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CHARACTERIZATION OF SILK-COTTON AND WOOL-COTTON BLENDS PATTERN BOOKS BY FIBER OPTICS REFLECTANCE SPECTROSCOPY. THE BOOMING MARKET OF FIRST SYNTHETIC TEXTILE DYES IN EARLY 20th CENTURY

Maria Cristina Caggiani [a,1], Tiziana Forleo [b], Giulio Pojana [a], Giovanni Lagioia [c], Annarosa Mangone [b,d], Lorena Carla Giannossa [b,d,*]

[a] Department of Philosophy and Cultural Heritage, Ca' Foscari University of Venice, Dorsoduro 3484/d, 30123 Venezia, Italy
[b] Department of Chemistry, University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy
[c] Department of Economy, Management and Business Law, Largo Abbazia Santa Scolastica, 70124 Bari, Italy
[d] Centro Interdipartimentale "Laboratorio di Ricerca per la Diagostica dei Beni Culturali" (LaBC), University of Bari Aldo Moro, via Orabona 4, 70126 Bari, Italy

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ABSTRACT

A remarkable number of early 20th century azo synthetic textile dyes was characterized by Fiber Optics Reflectance Spectroscopy (FORS). Items are part of silk-cotton and wool-cotton blends pattern books of *Leopold Cassella & Co.*, a leading firm at that time. Focusing on early dyes from this privileged point of view, meant for us providing our own scientific contribution to restore luster to a historical period that represented the keystone from upmarket natural dyes to synthetic ones on a large scale. A selection of spectra on silk-cotton blend with the same dye concentration was compared color by color. In the case of wool-cotton blend textiles, two concentrations were available for each dye. Therefore, spectra comparisons between the same dyes used in silk-cotton and wool-cotton blends were carried out, as well as between the same dyes in different concentration in the case of wool-cotton textiles, simulating possible fading conditions. In addition, almost each analyzed dye was linked to its molecular structure. Finally, the obtained set of data has been statistically treated. The complete dataset was subjected to an exploratory analysis using PCA that exhibited an organization of the samples based on brightness and colors. The generation and validation of a PLS-DA model confirmed the recognizability of the samples based on color and pointed out the excellent conservation conditions implemented.

The method provides a non-invasive, fast and low-cost approach for the recognition of azo dyes, based on the combined application of FORS, colorimetric parameters and chemometrics and lays the foundation for a reference database.

1. Introduction

The dyeing of textile fabrics with natural dyes, which was the only means available for textile coloration before the discovery of synthetic ones, was an expensive step of the production process, especially when strong and bright colors were looked for [1]. The accidental discovery in 1856 of Mauveine, the first industrially produced synthetic textile dye, changed the dye world [2,3].

From the 1860s, new products were developed and the textile dye industry burst. The innovations went hand in hand with organic chemistry advances (higher purity products, cheaper synthesis processes, etc.).

The pattern books here investigated are part of an extensive assembly of the Commodity Science Museum of the Department of Economics, Management and Business Law at the University of Bari Aldo Moro (Italy). This precious collection includes several rare pattern books of yarns and textiles dated to the end of the 19th – beginning of the 20th century, among which an important corpus of the *Leopold Cassella & Co.*

* Corresponding author at: Centro Interdipartimentale "Laboratorio di Ricerca per la Diagostica dei Beni Culturali" (LaBC), University of Bari "Aldo Moro", via Orabona 4, 70126 Bari, Italy.
E-mail address: lorenacarla.giannossa@uniba.it (L.C. Giannossa).
[1] Present address: Dipartimento di Scienze Biologiche Geologiche e Ambientali, Università di Catania, Corso Italia 57, 95129 Catania, Italy.

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editions is present.

In this paper, we paid attention to two specific *Cassella & Co.* pattern books, one covering dyed silk-cotton blend textiles and the other wool-cotton blend ones.

Fiber Optics Reflectance Spectroscopy (FORS), extensively used for the identification of dyes and pigments [4,5], has scarcely been employed in the study of textile dyestuff [6,7], the main applications being directed to the revelation of natural/traditional dyes in fabrics prior to the era of synthetic colors [8,9].

The FORS technique coupled with statistical treatment was employed with the aim of generating references for future characterizations of 20th century dyestuff. Though not by far comprehensive of the totality of the dyes produced in this period, this work can be considered a starting point in this field; furthermore, molecular structures, color index, C.A.S. and indication about Cassella's patent are given to help future comparisons. This analytical approach, at the same time non-invasive, simple, fast, and relatively cheap, was preferred because of the remarkable number of textile samples and their perfect conservation conditions. On the other hand, in order to consider possible problems of fading on other, "real" samples, we exploited the presence of textiles dyed with different dye concentrations. The comparison of spectra obtained on lighter and darker textiles dyed with the same colorant can be considered as a test for understanding if the spectra after fading would be recognizable as well. Furthermore, focusing on early dyes of the 20th century meant contributing to restore luster to a historical period that represents the decisive passage from the use of natural dyes, often in exclusive contexts, to synthetic ones on a large scale, marking an incredible scale-up in chemical industries and a turning point also in mass fashion business [10].

1.1. Technological and industrial background: The azo dyes

The prosperous trade in natural dyes changed dramatically with the invention of "coal tar dyes", based on products obtained by distilling coal-tar, namely aniline, benzene, naphthalene and anthracene [11]. All German dye factories founded in short succession (Kalle, Farbenfabriken Bayer, Farbwerke Höchst, BASF and AGFA) started to produce it.

The naphthalene chemistry was intensively and deeply investigated in the Cassella firm. It was found that naphthalene derivatives were excellent building blocks for the synthesis of azo dyes. Bis azo dyes were extremely effective: different colors could be obtained by changing groups used in diazotization and coupling and/or reaction conditions, and colorants became more suitable for dyeing and printing wool, silk and cotton, but also rayon, jute, etc. Bis azo dyes could be applied without the use of mordants, synthesized directly on the fiber, applied in sequence to obtain color variations, and even modified once applied on the fiber.

The diamine dyes were a huge economic success for the Cassella company. The downside part was imitation: competitors were able to change something in parameters, synthetic paths, etc., enough to avoid patent limitations, and resubmitted the same dyes naming them in another way (SI1a).

In less than 15 years, *Leopold Cassella & Comp.*, which was renamed *Leopold Cassella & Co.*, had become the world's largest and most profitable azo dye factory with diamine dyes by the turn of the century. Even today, some names of primary important azo dyes products refer somehow to the production site or the inventor, such as Cassella C, Cassella F and H (Hoffmann) acid, etc. [12].

2. Materials and methods

2.1. The pattern books

Two pattern books, "Diaminfarben auf halbseide. (Seide und Baumwolle)/Diamine colors on half silk. (Silk and cotton)" (no date reported) and "Les Couleurs Diamine dans la teinture des tissus mi-laine/Diamine Colors in the dyeing of mid-wool fabrics" (1900), were investigated. Introductive pages are dedicated to describing in detail dyeing processes of textiles as well as reporting dyes classifications based on comparing final fibers coloring (same dye and same nuance in case of cotton and silk, same dye and different nuance in cotton and silk, dyes valuable only for cotton or silk, etc.). The core of both books is composed of systematic pages containing fragments of fabrics colored with the synthesized dyes, and reporting dye name, acid resistance, general description, and percentage of each dye, applied individually or as a mixture. Forty-three single dyes on silk-cotton blend from the first book were analyzed and compared with wool-cotton blend ones tinted with the same dye and reported in the second book. The declared dye concentration in silk-cotton blend textiles is 2% for almost all samples with few exceptions (0.25% : 2 dyes, 1% : 2 dyes and 6% : 2 dyes). In case of wool-cotton blend textiles, two concentrations (2% and 0.75%) are reported for each dye selected and were analyzed. For the colors presented, the concentrations of dyes indicated are those actually fixed on the fiber as mentioned in the textile sample books. All samples exhibited good conservation conditions, with intact fibers and brilliant and uniform colors.

2.2. Techniques

Fiber Optics Reflectance Spectroscopy (FORS) was employed to generate the spectra. All reflectance spectra were collected by means of the fiber optic spectrometer Quest U (B&W Tek Inc., Newark, DE, USA), it was connected to a tungsten light source through a silica glass fiber bundle with a Y-shape. 7 fibers (diameter = 200 μm each) enter a SMA 905 model reflection probe with a collecting spot of about 4 mm^2: 6 of them have the function of giving light to the sample, the seventh of collecting the reflected signal, which is focused on a slit (50 μm^2, leading to an optical resolution of about 1 nm). The light beam is then redirected and collimated by a system of $AlMg_2$ coated mirrors towards the grating and then through a refocusing mirror to a 2048-pixel linear silicon CCD array detector.

In order to perform the white calibration, a 99% Teflon diffuse reflectance metrological standard from Labsphere (North Sutton, NH, USA) was employed. Each spectrum was collected in the 370–850 nm range, averaging 500 cycles of 4–12 ms keeping the incident and acquisition angles at 45° from the surface normal, thus avoiding the collection of the specular reflection component. Three spectra were collected for each color patch and then averaged.

Also, colorimetric coordinates in the CIE L*a*b* color space were extracted for each of the three spots per sample and averaged (Illuminant = D65, Observer = CIE 1931).

Both obtained spectra and colorimetric data were acquired and collected by using the software BWSpec4 (B&W Tek).

The Principal Component Analysis (PCA) was applied to the obtained dataset [13]. This chemometric technique is based on a linear transformation of the original variables to new ones called Principal Components (PCs). The PCs are ordered by the direction of maxima variance and are mutually orthogonal.

The PCA was applied to reduce data dimensionality and to visualize patterns and relationships between data. The working matrix contains the objects (samples analyzed) along the rows and the variables along the columns.

The classification technique applied was the Partial Least Square-Discriminant Analysis (PLS-DA), which is a linear classification method based on the PLS2 regression algorithm searches for latent variables (LVs) with a maximum covariance with a Y block [14].

Instead of a regression technique, the X matrix is the matrix with the predictor variables and the Y matrix (also called "dummy variables") contains the degree of membership of a sample to the gth class and is expressed by a value of 1 or 0 [14].

Several parameters can be used to measure the quality of the classification model [15,16].

The non-error rate (NER) is the percentage of the correctly assigned objects and evaluates the quality of the classification model. It can be calculated as follow:

$$NER = \frac{\sum_{g=1}^{G} n_{gg}}{n} \cdot 100$$

Where G is the number of classes, n is the total number of objects and n_{gg} are the correctly classified objects.

The error rate (ER) is the percentage of wrongly assigned objects and is complementary to 1 of NER.

The sensitivity of the g^{th} class (Sn_g) describes the model ability to recognize objects belonging to the g^{th} class and is defined as:

$$Sn_g = \frac{n_{gg}}{n_g}$$

Where n_g is the number of objects belonging to the g^{th} class.

The specificity (Sp_g) of the g^{th} class is the ability of the g^{th} class to reject the object of all other classes and is defined as:

$$Sp_g = \frac{\sum_{k=1}^{G} (n_k^{'} - n_{gk})}{n - n_g} fork \neq g$$

Which n_{gk} is the number of the objects belonging to the g^{th} class and assigned to the k^{th} class and n_k' is the total number of objects assigned to the k^{th} class.

Sensitivity and specificity can assume only values between 0 and 1.

All the chemometric analyses were performed by means of the software R version 4.0.5 (R Core Team, Wien, Austria).

3. Results and discussion

3.1. Dyes data recovering

Dyes analyzed are reported in Table 1 (other relevant data in SI1b). Most of the found dyes are bis-azo compounds, except for few mono-azo, tri-azo, tetra-azo and azo compounds containing thiazole groups.

A meticulous work, considered the use of multiple names and codes for the same dye as well as the difficulties related to patent issues, allowed to identify most of the structural formulas linked to colorants analyzed (SI1b) [17–40]. Many dyes in that period were concurrently manufactured by many different firms, and competitors used different names for the same structural formula [40]. In the early days of artificial dyestuff industries, different shades were identified by letters, e.g. B (blue), R (red) and G (Gelb = yellow), as the dyes increased, an additional degree of detail was necessary and numbers in addition to letters were introduced (2B, 2R, etc.). For instance, C may stand for Cassella and W for the preferable use for wool, while HW for half wool. Still, some names included appended letters indicating their sources or the starting materials. In short, it is not surprising that some experts consider synthetic dye designation a hopeless problem to untangle [40].

Table 1
Color, code and name of the investigated dyes.

Color	Code	Name	Color	Code	Name
	1	Thioflavin S		23	Diaminblau RW
	2	Diamingelb N		24	Diaminblau 3B
	3	Diamingoldgelb		25	Diaminblau 2B
	4	Diaminechtgelb A		26	Diaminblau BG
	5	Diaminechtgelb B		27	Diaminblau 3R
	6	Diaminorange GC		28	Diaminblau BX
	7	Diaminorange DC		29	Diamineralblau R
	8	Diaminorange B		30	Diaminazoblau 2R
	9	Oxydiaminorange G		31	Diaminbrillantblau G
	10	Oxydiaminorange R		32	Diaminstahlblau L
	11	Diaminescharlach 3B		33	Diaminblauschwarz E
	12	Diaminrot 5B		34	Diaminschwarzblau B
	13	Diaminrot 10B		35	Diamingrün B
	14	Diaminechtrot F		36	Diamingrün G
	15	Diaminbordeaux B		37	Diaminschwarz BH
	16	Diaminbordeaux S		38	Diaminschwarz BO
	17	Diaminrosa BD		39	Diaminschwarz RO
	18	Diaminviolet N		40	Diaminschwarz HW
	19	Oxydiaminviolet B		41	Halbwollschwarz S
	20	Diaminreinblau		42	OxydiaminschwarzS000
	21	Diaminreinblau FF		43	Oxydiaminschwarz D
	22	Diaminblau CB			

3.2. Diamine dyes spectroscopic characterization

The colorimetric coordinates of all 43 dyes and their FORS features on silk-cotton blend are listed in Table 2. As concerns the wool-cotton blend pattern book, the same dyes investigated for silk-cotton blend were selected for the analysis and their 0.75 and 2% concentrations together with their colorimetric coordinates and FORS features are also listed in Table 2.

3.2.1. Diamine dyes on silk-cotton blend

All the reflectance spectra are reported in SI2, whilst a selection of spectra of dyes on silk-cotton blend is shown in Fig. 1 to support the comparison color by color.

Yellow colors

The yellow dyes spectra, all showing the characteristic shape of yellow hue, are the most difficult to be differentiated - as already reported for traditional dyes [9] - being their absorbance maxima and inflection points respectively comprised between 415 and 437, and between 495 and 530 nm (Table 2, Fig. 1a). *Thioflavin S* (1) can be distinguished only for a small shift towards lower wavenumbers of these two features with respect to the others (Fig. 1a).

Orange colors

The spectra of the *Diaminorange* (7, 8) dyes are characterized by profiles comparable to those of the yellow dyes, but with a remarkable shift of the absorbance maxima and inflection points towards higher wavelengths (Fig. 1b). The spectra acquired on *Oxydiaminorange* dyes (9, 10), instead, are clearly distinguished by a higher reflection in the 400–500 nm range and a consequent slower increase with two inflection points located at about 530 / 540 and at 593 / 600 for the G and R molecules, respectively, the last one shown in Fig. 1b.

Red and violet colors

The red colors appear quite varied in their definitions distinguishing “rot” (red), “echtrot” (fast red), “scharlach” (scarlet) and “bordeaux”, generating reflectance spectra with differentiated profiles within the typical sigmoidal curve of red colors [41]. The most intense reflectance maximum is exhibited by *Diaminrot 5B* (12), located at 460 nm, followed by an absorbance maximum at 530 nm and two inflection points at 595 and 663 nm. On the contrary, in the spectrum of *Diaminechtrot F* (14) it is difficult to spot a reflectance maximum: a slow increase in the reflectance can be seen between 400 and 570 nm, followed by a sharper one with inflection point at 605 nm (Fig. 1c). The *Diaminechtrot F* (14) dye showed a different structure with respect to “rot” *Diaminrot 10B* (13), namely the substituents are not symmetrical, i.e., the amine was not used for the two diazo-copulations (SI1b) [32].

The *Diaminscharlach 3B* (11) spectrum is characterized by a much steeper increase in the reflection with inflection point at 615 nm and an almost flat shape of the profile between 700 and 850 nm (Fig. 1c). It is a not symmetrical bis-azo compound: in the second step of the reaction the phenol was used, while in case of *Diaminechtrot F* (14) salicylic acid was employed. The *Diaminbordeaux S* (16) spectrum exhibits a considerable shift in the inflection point position (650 nm) with respect to the other red dyes (Fig. 1c). On the other hand, it is remarkably similar to those of the two violet dyes (Fig. 1c, d): the inflection points are very close in both cases, while the *Diaminviolet N* (18) dye is better differentiated for

Table 2
FORS features and colorimetric coordinates of analyzed dyes on silk-cotton and wool-cotton blends (λ_r = reflectance maximum, λ_{max} = absorbance maximum, i = inflection point).

Cod.	Textile	Uniform color	% (w:w), dry	FORS features			Colorimetric coordinates			
				λ_r [nm]	λ_{max} [nm]	i [nm]	L*	a*	b*	C*
1	Silk/Cotton	Yes	2		415	495	84.622	−4.063	67.601	67.723
2	Silk/Cotton	Yes	2		430	520	76.699	10.843	79.780	80.514
3	Silk/Cotton	Yes	2		437	520	81.326	8.029	78.498	78.907
4	Silk/Cotton	Yes	2		435	530	75.824	9.902	61.173	61.97
5	Silk/Cotton	Yes	2		415	513	78.961	4.096	63.527	63.659
6	Silk/Cotton	Yes	2		440	540	72.615	18.993	63.483	66.264
7	Silk/Cotton	Yes	2		450	560	69.701	27.319	59.405	65.385
8	Silk/Cotton	Yes	2		470	580	63.801	41.128	53.803	67.722
9	Silk/Cotton	Yes	2			535, 593	54.208	21.673	66.465	69.91
10	Silk/Cotton	Yes	2			540, 600	53.304	22.837	43.054	48.736
11	Silk/Cotton	Yes	2	450	535	615	37.273	68.914	28.484	74.569
12	Silk/Cotton	Yes	2	460	530	595, 663	45.187	40.811	27.214	49.052
13	Silk/Cotton	Yes	2	465	525	587	58.860	30.707	31.897	44.753
14	Silk/Cotton	Yes	2			605	40.952	37.978	23.676	44.753
15	Silk/Cotton	Yes	2	445	530	607	44.361	40.032	16.544	43.315
16	Silk/Cotton	Yes	2	450	550	650	21.347	39.712	2.238	39.775
17	Silk/Cotton	Yes	2	425	535	595	59.710	60.984	−5.530	61.235
18	Silk/Cotton	Yes	2	450	535	637	49.467	26.944	0.963	26.961
19	Silk/Cotton	Yes	2	440	550	653	35.684	33.256	−11.717	35.26
20	Silk/Cotton	Yes	0.25	480	615, 650	700	64.240	−9.856	−15.062	18
21	Silk/Cotton	Yes	0.25	475, 635	615, 660	710	56.570	−12.077	−16.849	20.73
22	Silk/Cotton	Yes	1	450	615	710	52.109	−3.033	−20.620	20.841
23	Silk/Cotton	Yes	2	450	600	720	29.016	9.889	−32.378	33.854
24	Silk/Cotton	Yes	2	440	600	707	34.761	9.274	−34.811	36.025
25	Silk/Cotton	Yes	2	435	600	713	35.332	7.152	−29.553	30.406
26	Silk/Cotton	Yes	2	440	590	700	30.093	13.948	−32.598	35.457
27	Silk/Cotton	Yes	2	440	570	690	19.895	18.220	−15.537	23.945
28	Silk/Cotton	Yes	2	440	590	700	26.772	12.757	−23.482	26.724
29	Silk/Cotton	Yes	2	447	600	740	29.879	2.422	−17.727	17.298
30	Silk/Cotton	Yes	2	445	565	700	32.909	12.734	−11.600	17.226
31	Silk/Cotton	Yes	2	440	585	715	24.969	14.857	−31.167	34.527
32	Silk/Cotton	Yes	2	480	635	777	27.924	−7.051	−12.706	14.531
33	Silk/Cotton	Yes	2	447	575	730	28.613	9.281	−18.975	21.123
34	Silk/Cotton	Yes	2	453	615	795	17.875	0.175	−9.765	9.766
35	Silk/Cotton	Yes	2	513	650	750	19.942	−16.918	8.888	19.11
36	Silk/Cotton	Yes	2	513	660	740	25.892	−17.858	5.598	18.715
37	Silk/Cotton	Yes	2	440	580	735	33.073	6.254	−14.793	16.06
38	Silk/Cotton	Yes	2	450	575	730	20.282	9.088	−12.821	15.715
39	Silk/Cotton	Yes	2	455	575	710	20.085	7.107	−9.704	12.028
40	Silk/Cotton	Yes	2	480	640	770	17.988	−6.047	−9.367	11.15
41	Silk/Cotton	Yes	6			800	11.359	−3.303	10.369	10.883
42	Silk/Cotton	Yes	1	460	575	725	30.162	4.253	−4.092	5.902
43	Silk/Cotton	Yes	6			770	7.579	−0.211	9.471	9.473
1	Wool/Cotton	Yes	2		425	510	76.176	0.981	66.874	66.881
			0.75		410	480	75.874	−5.977	53.456	53.789
4	Wool/Cotton	No	2			535	77.026	15.647	74.108	75.741
			0.75		440	530	81.285	10.105	77.936	78.588
8	Wool/Cotton	Yes	2		460	587	54.928	31.78	44.786	54.916
			0.75		450	570	57.855	20.79	33.629	39.537
9	Wool/Cotton	Yes	2			547, 590	50.762	22.393	52.923	57.465
			0.75			523, 580	67.747	8.013	41.963	42.721
10	Wool/Cotton	Yes	2			552	55.325	22.774	45.625	50.993
			0.75			540, 590	67.111	12.612	33.693	35.976
12	Wool/Cotton	Yes	2	475		600	45.573	39.208	24.443	46.203
			0.75	500		590	67.821	21.9	25.526	33.633
14	Wool/Cotton	Yes	2	413	510	600	37.134	35.687	8.452	36.674
			0.75	420	510	587	58.41	26.017	7.843	27.174
16	Wool/Cotton	No	2	415	520	620	37.134	35.687	8.452	36.674
			0.75	445	520	605	58.41	26.017	7.843	27.174
18	Wool/Cotton	Yes	2	425	540	623	50	41.076	17.225	44.542
			0.75	430	540	600	61.693	34.156	15.687	37.586
19	Wool/Cotton	No	2	430	535	645	31.209	43.997	−0.593	44.001
			0.75	435	540	645	49.09	44.387	−2.292	44.446
25	Wool/Cotton	No	2	440, 467	580	685	39.301	11.359	−24.51	27.014
			0.75	440, 470	590	680	42.741	3.608	−19.904	20.228
30	Wool/Cotton	No	2	430	600	740	15.57	10.897	−22.856	25.321
			0.75	425	600	735	43.453	5.283	−20.53	21.199
32	Wool/Cotton	Yes	2	440	585	725	15.57	10.897	−22.856	25.321
			0.75	450	585	700	43.453	5.283	−20.53	21.199
36	Wool/Cotton	Yes	2	515	625, 660	753	26.055	−13.236	1.614	13.334
			0.75	510	620, 650	730	44.641	−17.523	−1.632	17.599
37	Wool/Cotton	Yes	2	515	615, 660	750	20.403	−13.373	2.849	13.674
			0.75	515	615, 650	723	40.472	−21.006	3.823	18.8

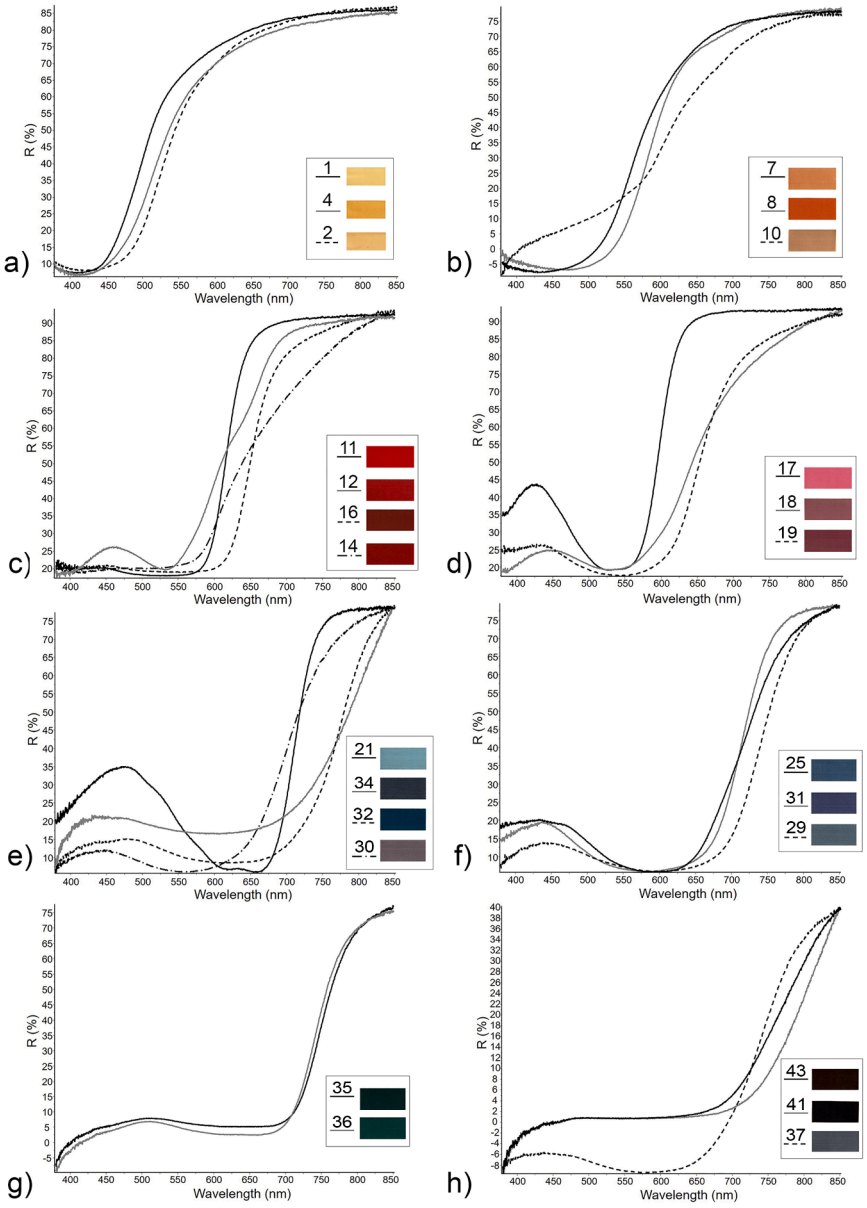

Fig. 1. Reflectance spectra of samples of silk-cotton blend colored with a) yellow, b) orange, c) red, d) pink and violet, e), f) blue, g) green, h) black dyes. The codes of the dyes are reported in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

its absorbance maximum position (Fig. 1d, Table 2).

Pink color

The high intensity reflectance maximum at 425 nm and the sharp increase with inflection point at 595 nm are the most significant features of the mono-azo dye *Diaminrosa BD* (17) reflectance spectrum (Fig. 1d).

Blue colors

The blue colors are the most represented in the considered pattern book with fifteen different shades ranging from sky blue to almost black. The light shade characterizing *Diaminreinblau FF* (21) is very well distinguished with the FORS spectrum thanks to its intense main reflectance maximum at 475 nm: the broad band includes two sub-bands, with another relative maximum centered at about 525 nm, furthermore, this spectrum is characterized by two absorbance maxima at 615 and 660 nm (Fig. 1e). At the opposite extreme, the darkest shade is provided by *Diaminschwarzblau B* (34) whose spectrum is indeed much less structured and typical of dark colors, where the correct features positions are difficult to be read [7] (Fig. 1e). The *Diaminstahlblau L* (32) color is slightly lighter, with an analogous profile, but more easily readable features (Fig. 1e). The *Diaminazoblau 2R* (30) dye is peculiar and not much blue-like, it can be differentiated by the combination of its features (Fig. 1e, Table 2). Finally, *Diaminblau RW* (23), *Diaminblau 3B* (24), *Diaminblau 2B* (25) and *Diamineralblau R* (29) share the position of the absorbance maximum at 600 nm and also the inflection point shift is not significative for all the different dyes (705–740 nm), while *Diaminblau 3B* (24), *Diaminblau BG* (26), *Diaminblau 3R* (27) and *Diaminbrillantblau G* (31) have the same position of the reflectance maximum (440 nm) and a tight interval of inflection points (690–715 nm) (SI2, Fig. 1f, Table 2).

Green colors

The FORS spectra of the only two green dyes are almost overlapped (except for more marked features of *Diamingrün G* (36)), mirroring the high similarity of their molecular structures (Fig. 1g, SI1b). Both dyes were obtained starting from benzidine which reacted with one mole of phenol (*Diamingrün B* (35)) or salicilic acid (*Diamingrün G* (36)) and one

mole of H acid (8-amino-1-naphtol-3,6-disulfonic acid) which in turn was coupled with p-nitroaniline [27].

Black colors

Many dyes defined as "black" are rather brownish or greyish like *Diaminschwarz BH* (37) (Fig. 1h); the darkest shades such as *Oxydiaminschwarz D* (43) and *Halbwollschwarz S* (41) (Fig. 1h) show reflectance spectra with a flat profile between 450 and 650 nm.

3.2.2. Diamine dyes on wool-cotton blend

All reflectance spectra are presented in SI3.

The two yellow colors show two different spectra patterns, depending on their corresponding structural formulas (SI1b). The profile of *Diaminorange B* (8) is very similar to the profile characterizing *Diaminechtgelb A* (4), but it can be easily distinguished thanks to a strong shift of its inflection point of more than 50 nm. It can be also differentiated from the two *Oxydiaminorange* dyes (9, 10) performing a less steep increase of its s-shaped spectrum. Both pink and violet dyes are hardly separated if not by the higher inflection point of the darker color.

Once again, the two green dyes spectra are very similar. Among the blues, the *Diaminblau 3B* (24) is identified by its double reflectance maximum at about 440 and 470 nm.

3.3. Variability of the Diamine dyes reflectance spectra

Since visible spectra were considered, it seemed important to state if there can be a variability of the colors obtained with the considered dyes, and consequently of their reflectance spectra, according to various factors [7], such as the supporting fibers [42] or the concentration [43], that can simulate fading conditions, and to what extent these variations can hinder the dye identification. Therefore, these aspects will be discussed in the following paragraphs.

Another important parameter not to be neglected is mordants employ. The use of the traditional alum mordant is not documented for these textiles, nor the employ of metallic ions, which could cause an interaction with the colorants [7].

Furthermore, as regards salts, such as sodium phosphate, sodium sulphate or sea salt, and sodium carbonate, they were added in bath for semi-silk fabrics, while sodium sulfate only was used in case of semi-wool: it is therefore not possible to discern which would be the effects of salts on the final color and which ones those of the fiber.

3.3.1. Same dye on different fibers

In the pattern book displaying the Cassella dyes applied to the wool-cotton blend, two different cases can be noticed: the great part of the dyes give color to wool and cotton at the same extent, while the remaining five provide a more intense color to cotton rather than to wool. In the former case, the final color is uniform, in the latter it results in stripes: considering that the collection spot of the instrument is of about 4 mm^2 and that each stripe measures about 1.5 mm, differently colored yarns could be analyzed at the same time. A still recognizable reflectance spectrum is generated, but it could be misleading in the perspective of the discussion here carried out.

Therefore, we stick to uniformly-coloring dyes: here, a different behavior was noted in the comparison of the two types of blend for darker dyes and lighter ones if applied in the same concentration (2%).

The darker dyes (31, 35, 36: L*= between 15 and 26 for wool and between 19 and 25 for silk) display almost superimposable spectra for silk-cotton and wool-cotton blends in the visible region, slight

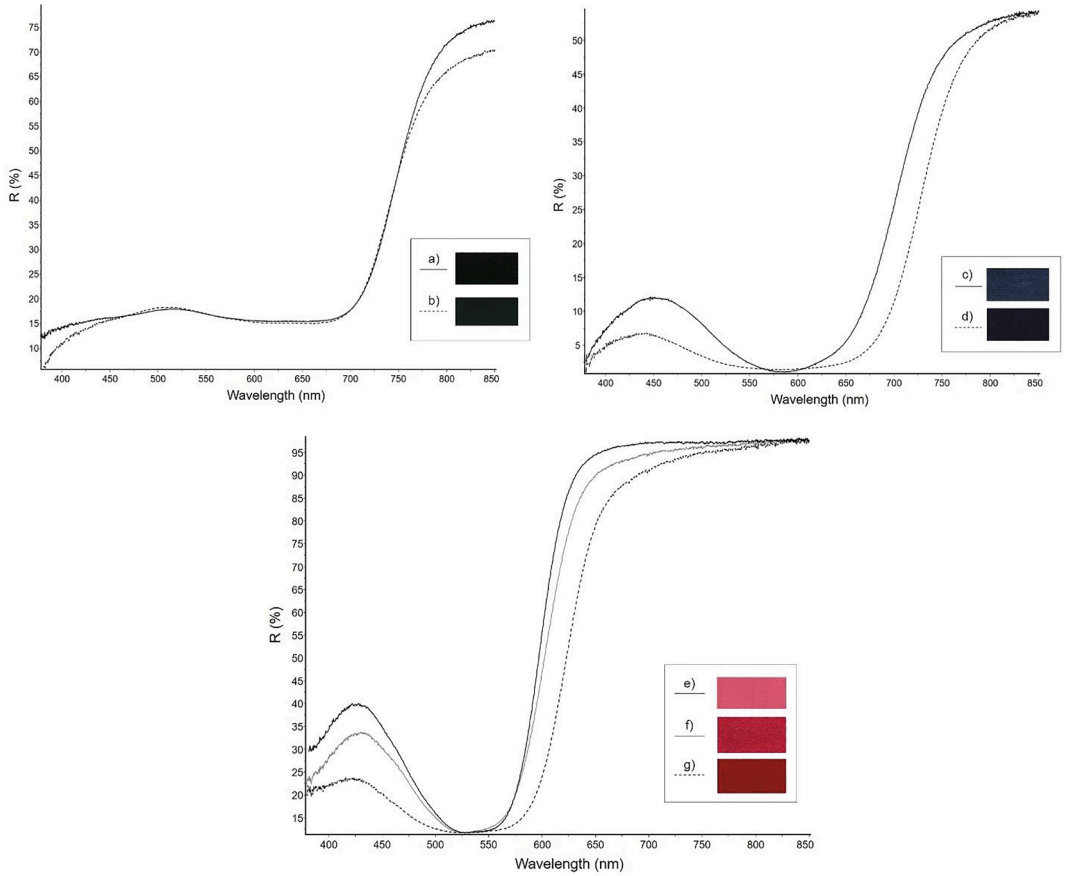

Fig. 2. Reflectance spectra comparing: same dark-coloured dye and same concentration (2%) on two different blends (Diamingrün B on a) wool-cotton and b) silk-cotton); same dye on the same blend (wool-cotton) in different concentrations (Diaminbrillanblau G in c) 0.75% and d) 2%); same bright-coloured dye on different blends and different concentrations (Diaminrosa BD in e) silk-cotton blend (2%), f) wool-cotton blend (0.75%) and g) wool-cotton blend (2%).

differences can be seen in the spectral regions towards ultraviolet and infrared (Fig. 2a & b). This is in accordance with the fact that the visible interval of the spectrum is the most suitable for the distinction of the colors, while the near infrared region could be more significant for additional fiber characterization [8].

Regarding the other dyes applied to wool, the lighter ones, though having the same spectral shape, they show a blue-shift of their reflectance maximum and/or a red-shift of their inflection point with respect to the same dyes applied to silk-cotton blends (Fig. 2e & g).

3.3.2. *Same dye in different concentrations*

The wool-cotton blend pattern book offered the opportunity to measure the same dyes applied to the same blend but at different concentration levels: 0.75 and 2%. The results of such comparison are similar to those discussed in the previous paragraph, showing that there is a hypsochromic shift of the reflectance maximum and/or a bathochromic one of the inflection point, when moving from the 0.75 to the 2% concentration level. It has been already reported that a dilution of the color induces a red-shift of the reflectance maximum [9].

3.4. *Chemometric treatment*

Multivariate statistical treatments have been applied to the dataset of spectra and colorimetric parameters (73 objects and 1291 variables). Some dyes are applied both on different (silk and wool) fabrics, and at different concentrations, therefore the number of measures available for the same dye is often greater than the unit.

We treated by PCA silk-cotton (43 objects) and wool-cotton (30 objects) blends items all together (Fig. 3a and b). The first 3 PCs contain respectively 39.7, 18.7 and 8.2% of the total explained variance. The graphs highlight an overall trend based on the discrimination between colors. In particular, a distribution ranging from darker to lighter samples can be observed.

It is interesting to notice how in the score plot (Fig. 3b), no separation is caused by different concentrations of dye or by different textile.

The loading plot in Fig. 3c shows that the samples contained in the third quadrant of the score plot (Fig. 3b) (yellow and a part of red and orange samples) are characterized by the four colorimetric parameters (in red) and by the spectral ranges from 527 to 718 cm^{-1} and from 721 to 730 cm^{-1}.

This indicates that the samples located at negative values of PC1 and negative values of PC2 are characterized by color tending to red and yellow (respectively positive values of a* and b*), with high saturation (positive values of C*) and brightness (positive values of L*) and higher intensities in the mentioned spectral ranges.

A classification method, the PLS-DA, was applied to the data to evaluate if the fabrics colored with dyes at lower concentration (equal to or less than 0.75%) are recognizable by the chemometric method. The dataset was divided into training and test sets, containing textiles with dye concentrations greater than 0.75% and equal to or less than 0.75%, respectively. The training set was used to calibrate the PLS-DA classification model and the test set to evaluate the predictive ability of the calibrated model.

The classes containing a number of samples greater than 4 for the training set were chosen for the calculation. For this reason, the following colors were excluded: pink, violet and green. The resulting dataset contains 47 objects in the training set and 13 objects in the test set.

The first three factors of PLS-DA explained 69.7% of the X-explained variance. The cross-validation was performed to internally validate the PLS-DA model. The optimal number of latent variables was chosen as the number associated with the minimum error rate.

The PLS-DA model on the training set was performed selecting 3, 2, 6, 3 and 3 latent variables for the yellow, orange, red, blue, black dyes classes respectively and 5 cross-validation groups for internal validation. The PLS-DA score plots of PC1 vs PC2 and PC1 vs PC3 associated with such model are shown in Fig. 4a and b. In both figures, a good discrimination of the yellow class can be observed. Fig. 4b displays a separation between the orange and the red classes, which slightly overlap in Fig. 4a. The blue and black classes, on the contrary, seem to be overlapped in the two scores plot.

The output of the classification model and the other classification parameters, sensitivity, specificity and NER, are shown in Table 3, according to Ballabio and Consonni [14].

The class thresholds (Table 3) were chosen in order to have a restrictive rule for the class assignment and were evaluated as the point where the specificity line crosses the sensitivity line in function of values of threshold ranging from 0.1 and 1.1.

At this point, the test set was projected onto the PLS-DA model to validate it and all 13 samples result classified to the a priori classes. The projection of the test set onto the model is presented in Figs. 4c and d.

From the results obtained by PCA and PLS-DA, it can be deduced that the samples are still distinguishable from each other, notwithstanding their different dye concentrations.

4. Conclusions

A first attempt to a spectroscopic characterization by FORS technique, assisted by the statistical treatment was carried out within the process of study and recovery of data concerning the diamine colors proposed by *Leopold Cassella & Co*.

The collected colorimetric and spectral information treated by PCA is

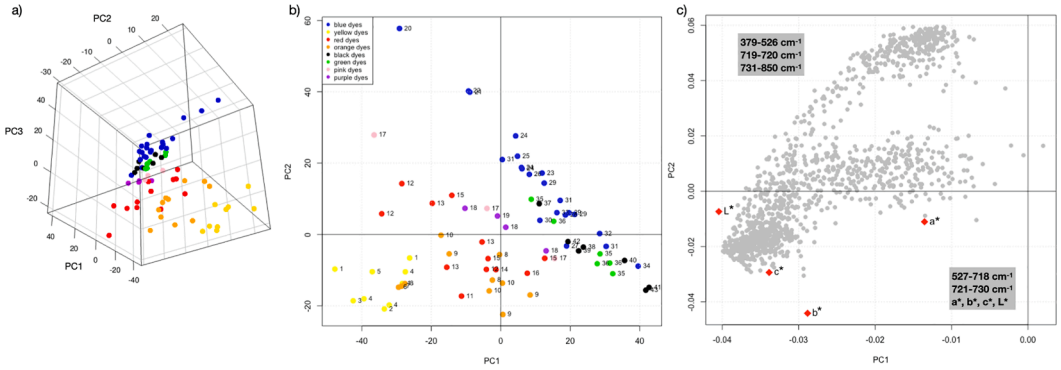

Fig. 3. a) Score plot (3D) considering all samples analyzed (silk-cotton and wool-cotton blend); b) Score plot (2D) PC1 vs PC2; c) Loading plot (2D) PC1 vs PC2. Grey points are the spectra points (spectral range of the quadrants are indicated in the grey insets), red ones are the colorimetric variables. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

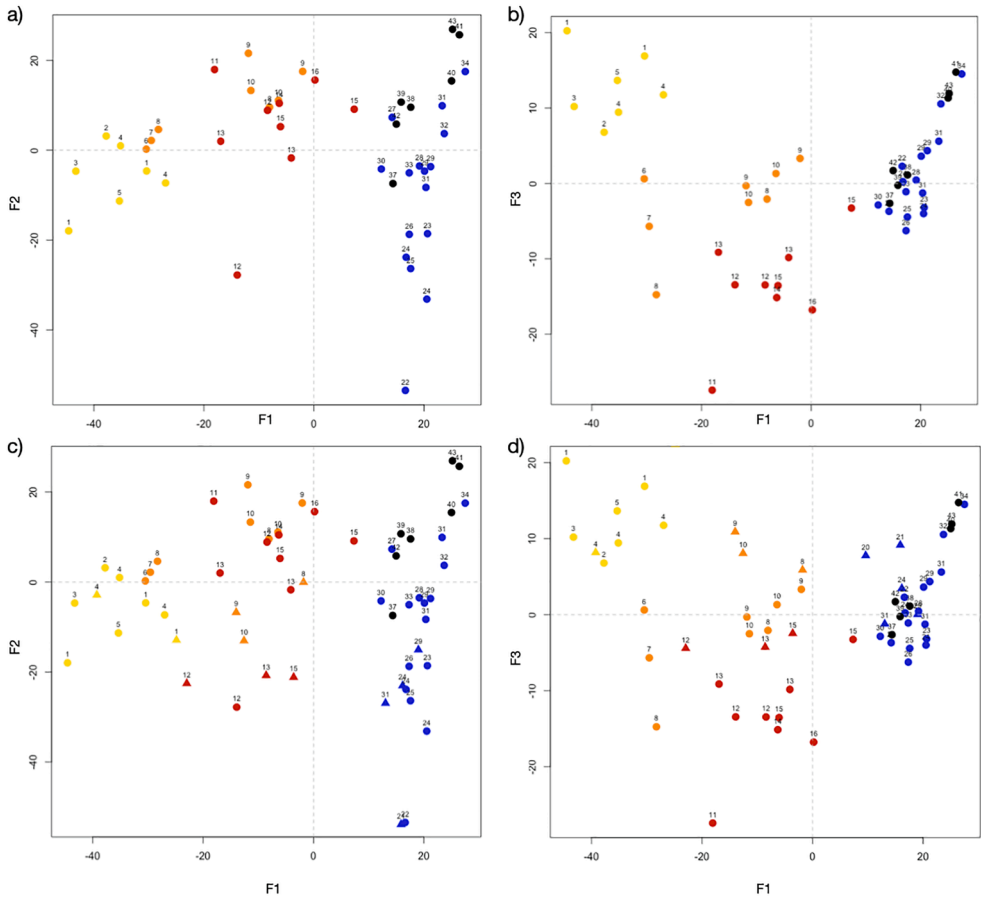

Fig. 4. Score plot of PLS-DA model (points): a) Factor-1 vs Factor-2; b) Factor-1 vs Factor-3. Score plot of PLS-DA model adding the prevision of the test set (triangles): c) Factor-1 vs Factor-2; d) Factor-1 vs Factor-3.

Table 3
Classification parameters (non-error rate NER, error rate ER, class sensitivity SN and specificity SP, ratio of not assigned samples N.A.) calculated in cross validation and on test set to obtain calibration and validation.

	Calibration			Validation			
	NER	0.81		NER	0.85		
	ER	0.19		ER	0.15		
Classes	SN	SP	N.A.= 0.09	SN	SP	N.A. = 0.07	Threshold
Yellow dyes	1.00	0.90		1.00	0.92		0.60
Orange dyes	1.00	0.92		1.00	0.94		0.26
Red dyes	0.89	0.89		0.92	0.92		0.38
Blue dyes	1.00	0.87		1.00	0.90		0.50
Black dyes	0.71	0.85		0.71	0.89		0.26

the first in the literature, to the best of our knowledge, about this class of historical synthetic dyes and could constitute a reference for future investigations on real case studies. The PCA model showed a gradual distribution of samples based on the different colors, that were ordered from the darkest to the lightest. No clustering was observed based on the different kinds of textile or the concentration of the dye. A PLS-DA analysis was applied to the data in order to further highlight the discrimination between the dyes. The PLS-DA model showed a good calibration ability with a NER of 81%, evaluated by cross-validation, and a good prediction ability, evaluated by projecting external test samples that have a low dye concentration (NER: 85%).

The testing on lighter and darker textiles dyed with the same colorant in different concentrations provided good results and was encouraging in view of generating references also for possibly faded real samples. Even though the association of other techniques must be surely considered to strengthen future attributions, we observed that the changing variables did not hinder the recognizability of these dyes with the proposed approach.

The combination of FORS spectroscopy, colorimetric parameters and chemometrics demonstrated to offer a non-invasive, fast, simple and low-cost approach to studying azo dyes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2022.107178.

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