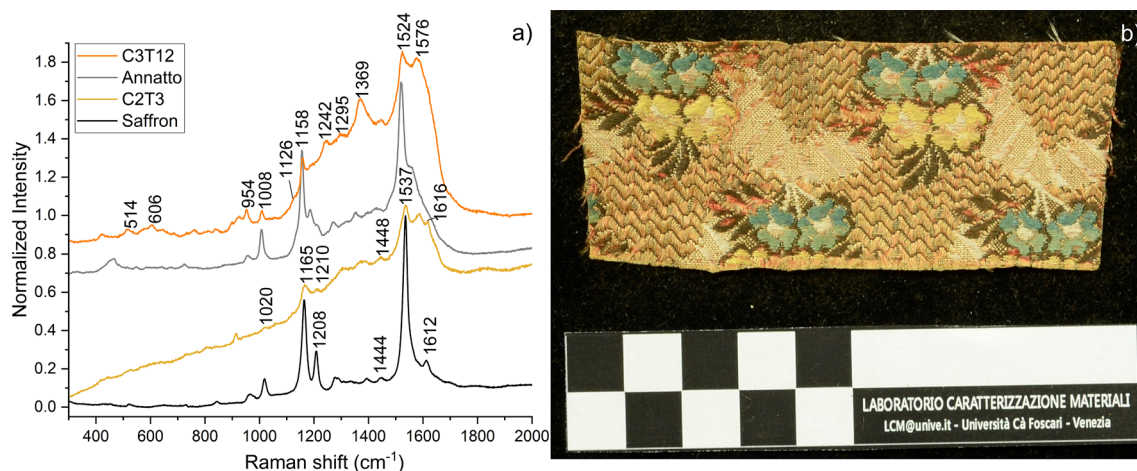


Fig. 5 a SERS spectra of C2T3 and C3T12, and annatto and saffron references. Spectra were normalised and vertically shifted for ease of comparison, with no smoothing or baseline correction; b VIS image of C3T12

The fabric was in fact supposed to be manufactured in Italy, so it can be assumed that artisans were aware of both materials and dyeing routines from other geographical areas.

Considering the combined information obtained by FORS and SERS, the most probable scenario foresaw the use of a mixture of an anthraquinone and annatto. Furthermore, both the analytical methods are not separation techniques, and the study of mixtures can be challenging: it is known that often not all components of a blend can be identified using a single methodology, but each one can preferably be detected by one technique. For this reason, the contemporary use of both methodologies is fundamental to obtain a clear understanding of the complexity of the employed dyestuff.

Figure S1 shows the IRFC image of C3T12, in which all red areas appear yellow. As already pointed out, anthraquinones are supposed to provide a golden yellow colour in IRFC [7, 49], so cochineal seems to affect the appearance of the fibre.

In addition to the red threads, also two pink fibres collected from darker and lighter embroideries of sample C3T9 were analysed by SERS (Fig. 4b, Table 1). In both cases, the spectra showed orcein as the main dyestuff, coupled with annatto, whose contribution is evident in the darker fibre. On the other hand, FORS spectra suggested the presence of an anthraquinone coupled with another component. The FORS spectrum acquired on darker areas displayed a broad and weak absorption band centred at approx. 590–600 nm (Fig. 4a) that could be compatible with orcein. Despite none of the typical absorptions of this dye being clearly visible, the second derivative of the spectrum revealed many maxima, presumably due to the presence of more than one compound (Fig. 4a).

This mixture could involve the use of anthraquinones, but it was not common, since only one work in the literature reported the occurrence of this blend: a Viennese swatch book of Benedict Codecasa, a silk merchant active between the late 1700s and early 1800s. The presence of both anthraquinones and lichen dyes was reported for several red, orange and purple colours, with madder coupled to lichen dyes, specifically in colour 356 [57]. However, the simultaneous presence of annatto was never reported in the literature.

The FC images of C3T9 are shown in Fig. 4c–e: pink details appeared greyish in UVFC and yellow in IRFC. The UVFC hue is not compatible with annatto, for which a red colour is expected, as reported for carotenoids [2]. The grey colour of the UVFC image is not consistent with any anthraquinone either, since both insect-based ones and madder should show shades of green. On the other hand, a yellow hue in IRFC is typically generated by this class of materials [7, 49]. However, and as already stated above, no information is currently available in the literature about orcein, to the best of authors' knowledge.

3.3 Yellow hues

The FORS spectra of the golden-yellow areas evidenced only one class of dyestuffs, flavonoids [3] (Fig. 5a, Table 1), the most common compounds exploited in the past to obtain yellow colours. However, SERS spectra collected on C2T3 and C3T12 (Fig. 5b) show bands at 1007, 1156 and 1523 cm^{-1} , attributable to annatto in C3T12 and to another yellow dye, possibly luteolin (514, 606, 952, 1126sh, 1242, 1295, 1369, 1576 cm^{-1}) [58], whose presence would match the results of FORS analysis.

Unfortunately, the FC colours are often not very specific when working on yellow dyestuff, most of them exhibiting white or light-yellow shades in IRFC [2, 7, 49], as observed in the C3T12 fragment (Figure S1). Annatto is expected to appear as red in UVFC and white in IRFC [2]; however, the same colour is also indicated as the IRFC hue of weld (a flavonoid, see below) [2].

The presence of annatto is also possible in C2T3, yet the positions of peaks seem to match better with the spectral profile of crocin, the glucoside of another apocarotenoid, crocetin, typical of saffron (Fig. 5b, Table 1). Other bands in the spectrum of C2T3 were observed at 1587, 1299 and 911 cm^{-1} and were possibly attributable to luteolin [58]. Crocin shows two absorbance bands at 445 and 470 nm that may be compatible with the change of slope in the FORS curve of sample C2T3 (Fig. 5a).

The UVFC image of this sample (Figure S2) was dominated by a reddish hue in correspondence with the yellow background, apart from some effects due to the shining of silk. The appearance of this colour is compatible with the presence of saffron, supposed to provide a pinkish hue in UVFC images [19]. On the other hand, the IRFC hue of the yellow background appears light blue, not allowing any clear interpretation.

As already mentioned in Sect. 3.2, the presence of annatto in C3T12 matched quite well with the date previously reported for these samples, i.e. the last quarter of the eighteenth century [3]. On the other hand, saffron has a long history of use as a direct dye and its presence in C2T3 is indeed compatible with the date reported for this textile fragment (fifteenth–sixteenth century). Saffron is a direct dye extracted from the stigmata of *Crocus Sativus* and already used in Egypt and in Persia for dyeing textiles in orange-yellow hues. It was also coupled with alum mordant [59] to obtain orange hues. It was particularly important for Romans and Greeks, but starting from the Middle Ages its use became more limited due to the availability of cheaper dyes such as weld, fustic and fiset. The main exception was Spain, where saffron was cultivated [50].

On the other hand, weld (*Reseda luteola*) is usually considered the most probable source of luteolin since the early Middle Ages and it remained the most used yellow dyestuff in Western Europe before the discovery of America. It continued to be one of the most relevant dye also later, until 1775 when quercitron became easily available [46], though also other plants can be considered as historically compatible sources. Luteolin is, in fact, a very diffuse compound in nature and can be found in many species, as well as most flavonoids. For example, dyer's broom (*Genista tinctoria*) and saw-wort (*Serratula tinctoria*) can also contain relevant amounts of such dye [60]. Dyer's broom has been used to dye wool since prehistoric times; it was first mentioned by Pliny in his *Naturalis Historia* and remained one of the most important yellow dyes [60]. Finally, also saw-wort was widely used by European textile dyers since the Middle Ages to dye wool and silk, but it was often coupled to weld or dyer's broom [50].

3.4 Brown hues

Brown threads were present in several textile fragments of the Guggenheim collection, mostly in embroideries. The previous FORS results reported tannins as the main dyestuff responsible for the colour in the analysed areas [3]. Data obtained through SERS integrated those results identifying annatto (bixin) in samples C2T3, C3T12-dark and C2T6 (Fig. 6a, Table 1). The use of this dye was already reported in Sects. 3.2 and 3.3 as responsible for the red and yellow colours on C3T12, but it was widely known also as a brown dye, especially when employed in combination with other dyes [53].

The reflectance spectrum of C2T6 (Fig. 6b) displayed the general shape attributable to flavonoids (Table 1), associated with broad and barely detectable bands possibly indicating the presence of a second compound, probably annatto as shown by SERS results. The FC images obtained for C2T6 may confirm the presence of annatto in the darker areas due to the red colour shown in the UVFC image (Fig. 6e). Tamburini and Dyer 2019 [2] reported about a similar appearance for an object containing carotenoids. The presence of a second compound may explain the reddish-brown hue displayed in the IRFC image (Fig. 6f).

On the contrary, two different typologies of FORS profile were obtained on C3T12 (Fig. 6b). The first one, which includes both dark and light brown hues on the back of the fragment, presents an inflection point at approx. 595 nm. The position of the feature seemed to be shifted towards higher wavelengths with respect to annatto for which, however, a precise value was never reported [53, 57]. Such shift could be attributed to the presence of a second compound, able to modify the spectrum and possibly to mask the absorbance features of annatto, which was detected by SERS on darker fibres. Other reflectance spectra acquired on the front of the same sample exhibited the previously reported typical concave shape of tannins [3]. Consequently, the analysis seemed to indicate that the two brown threads used to realise the C3T12 embroidery were altered on the front side. This led to the sole detection of tannins, better preserved than annatto, by FORS. The UVFC images (Fig. 6d) showed dark areas in correspondence with the brown parts, while a brown-reddish hue is evident in the IRFC image (Fig. 6e). Tannins are already known to generate dark brown hues in UVFC images and brown to red–orange colours in IRFC images. However, the reddish colour can be considered compatible with the presence of carotenoids [2], such as annatto.

Finally, the SERS spectrum collected on C3T4 (Fig. 6c) resulted more complex, showing features referable to the flavonoid quercetin (at 1642, 1560, 1526, 1407, 1366, 1187, 1003 and 521 cm^{-1}), annatto (1526, 1187, 1157 and 1003 cm^{-1}) and tannins (Table 1). Thus, it was difficult to determine which type of tannin could have been applied. Despite a partial overlap of bands belonging to different molecules, features shown in Fig. 6c seem to match quite well with data reported by Bruni et al., (2011) for sumac berries and/or ellagic acid, being one of the compounds in the berries extract [61].

The contemporary presence of tannins and quercetin could suggest two different scenarios: i) investigated threads were dyed with a plant extract yielding both compounds; ii) the two molecules derive from different sources and tannins were used both as mordants and to modify the final hue. The distinction between these two scenarios was not possible through the employed spectroscopic methods, and chromatography techniques (such as HPLC–MS) would be necessary to determine the relative amounts of the substances. The FC images (Figure S3) were not helpful to discriminate the two scenarios and only showed the dark and dark-reddish hues of tannins in UVFC and IRFC, respectively.

When considering this second hypothesis, Persian berries (Buckthorn berries) and quercitron bark can be considered as the main historical sources of quercetin [48, 62]. The former term was used to indicate berries from different plants of the *Rhamnus spp*, growing in both south-central Europe and in Asia Minor, providing earth brown hues when berries were well mature. This dye had been used since antiquity for dyeing textile fibres: it was already attested in Rome at the beginning of the Christian era and

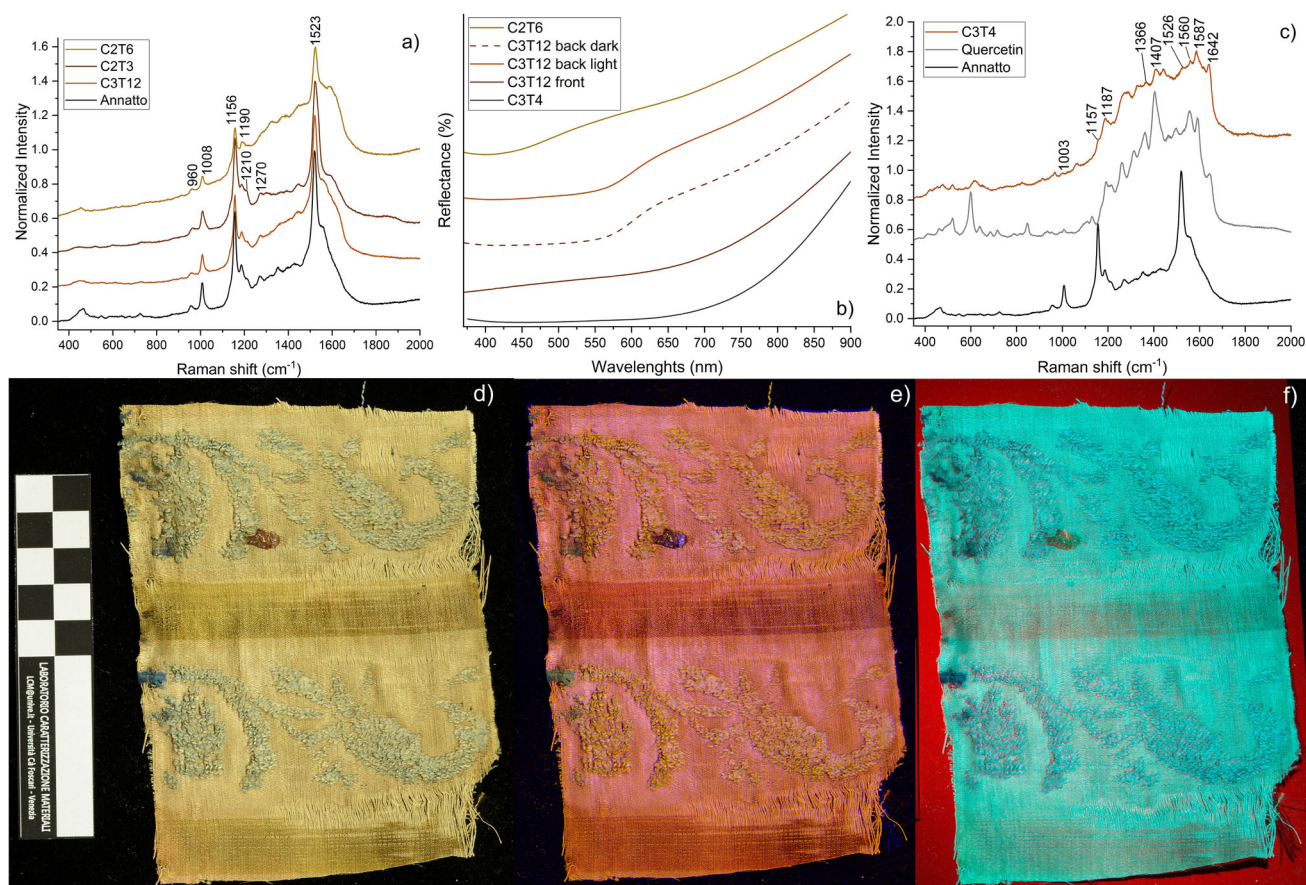


Fig. 6 **a** SERS spectra of C2T6, C2T3, C3T12 and annatto reference. Spectra were normalised to 1 and vertically shifted for a better comparison, with no smoothing or baseline correction; **b** FORS spectra of C2T6, C3T12 (dark and light back, and front) and C3T4; **c** SERS spectra of C3T4 and quercetin and annatto references. SERS Spectra were normalised and vertically shifted for ease of comparison, with no smoothing or baseline correction. **d** VIS image of C2T6; **e** UVFC image of C2T6; **f** IRFC image of C2T6

in Germany during the Middle Ages [63]. In parallel, quercitron bark indicates the inner bark of *Quercus velutina* (or *tinctoria*) Lamk [48], imported from North America (Pennsylvania, Georgia and Carolinas) starting from the end of the eighteenth century. The sample C3T4 dated back to the sixteenth century, so the use of Persian berries as a quercetin source would be the most reliable if hypothesis ii) is assumed.

3.5 Green hues

Green and purple hues can be quite challenging to analyse because they were often generated with mixtures of at least two components. Usually, indigotin and a yellow dye were used to produce a green colour and both the absorption band at ~660 nm and the inflexion point between 690 and 730 nm [64] of indigotin are strong features normally preserved and prevailing in all FORS spectra collected on green hues [3]. Indigotin was exclusively identified by SERS in two green threads, C3T6a and C3T6b (FORS spectra reported in [3], Table 1), for which no additional information could be obtained. In both cases, the relative amounts of the yellow component were probably too low for the sensitivity of the utilised methods. This could be attributed both to a choice of the dyer, especially for C3T6b, showing a darker hue, or to the well-known fastness of most of yellow dyes [65].

The identification of yellow dyes was not possible with FORS [3], but SERS spectra clearly evidenced the presence of luteolin in two samples, i.e., C1T3 and C3T1b (Fig. 7a–d), confirming the usefulness of a combined approach involving these two complementary techniques. The presence of turmeric was previously hypothesised in sample C1T3 [3], due to some structures observed at low wavelengths in the FORS spectrum. However, the SERS results were much more reliable in the matching of the yellow dye luteolin, not detectable by UVFC imaging, showing only the yellowish colour due to indigotin (Fig. S4).

As already mentioned in Sect. 3.3, such a compound can be associated with several natural sources, and it was one of the most common yellow dyes in the past. Luteolin was often used to dye green together with indigo or woad due to its intrinsic yellow-greenish hue [50]; this is particularly true when copper was used as mordant. Saw-wart was also known for producing slightly different hues when combined with different mordants, such as greenish-yellow with alum and olive brown with iron [50].

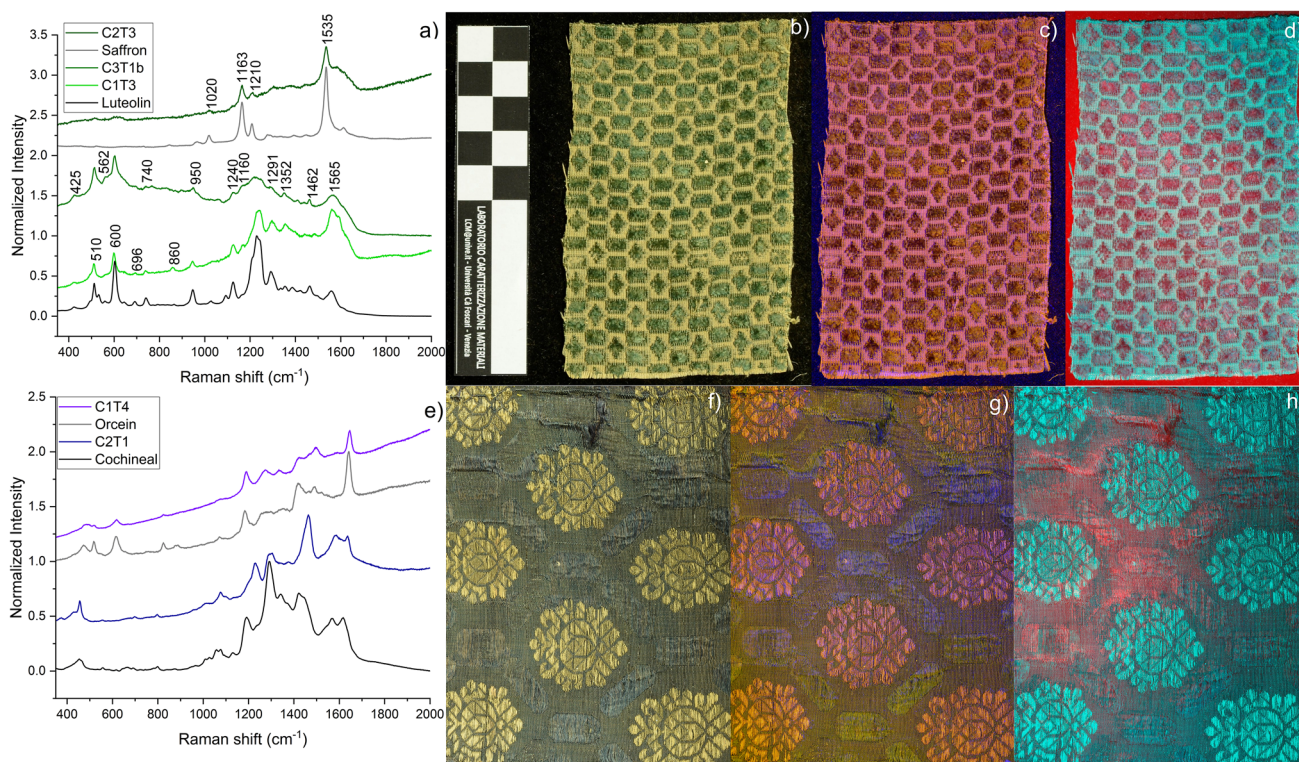


Fig. 7 **a** SERS spectra of C1T3, C3T1b, C2T3 and luteolin and saffron references. Spectra were normalised and vertically shifted for ease of comparison, with no smoothing or baseline correction; **b** VIS image of C3T1b; **c**: UVFC image of C3T1b; **d** IRFC image of C3T1b; **e** SERS spectra of C1T4 and C2T1. Spectra were normalised and vertically shifted for ease of comparison, with no smoothing or baseline correction; **f** VIS image of C1T4; **g** UVFC image of C1T4; **h** IRFC image of C1T4

Interestingly, the SERS spectrum of sample C2T3 (Fig. 7a) evidenced the presence of another yellow dye, being saffron (Table 1): the collected profile exhibited the two typical bands of carotenoids at 1163 (C–C stretching mode) and 1535 cm^{-1} (C = C stretching mode), as well as other less intense but diagnostic bands located at 1446, 1210 and 1020 cm^{-1} [66]. This is one of the few cases where the FORS profile seemed to be highly affected by the yellow dye [3], which played also a relevant role in the UVFC image. As stated in Sect. 3.3, saffron exhibits a pinkish hue in UVFC, and the light-green embroidery in C2T3 was found to display a brownish hue possibly due to the combination of the pink colour generated by saffron with the yellow-green one provided by indigotin [2] (Figure S2). In parallel, the IRFC image showed the green embroidery as quite light pink areas (Figure S2), possibly compatible with the presence of carotenoids [2].

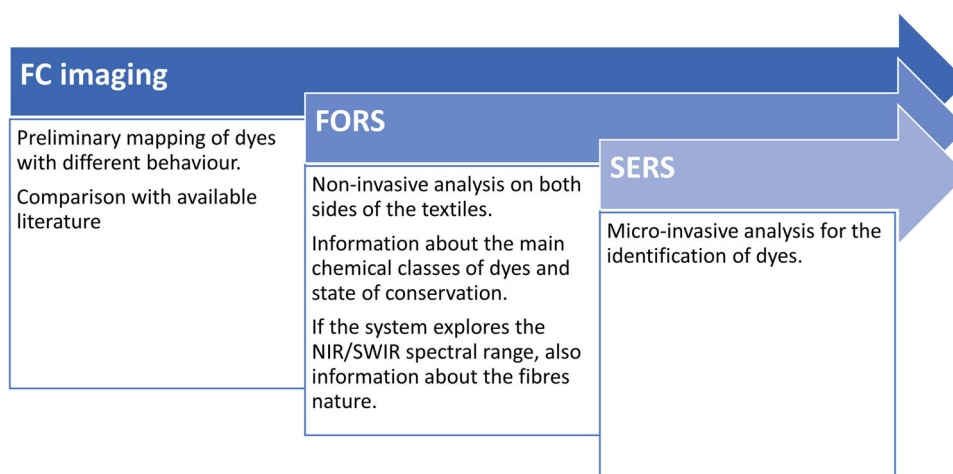
3.6 Purple hues

Purple hues were often obtained by blending a blue and a red dyestuff, the blue one usually being indigotin. However, few dyes are also reported as purple dyestuff; the most famous being orcein.

SERS spectra were collected on two samples from fragments C1T4 and C2T1. Previous results obtained from FORS [3] were partially confirmed for the latter (Fig. 7e), where the use of anthraquinones was detected, probably associated with alum as mordant to obtain the purple hue [3] (Table 1). Additional SERS measurements allowed for the identification of cochineal instead of the originally hypothesised madder (Table 1). This result was further confirmed by UVFC imaging showing the dark green hue typical of this animal dye (Figure S5) despite its high concentration and the type of fabric (velvet).

Interestingly, SERS results obtained on C1T4 fragment (Fig. 7e) clearly allowed to attribute the colour to orcein (Table 1); the same dye was previously detected in the blue threads of the same textile fragment (Sect. 3.1). While a production date was not available for C2T1, the C1T4 fragment dated back to the sixteenth century, so being compatible with the use of this dye (Sect. 3.1). However, this result seemed to be in contrast with what previously reported since the purple colour was attributed to a mixture of indigotin and cochineal [3] based on the comparison with literature [4] (Table 1). Re-analysing the FORS spectrum in light of the latest SERS results, it might be possible to attribute some of the observed features to orcein, whose spectrum [67], however, did not seem to fully match with the one recorded on sample C1T4. This case is, consequently, worthy of further investigation in order to figure out which hypothesis is the correct one: i) a mixture of indigotin and orcein, since the main features of the blue dye are clearly visible in the FORS spectrum, or ii) a mixture of three dyes including cochineal.

Fig. 8 Flowchart showing the sequence of analysis for the study of historical textiles



Unfortunately, the FC images (Fig. 7f–h) did not provide any relevant information, probably due to the poor conservation condition of some sections of the fragment, together with the coexistence of areas with different characteristics. As displayed in Fig. 7f, C1T4 contains opaque parts alternated to shining ones and to embroideries realised with a metallic thread, generating many reflections and effects difficult to eliminate during images collection and elaboration. While the UVFC image (Fig. 7g) showed a barely visible yellow-greenish hue, the IRFC one (Fig. 7h) exhibited instead the red colour typical of indigotin. However, no standard references, clearly allowing for evaluating whether or not orcein could be present in the mixture, are available.

To the best of the authors' knowledge, the three-component blend involving cochineal was never reported in the literature, while madder was found in combination with indigotin and orcein only in silk vestments from collections of twenty Krakow churches dating back to the fifteenth–seventeenth centuries [45]. On the other hand, orcein, probably as cudbear, was found coupled with indigotin in samples from a Norwich pattern book dating to 1790–1793 [57] and from Polish liturgical paraments of the fourteenth–fifteenth centuries [43].

4 Conclusions

A set of historical textile fragments belonging to the collection of M. Michelangelo Guggenheim was further investigated in detail by Surface Enhanced Raman Spectroscopy (SERS) and False Colour imaging to clarify some attributions previously given on the basis only of FORS spectra. As shown in Fig. 8, the proposed multi-technique approach foresees the initial use of FC imaging methods to obtain a preliminary mapping of areas displaying different behaviours presumably due to the use of diverse dyeing materials. Successively non-invasive analysis such as FORS can be performed to determine the main chemical classes of dyestuff present in the studied textile fragments. SERS is applied eventually to assess and complete the study since it can be considered a complementary analytical tool to FORS, able to provide information integrating those obtainable non-invasively.

The coupling of these two spectroscopic techniques, supported by FC images, both in the ultraviolet (UVFC) and infrared (IRFC) range, allowed for defining a more complex situation, involving the concurrent use of several dyes in most of the studied threads. In addition to identifying some of the yellow dyestuffs, previously generally indicated only as flavonoids, the SERS allowed detecting additional dyes such as annatto and orchil in many red, brown, yellow, blue and purple threads.

These results were consistent with the dates and geographical origins previously reported for these textile fragments and allowed increasing the knowledge about this collection.

In general, since nor Raman and FORS are separative methods, the use of both techniques, exploiting different principles, demonstrated once again their complementarity in investigating the complexity of historical materials, specifically traditional dyes.

Finally, the need for the generation of a complete database of false colour images, both in the UV and in the IR spectral range, is evident. Something has been recently made available in the database of *Centro Restauro la Venaria Reale* [68]; however, the mockups have been realised as painting panels, i.e. mixing the dyes with binders (Arabic gum and PVAc) and adding two finishing (terpene and acrylic resin), that can interfere with the colours generated by the dyes themselves. Instead, it could be particularly useful not only making such a database available for a comparison of the behaviour of the main dyes used in Europe starting from the renaissance, but also including their combination with different mordants, dyeing methods and mixtures of dyes in various proportions.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1140/epjp/s13360-023-04248-y>.

Acknowledgements The authors are grateful to the Liceo Artistico Statale "Michelangelo Guggenheim" (Venice, Italy) for allowing the current study on their fabrics collection. The authors want to thank also Mr. Isam Al Salem and Mr. Riccardo Orlandi of the Istituto d'Istruzione Superiore "Bruno Franchetti" (Venice) for helping in the acquisition of Reflected UV (UVR) and IR images during their school work alternation period spent at the Laboratory of Materials Characterization (LCM) of the Department of Philosophy and Cultural Heritage, University Ca' Foscari of Venice, Italy.

Funding Open access funding provided by University of Oslo (incl Oslo University Hospital). This research did not receive any specific grant from funding agencies in the public, commercial or from not-for-profit sectors.

Data availability No data associated in the manuscript.

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