

Non-invasive identification of dyed textiles by using Vis-NIR FORS and hyperspectral imaging techniques

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ABSTRACT

Natural dyes have been utilized since ancient times to produce colorful garments and, at the same time, each culture has developed its own traditional designs and techniques during the centuries. Hence, in order to accomplish a proper conservation program of these artefacts, it is fundamental the importance of studying the used dyes on historic textiles. Traditionally, the identification is carried out through invasive or micro-invasive techniques such as HPLC or Raman-SERS. However, a first screening using non-invasive approaches, that could tentatively identify some of the dyes in a contactless mode, is strongly recommended. The present study focuses on the application of non-invasive spectroscopic techniques, namely FORS and hyperspectral imaging in the visible and near infrared range, for the identification of dyes on textiles. Twelve natural dyestuffs (twelve from plant, two insect dyes and a lichen) and three mordants ($KAl(SO_4)_2$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$) were selected and combined to create a set of wool samples whose reflectance spectra, acquired using FORS technique, were the basis for a spectral database. The same set was used to test the Specim IQ hyperspectral camera, with positive results for a non-invasive investigation on wider areas. The application of Spectral Angle Mapping (SAM) gave the possibility to map directly on the image pixel with similar spectral features. Finally, colorimetric data were acquired with a spectrophotometer to obtain chromaticity coordinates.

KEYWORDS Natural dyes, wool fiber, FORS, hyperspectral imaging, textiles, non-invasive

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1. Introduction

Natural dyestuffs have been used since ancient times to dye fabrics and yarns to obtain colorful clothes. Every culture has its own traditions, which include materials and processes of manufacturing. For this reason, in order to accomplish a complete investigation on ancient textiles it is fundamental to be able to recognize which dye has been used to understand those techniques and materials, both to pursue a proper conservation program and to discover more about the manufacturer who made the object.

Natural dyes can be classified according to two criteria: color or dyeing method (Hofenk de Graaff, Roelofs and Bommel, 2004; Cardon, 2007). The classification based on the dyeing methods includes direct-, mordant-, and vat-dyes. Direct dyes are chemical compounds, soluble in water, whose structures are full of polar groups that can bind directly to the fibers without using any other compound. Mordant dyes, on the other hand, need a medium, the mordant, which is a metal salt with a chelating structure that binds the color to the fiber. Some typical mordants are alum, sulphates (mainly iron or copper), stannous chloride and potassium chromate, but also tannins were used (Cardon, 2007). Vat dyes are chemical compounds that are not soluble in water; therefore, they must undergo a redox reaction to give the thread a color. First, the dye is dissolved in an alkaline bath where the fibers are impregnated with the soluble form of the dye and then exposed to air to oxidize and reach the final color.

Traditionally the possibility to make an accurate identification of dyes on archaeological and historical clothes and textiles is accomplished through invasive or micro-invasive methods. In this sense, the most used technique is High Pressure Liquid Chromatography (HPLC) (Ferreira et al., 2000; Rosenberg, 2008) which involves the extraction of the dye from the fiber. A more recent application to the identification of dyes is Raman-SERS (Leona, 2004), that involves the use of metal colloids to enhance the Raman signal and avoid fluorescence, but that is still micro-invasive (Leona, Stenger and Ferloni, 2006; Zaffino et al., 2014; Bernardino, de Faria and Negrón, 2015; Ricci et al., 2016). Nonetheless, the use of non-invasive methodologies is fundamental when working with object of artistic and cultural importance. That is the reason why a spectroscopic approach could be useful as a first screening to try to identify some of the dyes without direct contact with the analyzed object.

Dyeing molecules contain functional groups (chromophores) that cause color and other groups, called auxochromes, which – although not directly responsible

of color – can influence the absorption of radiation and consequently make the molecule colored (McMurry, 2012). The possibility of acquiring reflectance spectra in the ultraviolet (UV), visible (Vis) and near infrared (NIR), in some cases, can lead to the identification of the main spectroscopic features of each dye and to distinguish the dyes, or at least their nature (flavonoids, anthraquinones, etc.), despite all the boundary conditions that can affect the spectrum (McMurry, 2012). In particular, fiber optics reflectance spectroscopy (FORS) in the UV-Vis-NIR range, which has been used for the investigation of works of art since the 1990s and has become an established technique for the study of artists' materials (Bacci, 2000), represent a valid option because of its portability and ability to perform non-invasive fast in situ analysis. Moreover it is reported in many recent studies, as for example (Angelini et al., 2010; Gulmini et al., 2013; Maynez-Rojas, Casanova-González and Ruvalcaba-Sil, 2017; de Ferri et al., 2018; Aceto et al., 2020) that this technique has shown positive results for a preliminary identification of dyes on textiles.

The present study is focused to create a UV-Vis-NIR spectroscopic database on colored wool fibers, whose aim is to help conservation scientists and conservators – albeit in the preliminary stages of their investigation – to recognize dyes in a non-invasive way. Therefore, twelve natural dyestuffs, selected among those sources of color historically used to dye textiles, and three mordants were employed to tint raw wool according to ancient recipes. Data were collected in the 350-1000 nm range using FORS technique. Also colorimetric data were acquired using a spectrophotometer to calculate for each sample its chromaticity coordinates.

Furthermore, the application of the emerging imaging spectroscopic technique (Casini et al., 2005; Delaney et al., 2010; Vitorino et al., 2015; Cucci, Delaney and Picollo, 2016; Blanch-Perez-del-Notario, Saeys and Lambrechts, 2019; Striova, Dal Fovo and Fontana, 2020) which combines the potentiality of spot spectroscopic with imaging techniques, made it possible to extend the FORS analysis to larger areas. This was the reason for testing the Specim IQ (Cucci et al., 2017, 2018; Picollo et al., 2020) hyperspectral camera (Specim, Spectral Imaging Ltd, Oulu, Finland) which is compact and portable, to the same samples used to create the spectroscopic database.

2. Method

2.1. Preparation of samples

In the present work, twelve dyes and three mordants were selected within those historically used in dyeing.

Among the selected dyes, nine are from plants (*Alkanna Tinctoria*, *Anthemis Tinctoria*, *Indigofera Tinctoria*, *Haematoxylum Campechianum*, *Rubia Tinctorum*, *Carthamus Tinctorius*, *Curcuma Longa*, *Juglans Regia*, *Reseda Luteola*), two are insect dyes (*Dactylopius Coccus Cacti* and *Kerria Lacca*) and one is a lichen (*Roccella Tinctoria*). The preparation of samples was made by a specialist in the field following historical recipes on a set of skeins of raw wool, each of 20 g, that was prepared with three selected mordants ($KAl(SO_4)_2$, $CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 7H_2O$) to enrich the color palette.

The cochineal dyed wool was etched with both alum and a mixture of alum and iron sulfate. The indigo and orchil dyes were employed with a vat procedure. The quantity of material used (% weight/weight is referred to dry material) is reported in table 1.

Table 1: Percentage of the amount of dyeing material used referred to dry weight.

		%w/w
Alkanet	<i>Alkanna Tinctoria</i>	100%
Chamomile	<i>Anthemis Tinctoria</i>	100%
Cochineal	<i>Dactylopius Coccus Cacti</i>	12%
Indigo	<i>Indigofera Tinctoria</i>	5-6%
Lac	<i>Kerria Lacca</i>	8%
Logwood	<i>Haematoxylum Campechianum</i>	30%
Madder	<i>Rubia Tinctoria</i>	100%
Orchil	<i>Roccella Tinctoria</i>	unknown amount of lichen macerated for a month in water and ammonia solution
Safflower	<i>Carthamus Tinctorius</i>	100%
Turmeric	<i>Curcuma Longa</i>	100%
Walnut	<i>Juglans Regia</i>	100%
Weld	<i>Reseda Luteola</i>	100%

The extraction of the dyes was carried out by soaking most of the plants and cochineal in water for twelve hours and then boiling the mixture for at least one hour. The alkanet dye was extracted in alcohol and the *Kerria Lacca* insect was left in a solution of water and citric acid. Subsequently, the whole was filtered to obtain the bath-color in which the skeins were soaked. Some skeins were mordanted before the dyeing process using alum 25% by weight, while iron and copper sulfate (both 10%) were used simultaneously with dyes in the bath-color.

The vat dyeing process was carried out for indigo and orchil. The indigo was left to ferment in a solution with 5% indigo, 5% sodium hydrosulfite, 10% soda Solvay to obtain the water-soluble compound. The yarn was then

soaked in the bath for twenty minutes at 55°C and subsequently exposed to air to oxidize and reach the final color. Orchil dye was instead extracted by leaving the lichens in a solution of water and ammonia for one month. Therefore, the dyeing process was similar to the indigo vat process.

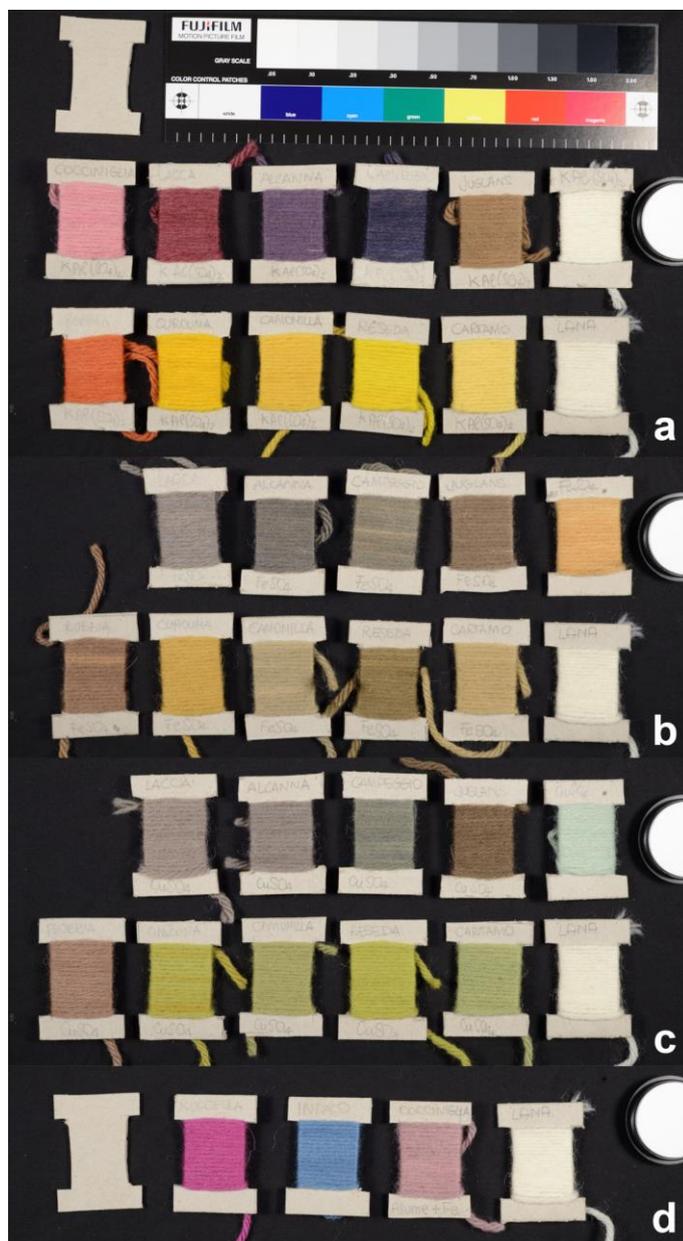


Figure 1: Overall of the set analyzed. Samples etched with alum (a), iron sulfate (b) and copper sulfate (c), without mordant (d).

2.2. Experimental

Colorimetric analysis were carried out using a Konica Minolta CM-700d spectrophotometer, operating in the 360-740 nm range with a 10 nm wavelength pitch. The instrument features a diffraction grating, a silicon photodiode

double array and a pulsed xenon lamp with UV cut filter. The measurement setup was: 8mm \varnothing illumination area, d/8° geometry with both specular component included (SCI) and excluded (SCE). The colorimetric calculation was done for CIE 10° standard observer and D65 illuminant.

The FORS data were acquired using a compact module, which is portable and features in a unique chassis two spectroanalysers equipped with fiber optics. Here, it was decided to use only the Zeiss MCS601 UV-NIR spectroanalyser, which is equipped with a multi-channel spectrometer (MCS) polychromator with 1024 diodes, 0.8 nm spectral pixel pitch and 2.4 nm spectral resolution. The reflectance spectra were acquired in the 350-1000 nm range with 298.5 ms integration time, continuous dark current mode, and each spectrum was the average of three acquisitions to improve the s/n ratio. Silica fiber optic bundles were used to send and to collect the radiation to and from the samples with a 2x45°/0° geometrical configuration to avoid the reflected specular radiation (Bacci, 2000). All samples were previously analyzed using a Perkin Elmer Lambda 1050 UV-Vis-NIR spectrophotometer in the 200-2500 nm range to obtain full information over the UV-Vis-NIR range and to understand were to focus the FORS measurements. The 1000-2200 nm region was excluded from the FORS measurements as it is practically covered by the wool spectral features.

Hyperspectral data were acquired using a Specim IQ hyperspectral camera, compact and portable, with an user-friendly interface, reduced weight and dimensions compared to those instruments conventionally used in hyperspectral imaging. The IQ camera operates in the 400-1000 nm range with a 7 nm spectral resolution. It features a CMOS linear sensor with a sampling pitch of 3.5 nm for 204 spectral bands. Images resolution is 512x512 pixel and data (file-cube) are almost 300MB (Cucci *et al.*, 2017, 2018). The experimental setup chosen consists of an illumination system with a fiber optic bundle and two light diffusers to send the radiation from the source (150W halogen lamp equipped with a IR cut filter) to the sampling zone, with a 2x45°/0° geometry. Integration time was fixed for all measurements at 55ms, for an overall of 50s acquisition time. The 'custom' modality was selected to collect data, and the reference was taken using a 99% reflectance Spectralon® Labsphere. Calibration of wavelengths was done using a reference of orange plexiglass. Furthermore, a luxmeter was employed during the data acquisition to record the amount of radiation sent over the sample, which was approximately 2000 lux, 45 mW/m² (almost 22.5 μ W/lm of UVa radiation). It is important to underline that these parameters are within the recommended values of UVa radiation dose for objects that are sensitive of UV-Vis radiation, such as dyes and textiles.

3. Results

3.1. Colorimetry

Measurements were carried out on all samples, including those with raw wool and cardboard only. Three spectra were recorded for each sample to assure repeatability and to evaluate the error for each set of measurements. In table 2 arithmetic averages are shown for both SCI and SCE L*a*b* (CIE1976) values and their color difference, ΔE , was obtained using the CIEDE2000 formula. Colorimetric data show that SCI and SCE values are not dissimilar and that ΔE is below the threshold of human difference color perception.

3.2. Fiber Optics Reflectance Spectroscopy (FORS)

For each sample, three FORS measurements were acquired, positioning the bundles parallel, orthogonal and oblique to the yarn's fibers. The three reflectance spectra compared did not show differences despite the reflectance intensity. Hence, it was decided to choose the orthogonal configuration to build up the spectral database, since it showed the highest reflectance values.

The comparison between spectra of wool with the three mordants highlights the influence of the metallic salts on the spectral features. In particular, wool samples etched with iron and copper sulfate show important absorptions in the UV-Vis region that can affect the spectral features of dyes, making it possible to distinguish dyes not only depending on their chemical nature but also on the mordant used.

Through the identification of dyes of the same color emerged the impossibility to distinguish yellows (chamomile, safflower, turmeric, weld) etched with iron and copper sulfate (Angelini *et al.*, 2010). Instead, it is possible to partially discern yellow dyes etched with alum (Fig.2) since all samples show a wide absorption band in the 300-450 nm region, but safflower and chamomile absorb at lower wavelengths compared to turmeric and weld. Moreover, weld and chamomile show a smooth shoulder at 660-670 nm. Regardless, to accomplish a deep discrimination of yellow dyes it would be useful to apply statistical and multivariate procedure, such as PCA (Cazenobe *et al.*, 2002).

Red dyes can be divided into animal and vegetal according to the $n \rightarrow \pi^*$ absorption of the anthraquinones' carbonyl group, which occurs at 500 nm and 540 nm for madder and at 524 nm and 560 nm for cochineal and lac (Gulmini *et al.*, 2013; Vitorino *et al.*, 2015; de Ferri *et al.*, 2018). Though, it is not possible to distinguish the two insect dyes except by studying their first derivative as reported in (Fonseca *et al.*, 2019) and shown in Fig. 3. The identification of animal and vegetal red, instead, it is not possible with samples etched with iron and copper sulfate.

Table 2: CIEL*a*b*1976 values and color difference (ΔE_{00}) between SCI and SCE measurements obtained with CIEDE2000 formula for each sample

SAMPLE	SCI			SCE			ΔE_{00}
	L*	a*	b*	L*	a*	b*	
Alk_Cu	45.71 ± 0.22	1.69 ± 0.24	6.56 ± 0.19	45.69 ± 0.25	1.70 ± 0.24	6.58 ± 0.19	0.03
Alk_Fe	39.95 ± 0.36	1.36 ± 0.05	5.39 ± 0.16	39.88 ± 0.38	1.38 ± 0.05	5.41 ± 0.16	0.06
Alk_Al	33.91 ± 0.15	7.24 ± 0.15	-5.06 ± 0.18	33.84 ± 0.12	7.26 ± 0.16	-5.04 ± 0.18	0.07
Card_	70.52 ± 0.01	1.25 ± 0.01	7.96 ± 0.01	70.36 ± 0.01	1.26 ± 0.01	7.99 ± 0.01	0.13
Cha_Cu	52.99 ± 1.06	-3.65 ± 0.28	26.11 ± 0.27	52.93 ± 1.10	-3.64 ± 0.28	26.12 ± 0.29	0.06
Cha_Fe	53.10 ± 0.38	2.80 ± 0.04	17.74 ± 0.15	53.01 ± 0.25	2.79 ± 0.05	17.76 ± 0.16	0.09
Cha_Al	62.39 ± 0.07	12.59 ± 0.05	49.83 ± 0.04	62.34 ± 0.09	12.60 ± 0.05	49.83 ± 0.04	0.04
Coc_Al	56.43 ± 0.04	25.88 ± 0.02	3.59 ± 0.01	56.40 ± 0.05	25.87 ± 0.03	3.62 ± 0.03	0.03
Coc_AlFe	53.13 ± 0.01	14.94 ± 0.01	2.57 ± 0.01	53.02 ± 0.01	14.95 ± 0.02	2.60 ± 0.01	0.08
Ind_	46.27 ± 0.03	-6.16 ± 0.01	-13.87 ± 0.01	46.22 ± 0.02	-6.18 ± 0.01	-13.84 ± 0.02	0.05
Lac_Cu	48.46 ± 0.02	2.76 ± 0.01	7.76 ± 0.01	48.44 ± 0.01	2.77 ± 0.001	7.79 ± 0.01	0.03
Lac_Fe	48.26 ± 0.02	3.08 ± 0.01	5.39 ± 0.01	48.15 ± 0.01	3.09 ± 0.01	5.42 ± 0.01	0.12
Lac_Al	32.14 ± 0.01	25.36 ± 0.02	2.34 ± 0.01	32.03 ± 0.02	25.38 ± 0.01	2.38 ± 0.02	0.09
Log_Cu	42.60 ± 0.18	-1.96 ± 0.03	8.44 ± 0.15	42.59 ± 0.18	-1.95 ± 0.03	8.46 ± 0.16	0.03
Log_Fe	46.48 ± 1.06	1.34 ± 0.06	10.34 ± 0.24	46.39 ± 1.06	1.35 ± 0.06	10.36 ± 0.23	0.09
Log_Al	25.26 ± 0.13	1.67 ± 0.01	-5.91 ± 0.03	25.21 ± 0.13	1.66 ± 0.01	-5.88 ± 0.03	0.05
Mad_Cu	46.62 ± 0.01	10.27 ± 0.01	10.38 ± 0.01	46.58 ± 0.01	10.28 ± 0.01	10.40 ± 0.01	0.04
Mad_Fe	43.17 ± 0.02	10.03 ± 0.01	11.67 ± 0.01	43.05 ± 0.01	10.04 ± 0.01	11.69 ± 0.01	0.11
Mad_Al	43.09 ± 0.01	37.73 ± 0.01	26.06 ± 0.01	43.05 ± 0.01	37.75 ± 0.01	26.10 ± 0.01	0.05
Orc_	39.97 ± 0.01	32.16 ± 0.01	-6.85 ± 0.01	39.95 ± 0.01	32.23 ± 0.01	-6.80 ± 0.01	0.05
Saf_Cu	55.68 ± 0.02	-7.27 ± 0.04	25.66 ± 0.16	55.62 ± 0.25	-7.25 ± 0.03	25.69 ± 0.18	0.07
Saf_Fe	55.85 ± 0.13	5.28 ± 0.02	24.28 ± 0.07	55.79 ± 0.09	5.28 ± 0.02	24.31 ± 0.06	0.07
Saf_Al	71.56 ± 0.04	5.43 ± 0.02	47.35 ± 0.01	71.56 ± 0.04	5.45 ± 0.02	47.45 ± 0.02	0.03
Tur_Cu	55.74 ± 0.10	-2.06 ± 0.05	37.56 ± 0.19	55.68 ± 0.06	-2.04 ± 0.06	37.58 ± 0.19	0.04
Tur_Fe	55.75 ± 0.42	11.35 ± 0.09	34.69 ± 0.09	55.78 ± 0.34	11.34 ± 0.06	34.69 ± 0.01	0.11
Tur_Al	63.78 ± 0.04	17.84 ± 0.04	74.99 ± 0.02	63.72 ± 0.03	17.96 ± 0.04	75.14 ± 0.04	0.06
Wal_Cu	34.70 ± 0.03	4.53 ± 0.02	11.83 ± 0.02	34.67 ± 0.03	4.55 ± 0.03	11.84 ± 0.02	0.03
Wal_Fe	42.10 ± 0.02	5.67 ± 0.01	11.60 ± 0.01	41.98 ± 0.01	5.69 ± 0.01	11.62 ± 0.01	0.11
Wal_Al	42.20 ± 0.03	8.90 ± 0.01	16.03 ± 0.02	42.07 ± 0.02	8.94 ± 0.02	16.07 ± 0.01	0.12
Wel_Cu	56.30 ± 0.06	-3.34 ± 0.01	42.10 ± 0.05	56.19 ± 0.07	-3.33 ± 0.01	42.11 ± 0.04	0.11
Wel_Fe	42.04 ± 0.03	3.86 ± 0.01	18.55 ± 0.01	42.02 ± 0.02	3.87 ± 0.01	18.59 ± 0.01	0.03
Wel_Al	68.46 ± 0.01	6.36 ± 0.01	77.51 ± 0.01	68.41 ± 0.03	6.37 ± 0.01	77.55 ± 0.02	0.04
Woo_Cu	69.93 ± 0.01	-9.59 ± 0.01	12.43 ± 0.01	69.87 ± 0.02	-9.57 ± 0.01	12.47 ± 0.02	0.06
Woo_Fe	58.48 ± 0.26	14.26 ± 0.03	30.42 ± 0.16	58.47 ± 0.25	14.27 ± 0.03	30.43 ± 0.16	0.02
Woo_Al	85.67 ± 0.01	-0.54 ± 0.01	15.75 ± 0.01	85.64 ± 0.03	-0.58 ± 0.01	15.82 ± 0.01	0.06
Woo_raw	84.16 ± 0.03	-0.20 ± 0.01	14.97 ± 0.01	84.12 ± 0.03	-0.22 ± 0.01	15.02 ± 0.01	0.04

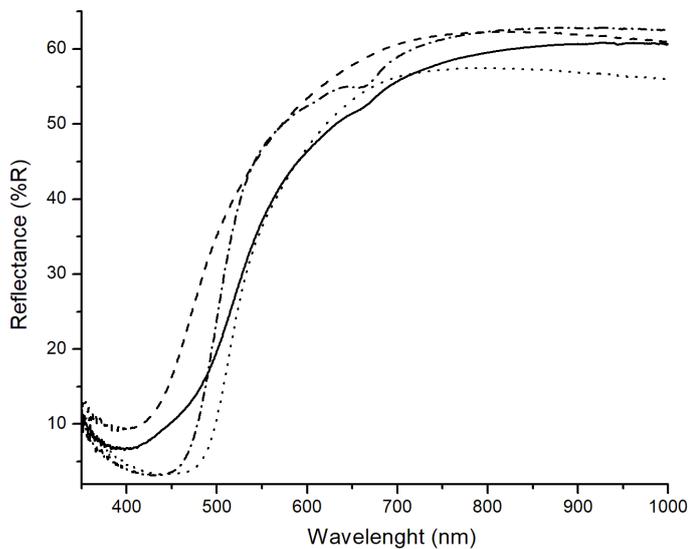


Figure 2: Reflectance spectra of yellow dyes etched with alum: chamomile (solid line), safflower (dash line), turmeric (dot line), weld (dash dot line).

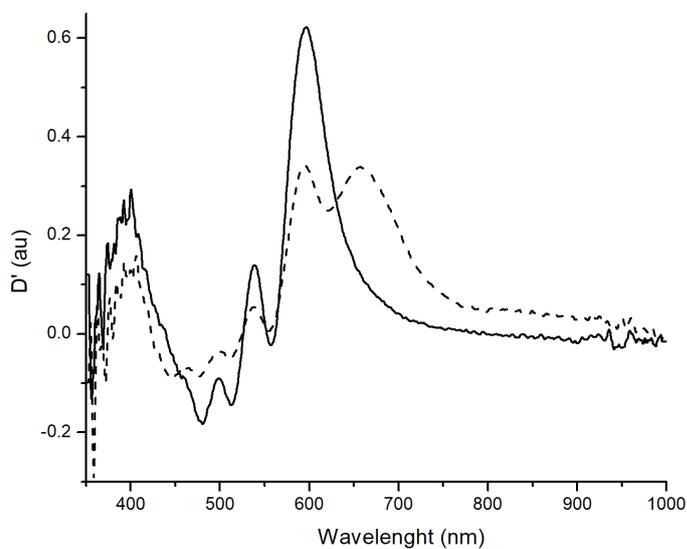


Figure 3: First derivative spectra of animal red dyes: cochineal (solid line) and lac (dash line), both etched with alum.

Purple-bluish samples (alkanet, logwood, orchil and indigo) show reflectance spectra that make their identification possible according to values reported in literature (Fig. 4). In particular it is possible to observe two bands at 424 nm and 588 nm (Gulmini *et al.*, 2013) for logwood with alum mordant and two bands at 545 nm and 580 nm (Aceto *et al.*, 2015) for the orchil dyed sample. Instead the indigo dyed sample shows the typical $\pi \rightarrow \pi^*$ absorption of the indigo molecule around 660 nm

and another weak band at 550 nm (Monahan and Kuder, 1972) and a shoulder at 345 nm (Gulmini *et al.*, 2013).

The only dark dye present in the investigated set of samples (walnut) did not show any characteristic absorption. However, its spectral features in the three spectra corresponding to different mordants makes walnut dye easily distinguishable from the others in the set.

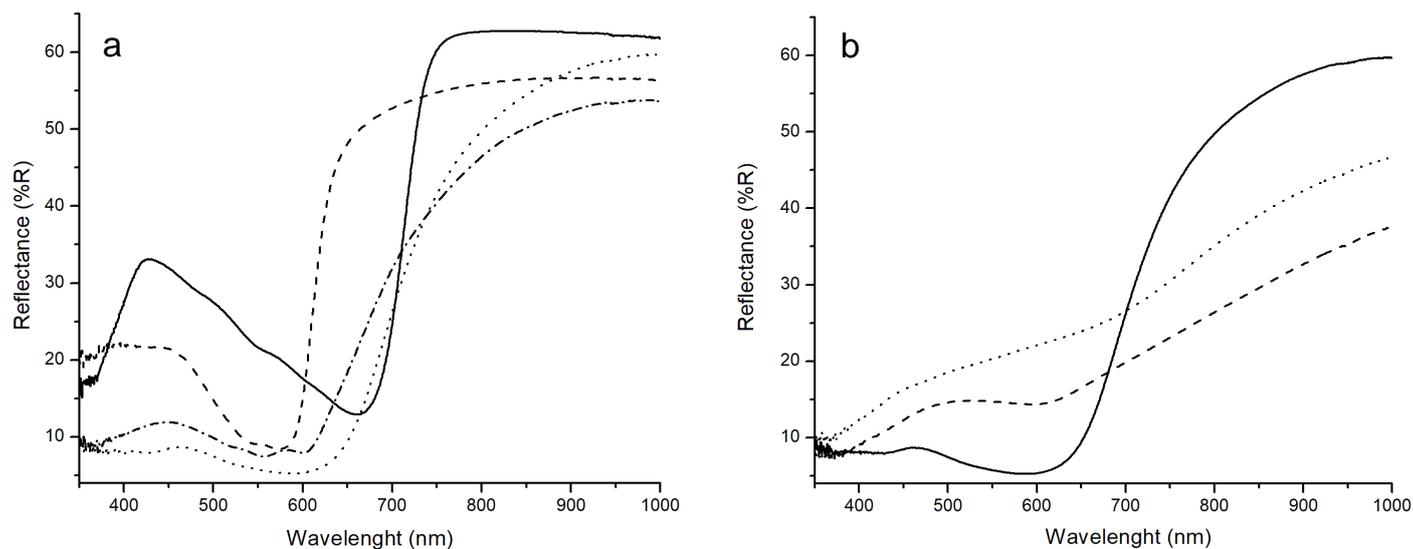


Figure 4: a) Reflectance spectra of indigo (solid line), orchil (dash line), logwood (dot line) and alkanet (dot dash line) both etched with alum. b) Reflectance spectra of logwood etched with alum (solid line), copper sulfate (dash line), iron sulfate (dot line).

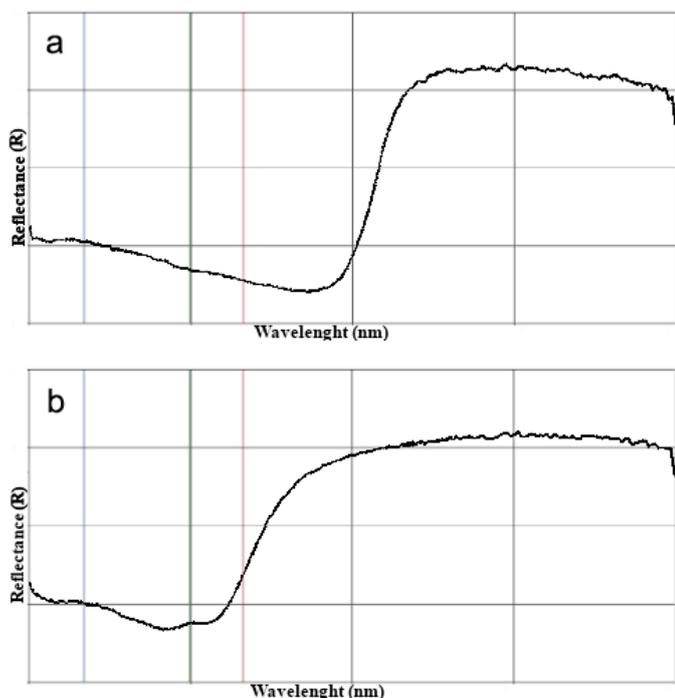


Figure 5: Reflectance spectra of indigo (a) and cochineal (b) extracted out of the file-cube using Specim IQ Studio.

3.3. Hyperspectral imaging

Hyperspectral data were acquired grouping samples both by hues (reds, yellows, etc.) and by the same type of dye in order to compare shades of the same dye etched with the three different salts.

Results show that spectra obtained with Specim IQ camera are comparable to those obtained with FORS. Indeed, for most of the samples it was possible to qualitatively identify the compound immediately after the acquisition of file-cube data. For examples, samples dyed with cochineal and indigo have the same spectroscopic features encountered in FORS spectra (Fig. 5). Quite the opposite happens with lac and madder both etched with alum which are difficult to discriminate, since spectra extracted out from file-cubes show a wide absorption band: at 400-550 nm in the case of madder and at 500-600 nm for lac.

The same consideration applies to the purple-bluish dyes, especially in the case of alkanet and logwood where spectra are not well resolved. Nevertheless, thanks to the use of the Spectral Angle Mapping (SAM)

algorithm, it is possible to map directly on the image pixels with similar spectral features to recognize areas where alkanet was used rather than logwood (Fig. 6).

Hyperspectral data of yellow dyes etched with alum show that, as predictable, it is impossible to identify dyes

because all spectra extracted out from the file-cube present similar features. However, the SAM algorithm permits to distinguish the four yellow dyes applying a high tolerance angle between 2.56 and 1.81 rad.

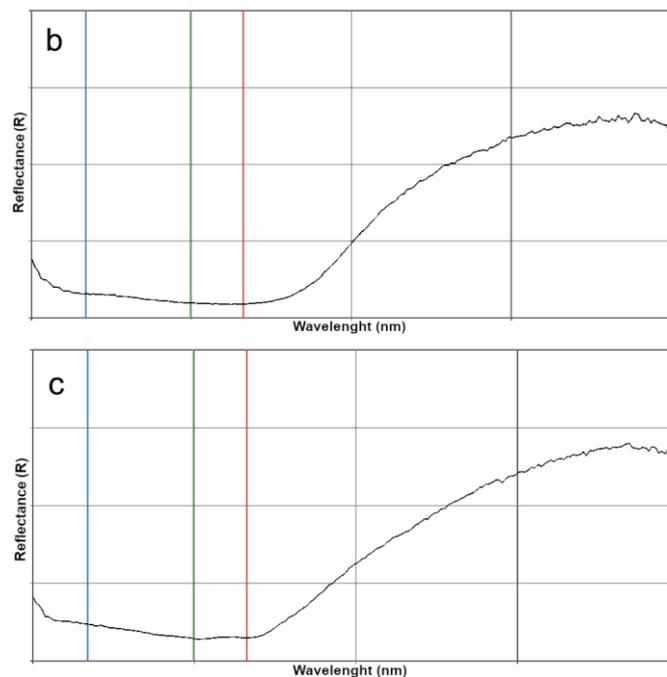
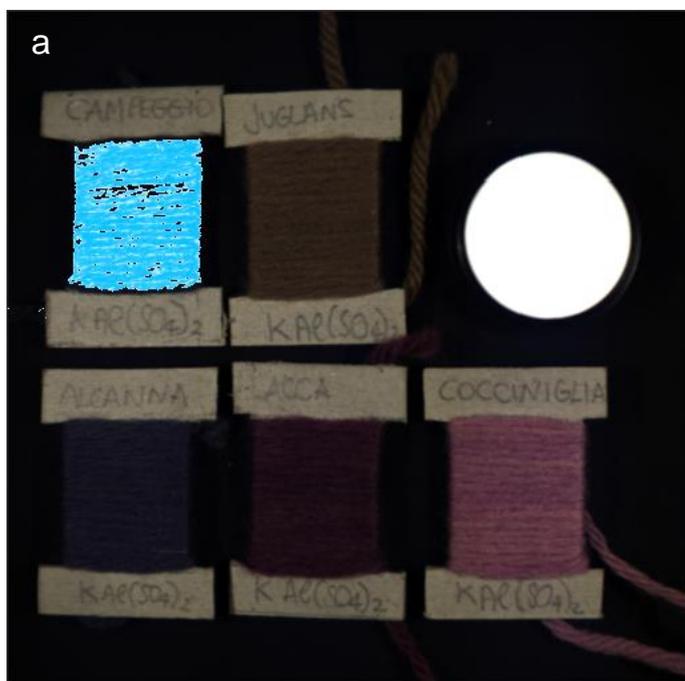


Figure 6: a) Areal distribution of pixel with the same spectral features obtained applying SAM algorithm on logwood file cube. Reflectance spectra of logwood etched with alum (b) and alkanet etched with alum (c), both extracted out of the file-cube using Specim IQ Studio.

4. Conclusion

Results obtained in the present study constitute the basis for the creation of a spectroscopic database that will be soon online on the IFAC-CNR website. The twelve dyes here analyzed represent only a starting point and it is already planned to include more dyes and typology of yarns in the future.

The acquired data show convincing results for a qualitative, in situ analysis to identify dyes. FORS was confirmed to be a valid technique to preliminary discern dyes according to their spectral features, being a non-invasive portable technique.

Finally, the Specim IQ camera permitted the non-invasive acquisition of imaging hyperspectral data on the set. Spectra extracted out of file-cubes were comparable to those obtained with FORS for most of the samples and made it possible a qualitative analysis on wider areas for each file-cube. Furthermore, the application of SAM algorithm permitted to map pixels with the same spectral features in order to recognize areas dyed with the same colorant.

5. Conflict of interest declaration

The authors state that no actual or potential conflicts of interest exist including financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

6. Funding source declaration

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8. Short biography of the authors

Greta Peruzzi - Master student in Conservation Science at Sapienza University in Rome. Her interests involve non-invasive investigation of archaeological and historical textiles using spectroscopic techniques.

Costanza Cucci - got her Physics “Laurea” and Ph.D. in Conservation Science at the Florence University. Currently she is a researcher at IFAC-CNR. Her research focus is on spectroscopic techniques and data-processing algorithms applied to the fields of cultural heritage, environmental monitoring, and safety food controls.

Marcello Picollo - Ph.D., is a researcher at IFAC-CNR. His interests include color measurement, Vis-NIR Hyperspectral Imaging, and spot size UV-Vis-IR spectroscopic investigations of 2D polychrome objects.

Franco Quercioli - is a senior researcher at the National Institute of Optics - CNR. He is an experimental physicist whose activities have covered the fields of: coherent optics, interferometry, optical metrology, holography, Fourier optics, optical engineering, confocal and non-linear microscopy and biophotonics.

Lorenzo Stefani - is a technician in telecommunications at IFAC-CNR. He is in charge of the development of hardware and software for computer-controlled instrumentation for the non-invasive and in situ study of artworks.

References

Aceto, M. *et al.* (2015) 'A diagnostic study on folium and orchil dyes with non-invasive and micro-destructive methods', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 142, pp. 159–168. doi: 10.1016/j.saa.2015.02.001.

Aceto, M. *et al.* (2020) 'Identification of the purple dye on the Vienna Genesis', in Hofmann, C. (ed.) *The Vienna Genesis*. 1st edn. Wien: Böhlau Verlag, pp. 103–118. doi: 10.7767/9783205210580.103.

Angelini, L. G. *et al.* (2010) 'CHARACTERIZATION OF TRADITIONAL DYES OF THE MEDITERRANEAN AREA BY NON-INVASIVE UV-VIS-NIR REFLECTANCE SPECTROSCOPY', *Studies in Conservation*, 55(sup2), pp. 184–189. doi: 10.1179/sic.2010.55.Supplement-2.184.

Bacci, M. (2000) 'UV-VIS-NIR, FT-IR, AND FORS SPECTROSCOPY', in *Modern analytical methods in art and archeology*. New York: Wiley (Chemical analysis, v. 155), p. 755.

Bernardino, N. D., de Faria, D. L. A. and Negrón, A. C. V. (2015) 'Applications of Raman spectroscopy in archaeometry: An investigation of pre-Columbian Peruvian textiles', *Journal of Archaeological Science: Reports*, 4, pp. 23–31. doi: 10.1016/j.jasrep.2015.08.029.

Blanch-Perez-del-Notario, C., Saeys, W. and Lambrechts, A. (2019) 'Hyperspectral imaging for textile sorting in the visible–near infrared range', *Journal of Spectral Imaging*, p. a17. doi: 10.1255/jsi.2019.a17.

Cardon, D. (2007) *Natural dyes: sources, tradition, technology and science*. London: Archetype.

Casini, A. *et al.* (2005) 'Fiber optic reflectance spectroscopy and hyperspectral image spectroscopy: two integrated techniques for the study of the Madonna dei Fusi', in Salimbeni, R. and Pezzati, L. (eds). *Optical Metrology*, Munich, Germany, p. 58570M. doi: 10.1117/12.611500.

Cazenobe, I. *et al.* (2002) 'Non-destructive spectroscopic investigation of dyed textiles: an application to yellow dyed wool samples', in *Preprints of the 13th Triennial ICOM Meeting*. Rio de Janeiro, pp. 238–244.

Cucci, C. *et al.* (2017) 'Bridging research with innovative products: a compact hyperspectral camera for investigating artworks: a feasibility study', in Pezzati, L. and Targowski, P. (eds). *SPIE Optical Metrology*, Munich, Germany, p. 1033106. doi: 10.1117/12.2270015.

Cucci, C. *et al.* (2018) 'The illuminated manuscript Corale 43 and its attribution to Beato Angelico: Non-invasive analysis by FORS, XRF and hyperspectral imaging techniques', *Microchemical Journal*, 138, pp. 45–57. doi: 10.1016/j.microc.2017.12.021.

Cucci, C., Delaney, J. K. and Picollo, M. (2016) 'Reflectance Hyperspectral Imaging for Investigation of Works of Art: Old Master Paintings and Illuminated Manuscripts', *Accounts of Chemical Research*, 49(10), pp. 2070–2079. doi: 10.1021/acs.accounts.6b00048.

Delaney, J. K. *et al.* (2010) 'Visible and Infrared Imaging Spectroscopy of Picasso's Harlequin Musician: Mapping and Identification of Artist Materials in situ', *Applied Spectroscopy*, (64), pp. 584–594.

Ferreira, E. *et al.* (2000) 'LC-Ion Trap MS and PDA-HPLC-Complementary techniques in the analysis of flavonoid dyes in Historical textiles: The case study of an 18th century Herald's Tabard', in.

de Ferri, L. *et al.* (2018) 'Non-invasive study of natural dyes on historical textiles from the collection of Michelangelo Guggenheim', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 204, pp. 548–567. doi: 10.1016/j.saa.2018.06.026.

Fonseca, B. *et al.* (2019) 'Seeing red: towards an improved protocol for the identification of madder- and cochineal-based pigments by fiber optics reflectance spectroscopy (FORS)', *Heritage Science*, 7(1), p. 92. doi: 10.1186/s40494-019-0335-1.

Gulmini, M. *et al.* (2013) 'Identification of dyestuffs in historical textiles: Strong and weak points of a non-invasive approach', *Dyes and Pigments*, 98(1), pp. 136–145. doi: 10.1016/j.dyepig.2013.02.010.

Hofenk de Graaff, J. H., Roelofs, W. G. T. and Bommel, M. R. van (2004) *The colourful past: origins, chemistry and identification of natural dyestuffs*. London: Archetype Publ.

Leona, M. (2004) 'Sub-nanogram level identification of alizarin by surface enhanced raman scattering', in *IRUG6. Sixth Infrared and Raman Users Group Conference (IRUG&)*, Florence, Italy: Marcello Picollo, pp. 105–112.

Leona, M., Stenger, J. and Ferloni, E. (2006) 'Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art', *Journal of Raman Spectroscopy*, 37(10), pp. 981–992. doi: 10.1002/jrs.1582.

Maynez-Rojas, M. A., Casanova-González, E. and Ruvalcaba-Sil, J. L. (2017) 'Identification of natural red and purple dyes on textiles by Fiber-optics Reflectance Spectroscopy', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 178, pp. 239–250. doi: 10.1016/j.saa.2017.02.019.

McMurry, J. (2012) *Organic chemistry*. 8e edn. Belmont, CA: Brooks/Cole, Cengage Learning.

Monahan, A. R. and Kuder, J. E. (1972) 'Spectroscopic differences between crystalline and amorphous phases of indigo', *The Journal of Organic Chemistry*, 37(25), pp. 4182–4184. doi: 10.1021/jo00798a048.

Piccolo, M. *et al.* (2020) 'Hyper-Spectral Imaging Technique in the Cultural Heritage Field: New Possible Scenarios', *Sensors*, 20(10), p. 2843. doi: 10.3390/s20102843.

Ricci, M. *et al.* (2016) 'Microanalysis of Organic Pigments in Ancient Textiles by Surface-Enhanced Raman Scattering on Agar Gel Matrices', *Journal of Spectroscopy*. Edited by C. Krafft, 2016, p. 1380105. doi: 10.1155/2016/1380105.

Rosenberg, E. (2008) 'Characterisation of historical organic dyestuffs by liquid chromatography–mass spectrometry', *Analytical and Bioanalytical Chemistry*, 391(1), pp. 33–57. doi: 10.1007/s00216-008-1977-0.

Striova, J., Dal Fovo, A. and Fontana, R. (2020) 'Reflectance imaging spectroscopy in heritagescience', *La Rivista del Nuovo Cimento*, 43(10), pp. 515–566. doi: 10.1007/s40766-020-00011-6.

Vitorino, T. *et al.* (2015) 'Non-invasive identification of traditional red lake pigments in fourteenth to sixteenth centuries paintings through the use of hyperspectral imaging technique', *Applied Physics A*, 121(3), pp. 891–901. doi: 10.1007/s00339-015-9360-4.

Zaffino, C. *et al.* (2014) 'Fourier-transform surface-enhanced Raman spectroscopy (FT-SERS) applied to the identification of natural dyes in textile fibers: an extractionless approach to the analysis: FT-SERS for extractionless identification of natural dyes in textile fibers', *Journal of Raman Spectroscopy*, 45(3), pp. 211–218. doi: 10.1002/jrs.4443.