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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.

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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 global 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. Dyes concentration in silk-cotton blend textiles was 2% for almost all samples, with few exceptions. In the case of wool-cotton blend textiles, two concentrations (2% and 0.75%) 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. In addition, almost each analyzed dye was linked to its molecular structure. Finally, the obtained set of data has been statistical treated. The PCA treatment highlighted the grouping of items based on colors, allowing some hypothesis of similarity and dissimilarity based on molecular structures. A reference database for future characterizations on real case studies by a

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non-invasive and fast approach, usually preferable when fabrics show perfect conservation conditions has been proposed. The PLS-DA analysis was applied to a part of the dataset to further study some clusters that emerged by PCA treatment. Most of the investigated dyes resulted quite well distinguishable, while few, such as those exhibiting very similar structures and equally named but supported by a different alphanumeric code, showed almost superimposable spectral features (i.e. green dyes *Diamingrun B* and *G*). The results highlighted also that, notwithstanding the changing variables, the dyes spectra were still recognizable and specific shifts or changes in the intensity values of the reflectance spectra could be predicted.

Keywords

Diamine, azo dyes, FORS, silk-cotton, wool-cotton, database, chemometric methods

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 part 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]. The purple colour thus obtained was of better quality than ‘false shellfish purples’ extractable from lichens and the mixtures of red and blue natural dyes (i.e. madder and indigo) and, on the other hand, was definitely cheaper than Tyrian purple. Mauveine was launched on the market in 1857, soon revealing itself a commercial triumph.

In a short period of time, a wide range of other aniline dyes had been synthetized, leading the way to an extensive variety of new bright colors for textiles. 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 *Aldo Moro* of Bari (Italy). The museum and the annexed chemical laboratory for the analysis of goods, were established by the Royal School of Commerce in 1886, and together with the library represented the central body of the school, the second in Italy after Ca' Foscari in Venice, founded in 1868. The museum was born to store and classify various samples of raw materials, semi-finished or finished products coming from all the world, with the aim of following the continuous technological and economic comparison of nations’ progress.

Starting from the fifties, the teaching approach of commodity science changed, including the study of production processes techniques as well as their impact on natural resources and the environment. At the same time, the museum began to lose its function in education and research, a common destiny for most of Italian commodity museums, inexorably unable to keep up with the rapid escalation of new technologies [4,5].

Nowadays, much of the original collection is still accessible. This precious assemblage includes also 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.* 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 [6,7], has scarcely been employed in the study of textile dyestuff [8,9], the main applications being directed to the revelation of natural/traditional dyes in fabrics prior to the era of synthetic colors [10,11].

The FORS technique was employed with the aim of generating a reference database for the future characterizations of 20th century dyestuff. A non-invasive and fast analytical approach was preferred because of the remarkable number of pattern books available and the perfect conservation conditions of most fabrics.

As the research progressed, unexpectedly, the objectives expanded. At this point, our purposes went beyond. Focusing on early dyes of the twentieth 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 [12].

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 [13]. While Mauveine (1856) had a short life as a fashion color due to intrinsic difficulties in synthesis and yield, Fuchsine rapidly expanded the aniline dye industry. All German dye factories founded in short succession (Kalle, Farbenfabriken Bayer, Farbwerke Höchst, BASF and AGFA) started to produce it.

The leadership of *Leopold Cassella & Comp.* quickly recognized the potential business in new synthetic dyes and the necessity to acquire knowledge in their manufacture to preserve profit.

During those years, innovations and scientific competition were both very raised and the research results had to be kept strictly secret to avoid imitations. From 1877, the adoption of the German Patent Act presented a new scene, making new discoveries legally more protected [14].

The naphthalene chemistry was intensively and deeply investigated in Cassella firm. It was found that naphthalene derivatives were excellent building blocks for the synthesis of azo dyes. Bis azo dyes were extremely effective thanks to their adaptability: different colors could be obtained by changing groups used in diazotization and coupling and/or the 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 (benzidine, tolidine, dianisidine, methoxy or ethoxy-benzidine) 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 (e.g. in SM1a).

Many of these bis azo dyes were mixtures of different chemical structures, the composition of which could be influenced by the choice of reaction. For example, diamine violet N [15] and diamine black RO [15] could be produced changing the synthetic routes from the same starting products benzidine and η'- (gamma) acid [16].

In less than 15 years, *Leopold Cassella & Comp*., which was renamed *Leopold Cassella & Co*. when the trade and manufacturing units were officially merged in 1894, had become the world's largest and most profitable azo dye factory with diamine dyes by the turn of the century. The patent ownership in the field of dyes arose to more than 150 German patents. 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. [17].

2. Materials and Methods

2.1 The Pattern Books

Two pattern books were investigated "*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). First introductive pages in both pattern books are dedicated to describing in detail dyeing processes of textiles and 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-two single dyes on half silk from the first book were analyzed and compared with wool 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, see Table 2). In case of wool-cotton blend textiles, two concentrations (2% and 0.75%, see Table 2) are reported for each dye selected and were analyzed.

2.1.1 Dyeing techniques

Here, we described the dyeing procedure reported in Cassella's pattern books.

Diamine colors in dyeing semi-silk fabrics

"The use of our diamine colors in the dyeing of semi-silk fabrics has acquired such importance that we believe it is useful to give an overview of the application and the qualities of diamine colors, which are mainly introduced into this industry."

The tourniquet tank was generally used for dyeing semi-silk fabrics using diamine colors. In isolated cases, when the nature of the textile to be dyed required it, the jigger was alternatively used.

Generally, the textiles were dyed with diamine colors on a soap bath with the addition of sodium phosphate, sodium sulphate or sea salt, and a little sodium carbonate.

The addition of these salts made the baths better exhausted; they were therefore used especially for dyeing dark and intense nuisances, while for light tones either soap alone, or soap and sodium phosphate were used instead. It was possible to obtain more or less dark tones by properly adjusting salt concentrations (e.g. the use of salts increased the amount of dye tied to the fiber, therefore providing a more intense color).

Specific guidelines which could be applied to all cases were not possible, depending the way of dyeing on the effect to be obtained as well as on the nature of the fabric to be treated.

The dyeing process was normally carried out at a temperature of about 80-90 °C, heating the bath with all the additives in, then the steam flow was stopped, the fabric entered, and all was turned for about 45 minutes -1 hour.

After dyeing and rinsing thoroughly, acetic acid was added. This operation was performed in a cold bath containing about 2 cc. acetic acid (50% per liter of water).

Diamine dyes, with some exceptions, are very resistant to acids, therefore, a change in shade or lightness will almost never occur.

Diamine colors in dyeing semi-wool fabrics

The use of dyeing process in one bath allowed the mid-wool industry to create a series of new items and its advantages contributed to a great development of this manufacture.

For dyeing mid-wool fabrics in a single bath, diamine colors were used either alone or combined in the same bath with specific dyes for wool. Generally, for dyeing, the fabrics to be dyed had to be carefully washed (degreased) earlier. For light shades, the fabric had to be wetted in advance, while for dark shades it was entered dry in the dye bath. Usually, the dyeing process was performed by the tourniquet tank.

The bath was heated with direct or indirect steam and sodium sulfate was added.

When tanks having previously contained with acid baths were used, it was necessary to neutralize the acid adsorbed by the wood by a following washing with sodium carbonate. A proper adjustment of the bath temperature was a crucial point for obtaining uniform and well-compliant shades on the two fibers.

2.2 Techniques

Fiber Optics Reflectance Spectroscopy (FORS) was employed to generate the spectra. The reflectance spectra were collected by means of the fiber optic spectrometer Quest U (B&W Tek Inc., Newark, DE, USA): it is 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 used. 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) is applied to the obtained dataset [18]. 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 information and are mutually orthogonal.

The PCA is 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 with the columns.

The classification technique applied to a part of the entire dataset is 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 [19].

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.

Several parameters can be used to measure the quality of the classification model [20-21].

The confusion matrix is a square matrix GxG, where G is the number of classes. Each element, n_{gk}, is the number of objects belonging to the gth class and assigned to the kth class. The diagonal elements n_{gg} are the correctly classified objects, while the off-diagonal elements represent the objects erroneously classified.

The other classification parameters can be evaluated by the confusion matrix.

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 n is the total number of objects.

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

The sensitivity of the gth class (Sn_g) describes the model ability to recognize objects belonging to the gth 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:

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

Which 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 have been performed by the software R version 4.0.5 (R Core Team, Wien, Austria).

3. Results and discussion

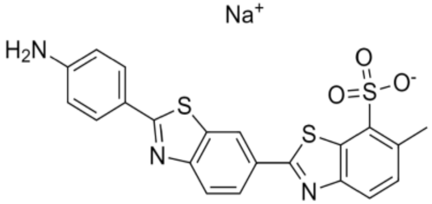
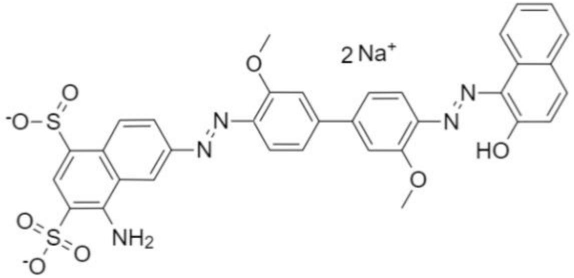
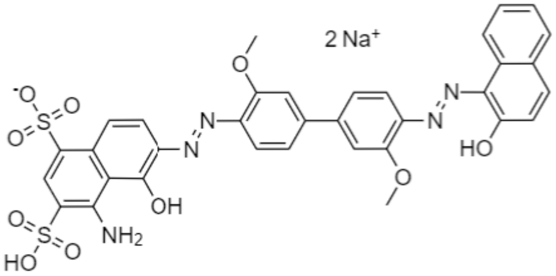
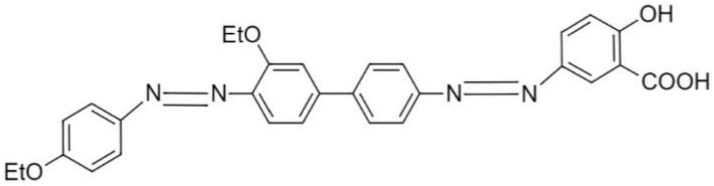
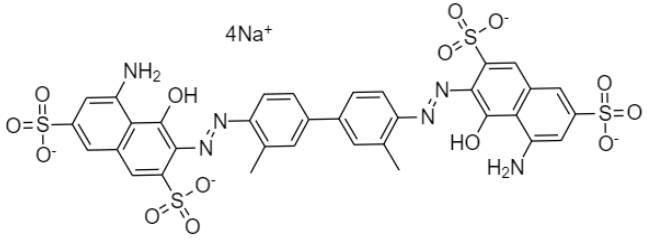
3.1 Dyes data recovering

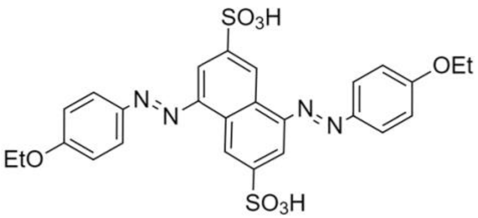
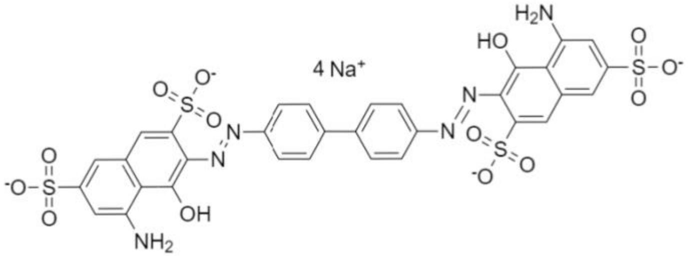
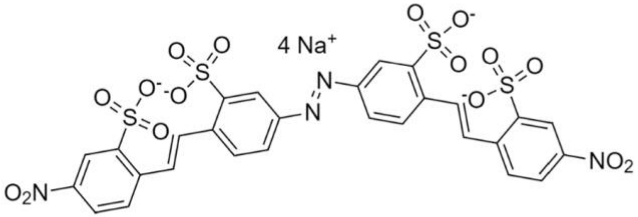
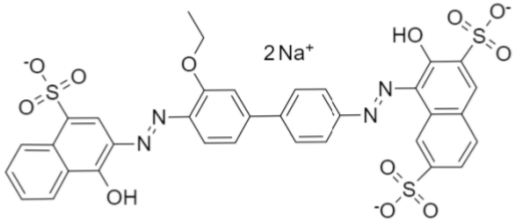
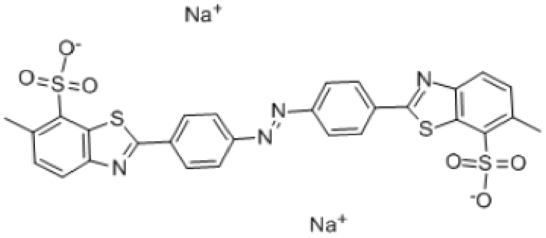
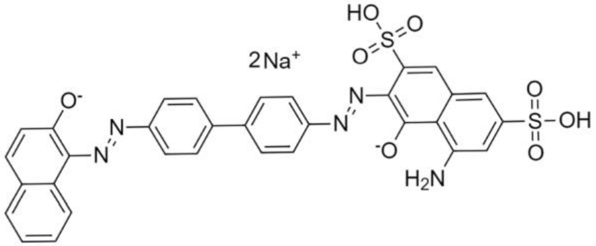
Dyes analyzed are grouped in a table as complete as possible (Table 1 and SM1b). Most of the found dyes are bis-azo compounds, except for few mono-azo, tri-azo, tetra-azo and azo compounds containing thiazole groups.

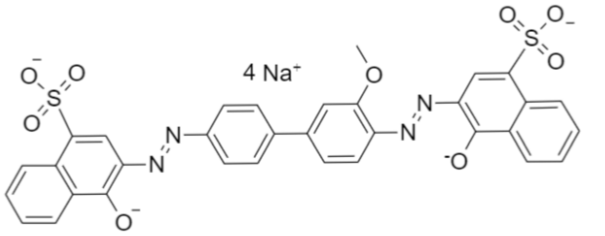
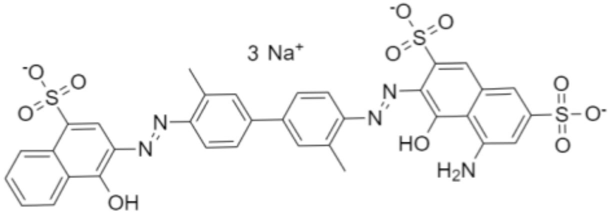
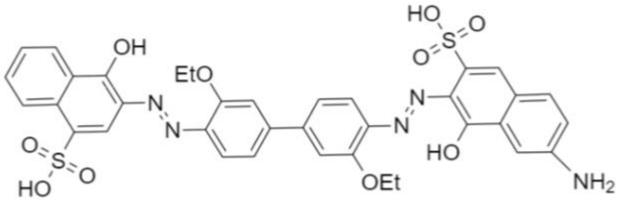
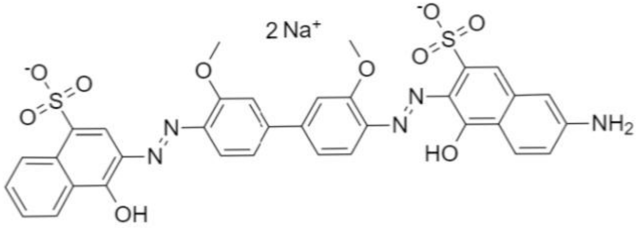
A meticulous editing and a detailed scouting work, considered the use of multiple names and codes for the same dye as well as the difficulties related to patent issues, allowed to identify most parts of structural formulas linked to colorants analyzed (Table 1) [22-45]. Many dyes in that period were concurrently manufactured by many firms in various countries, and competitors used different names for the same structural formula [45]. In the early days of artificial dyestuff industries, different shades were identified by letters 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, L may mean soluble or fast to light. In the same way, C may stand for Cassella and W the preferable use for wool, while HW for half wool. Still, some dyes 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 [45].

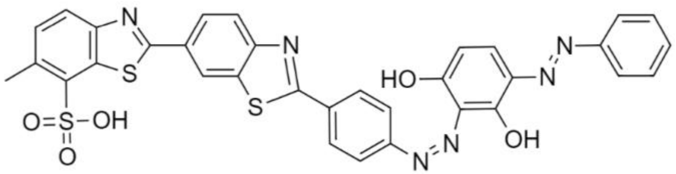
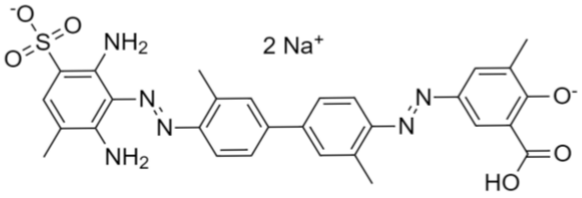
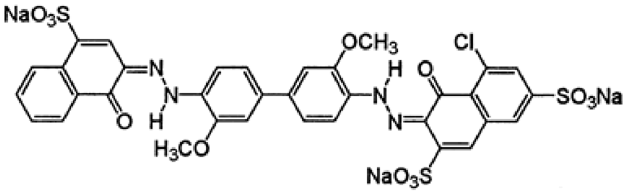
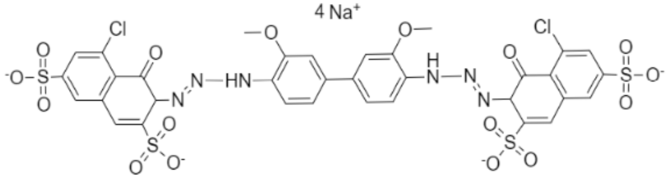
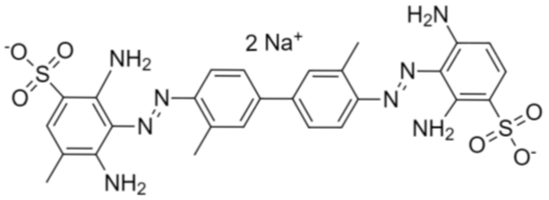
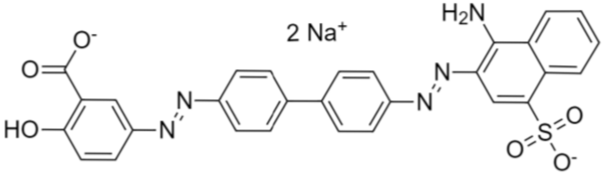
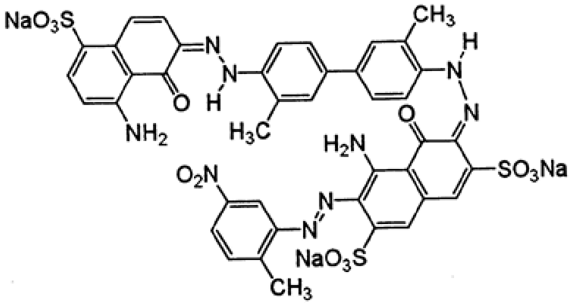
Both pattern books show samples perfectly preserved: brilliant and uniform colors in textiles neither discolored, frayed nor stained or worn.

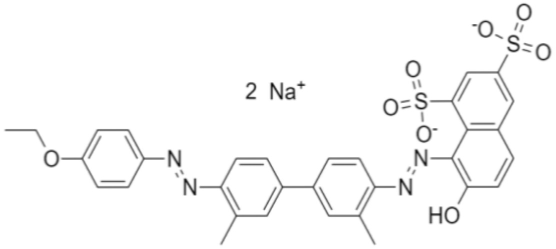
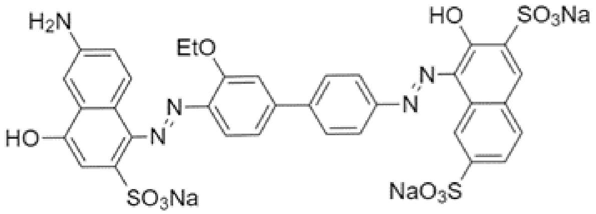
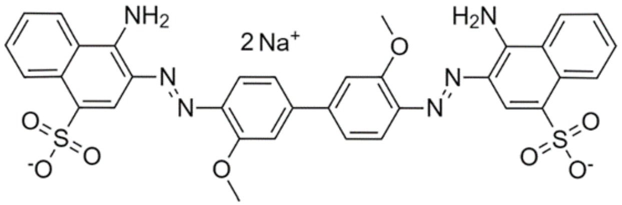
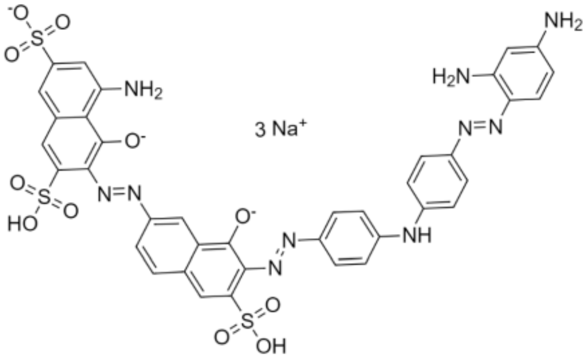
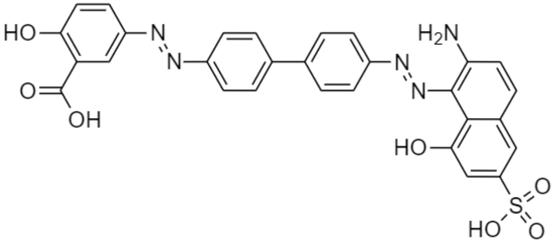
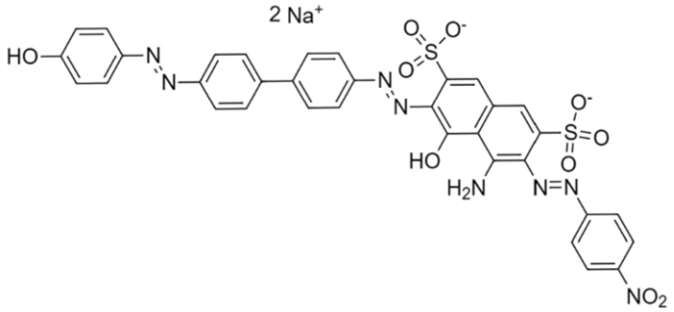
Table 1 Color (Y=yellow, O=orange, R=red, P=pink, V=violet, B=blue, G=green, Bk=black), code, pattern book name and molecular structure of investigated dyes.

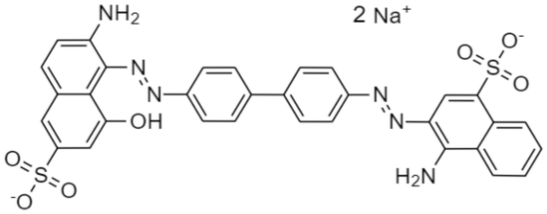
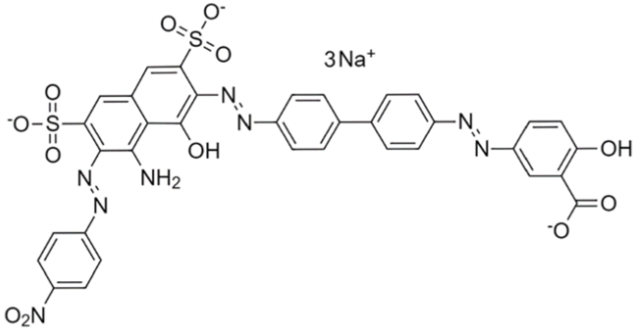
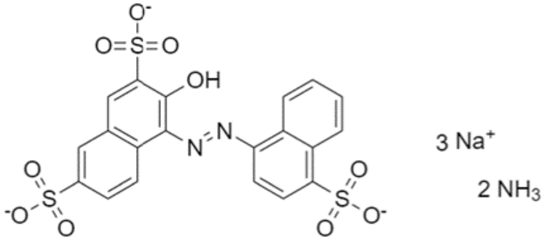
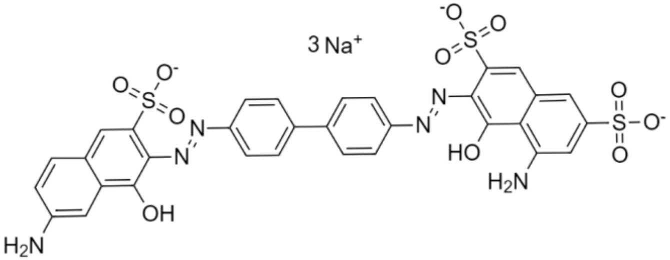
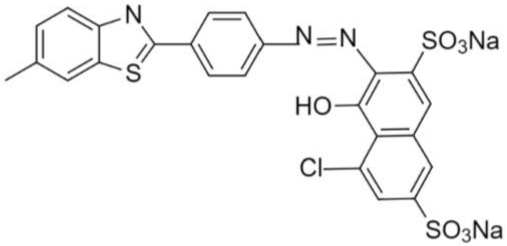
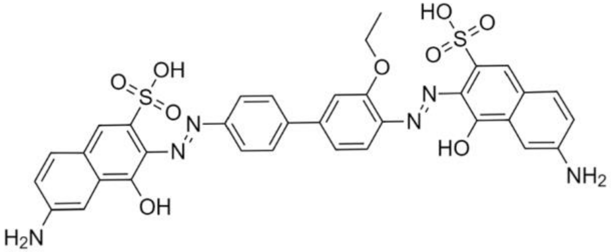
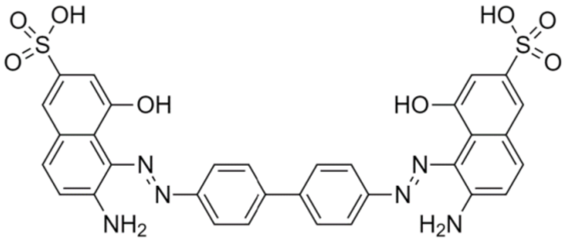
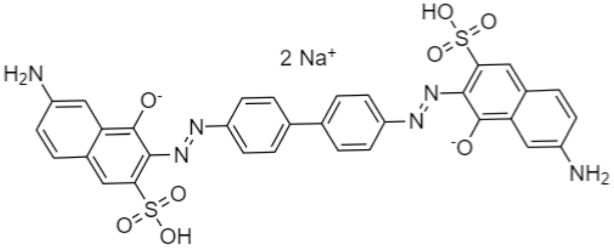
Color	Code	Pattern Book name	Molecular structure	Color	Code	Pattern Book name	Molecular structure
Y	1	Thioflavin S		B	22	Diaminblau RW	 
Y	2	Diamingelb N		B	23	Diaminblau 3B	

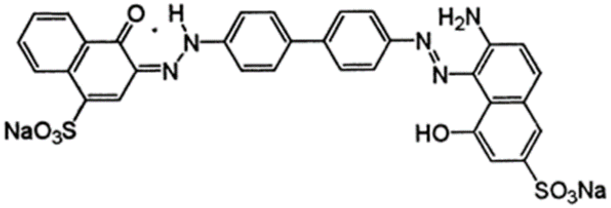
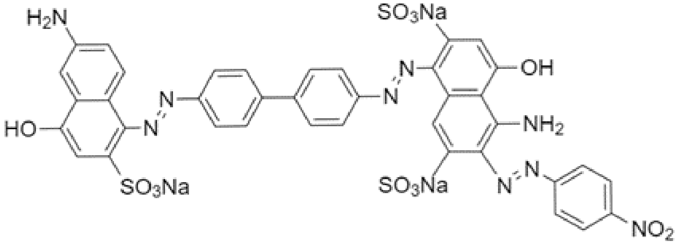
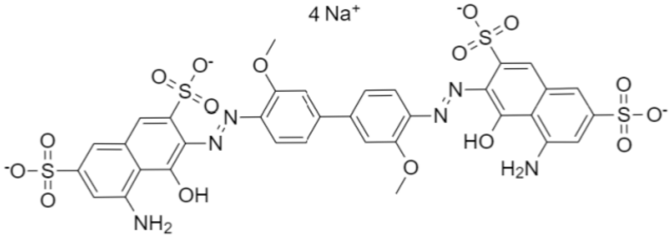
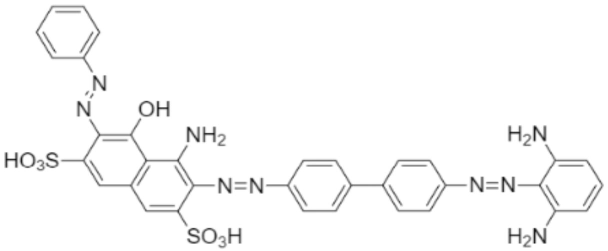
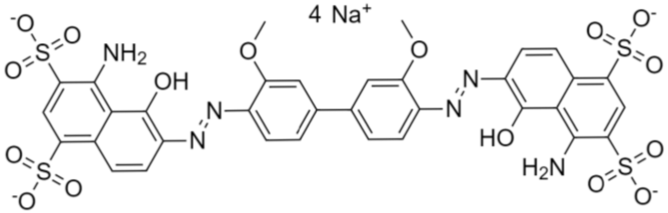
Y	3	Diamingoldgelb		B	24	Diaminblau 2B	
Y	4	Diaminechtgelb A	Primary reaction product: 	B	25	Diaminblau BG	Molecular structure Diamine Blue B. G should be for *gekupfert* copper. 
Y	5	Diaminechtgelb B		B	26	Diaminblau 3R	

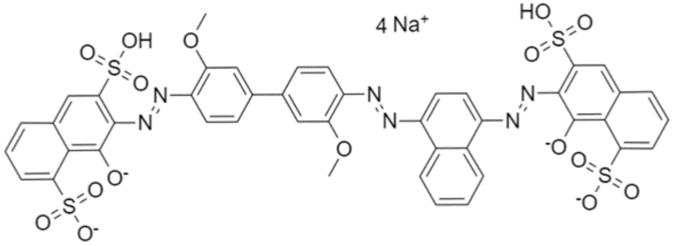
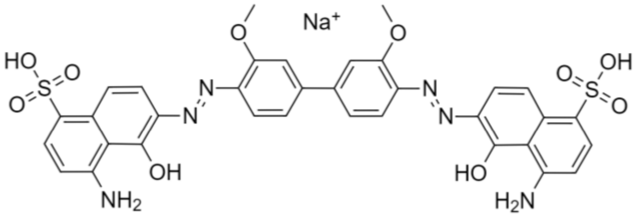
							
O	6	Diaminorange GC	C probably for Cassella. Diamine Orange G: A tetrazo dyestuff, which dyes cotton reddish-orange shades from an alkaline salt bath, and wool from a sodium sulphate bath.	B	27	Diaminblau BX	
O	7	Diaminorange DC	According to reference this dye is equal to Chloraminorange G, which structure is probably the same of Diaminechtgelb A.	B	28	Diamineralblau R	 

O	8	Diaminorange B		B	29	Diaminazoblau 2R	-
O	9	Oxydiaminorange G		B	30	Diaminbrillantblau G	 
O	10	Oxydiaminorange R	 	B	31	Diaminstahlblau L	

R	11	Diaminescharlach 3B		B	32	Diaminblauschwarz E	
R	12	Diaminrot 10B		B	33	Diaminschwarzblau B	 Tetrazo dyestuffs of a similar character to Diamine black HW.
R	13	Diaminechtrot F		G	34	Diamingrun B	

R	14	Diaminbordeaux B		G	35	Diamingrun G	
R	15	Diaminbordeaux S		Bk	36	Diaminschwarz BH	
P	16	Diaminrosa BD		Bk	37	Diaminschwarz BO	
V	17	Diaminviolett N		Bk	38	Diaminschwarz RO	

V	18	Oxydiaminviolett B		Bk	39	Diaminschwarz HW	
B	19	Diaminreinblau		Bk	40	Halbwollschwarz S	Structure of Halbwollschwarz 
B	20	Diaminreinblau FF		Bk	41	Oxydiaminschwarz S000	Tetrazo dye of a similar character to Diamine black HW.

B	21	Diaminblau CB	 	Bk	42	Oxydiaminschwarz D	Tetrazo dye of a similar character to Diamine black HW.

3.2 Diamine dyes

The colorimetric coordinates of all 42 dyes and their FORS features on silk-cotton blend are listed in Table 3. 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 3.

Table 3 Features and colorimetric coordinates of analyzed dyes on silk-cotton and wool-cotton blend as revealed by FORS investigation (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	Wool/Cotton	Yes	2		415	495	84.622	-4.063	67.601	67.723
2	Wool/Cotton	Yes	2		430	520	76.699	10.843	79.780	80.514
3	Wool/Cotton	Yes	2		437	520	81.326	8.029	78.498	78.907
4	Wool/Cotton	Yes	2		435	530	75.824	9.902	61.173	61.97
5	Wool/Cotton	Yes	2		415	513	78.961	4.096	63.527	63.659
6	Wool/Cotton	Yes	2		440	540	72.615	18.993	63.483	66.264
7	Wool/Cotton	Yes	2		450	560	69.701	27.319	59.405	65.385
8	Wool/Cotton	Yes	2		470	580	63.801	41.128	53.803	67.722
9	Wool/Cotton	Yes	2			535, 593	54.208	21.673	66.465	69.91
10	Wool/Cotton	Yes	2			540, 600	53.304	22.837	43.054	48.736
11	Wool/Cotton	Yes	2	450	535	615	37.273	68.914	28.484	74.569
12	Wool/Cotton	Yes	2	465	525	587	58.860	30.707	31.897	44.753
13	Wool/Cotton	Yes	2			605	40.952	37.978	23.676	44.753
14	Wool/Cotton	Yes	2	445	530	607	44.361	40.032	16.544	43.315
15	Wool/Cotton	Yes	2	450	550	650	21.347	39.712	2.238	39.775
16	Wool/Cotton	Yes	2	425	535	595	59.710	60.984	-5.530	61.235
17	Wool/Cotton	Yes	2	450	535	637	49.467	26.944	0.963	26.961
18	Wool/Cotton	Yes	2	440	550	653	35.684	33.256	-11.717	35.26
19	Wool/Cotton	Yes	0.25	480	615, 650	700	64.240	-9.856	-15.062	18
20	Wool/Cotton	Yes	0.25	475, 635	615, 660	710	56.570	-12.077	-16.849	20.73
21	Wool/Cotton	Yes	1	450	615	710	52.109	-3.033	-20.620	20.841
22	Wool/Cotton	Yes	2	450	600	720	29.016	9.889	-32.378	33.854
23	Wool/Cotton	Yes	2	440	600	707	34.761	9.274	-34.811	36.025
24	Wool/Cotton	Yes	2	435	600	713	35.332	7.152	-29.553	30.406
25	Wool/Cotton	Yes	2	440	590	700	30.093	13.948	-32.598	35.457
26	Wool/Cotton	Yes	2	440	570	690	19.895	18.220	-15.537	23.945
27	Wool/Cotton	Yes	2	440	590	700	26.772	12.757	-23.482	26.724
28	Wool/Cotton	Yes	2	447	600	740	29.879	2.422	-17.727	17.298
29	Wool/Cotton	Yes	2	445	565	700	32.909	12.734	-11.600	17.226
30	Wool/Cotton	Yes	2	440	585	715	24.969	14.857	-31.167	34.527
31	Wool/Cotton	Yes	2	480	635	777	27.924	-7.051	-12.706	14.531
32	Wool/Cotton	Yes	2	447	575	730	28.613	9.281	-18.975	21.123
33	Wool/Cotton	Yes	2	453	615	795	17.875	0.175	-9.765	9.766
34	Wool/Cotton	Yes	2	513	650	750	19.942	-16.918	8.888	19.11
35	Wool/Cotton	Yes	2	513	660	740	25.892	-17.858	5.598	18.715
36	Wool/Cotton	Yes	2	440	580	735	33.073	6.254	-14.793	16.06
37	Wool/Cotton	Yes	2	450	575	730	20.282	9.088	-12.821	15.715
38	Wool/Cotton	Yes	2	455	575	710	20.085	7.107	-9.704	12.028
39	Wool/Cotton	Yes	2	480	640	770	17.988	-6.047	-9.367	11.15
40	Wool/Cotton	Yes	6			800	11.359	-3.303	10.369	10.883
41	Wool/Cotton	Yes	1	460	575	725	30.162	4.253	-4.092	5.902
42	Wool/Cotton	Yes	6			770	7.579	-0.211	9.471	9.473

1	Silk/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	Silk/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	Silk/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	Silk/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	Silk/Cotton	Yes	2			552	55.325	22.774	45.625	50.993
			0,75			540, 590	67.111	12.612	33.693	35.976
13	Silk/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
15	Silk/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
17	Silk/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
18	Silk/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
24	Silk/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
29	Silk/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
31	Silk/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
35	Silk/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
36	Silk/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

3.2.1 Diamine dyes on silk-cotton blend

All the reflectance spectra can be found in SM2, whilst a selection of dyes on silk-cotton blend is shown in Fig.1 to the comparison color by color.

Yellow colors

The yellow dyes spectra, all showing the characteristic shape of yellow color, are the most difficult to be differentiated - as already reported for traditional dyes [11] - being their absorbance maxima and inflection points respectively comprised between 415 and 437, and between 495 and 530 nm (Table 3, Fig.1), respectively. *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 in 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.

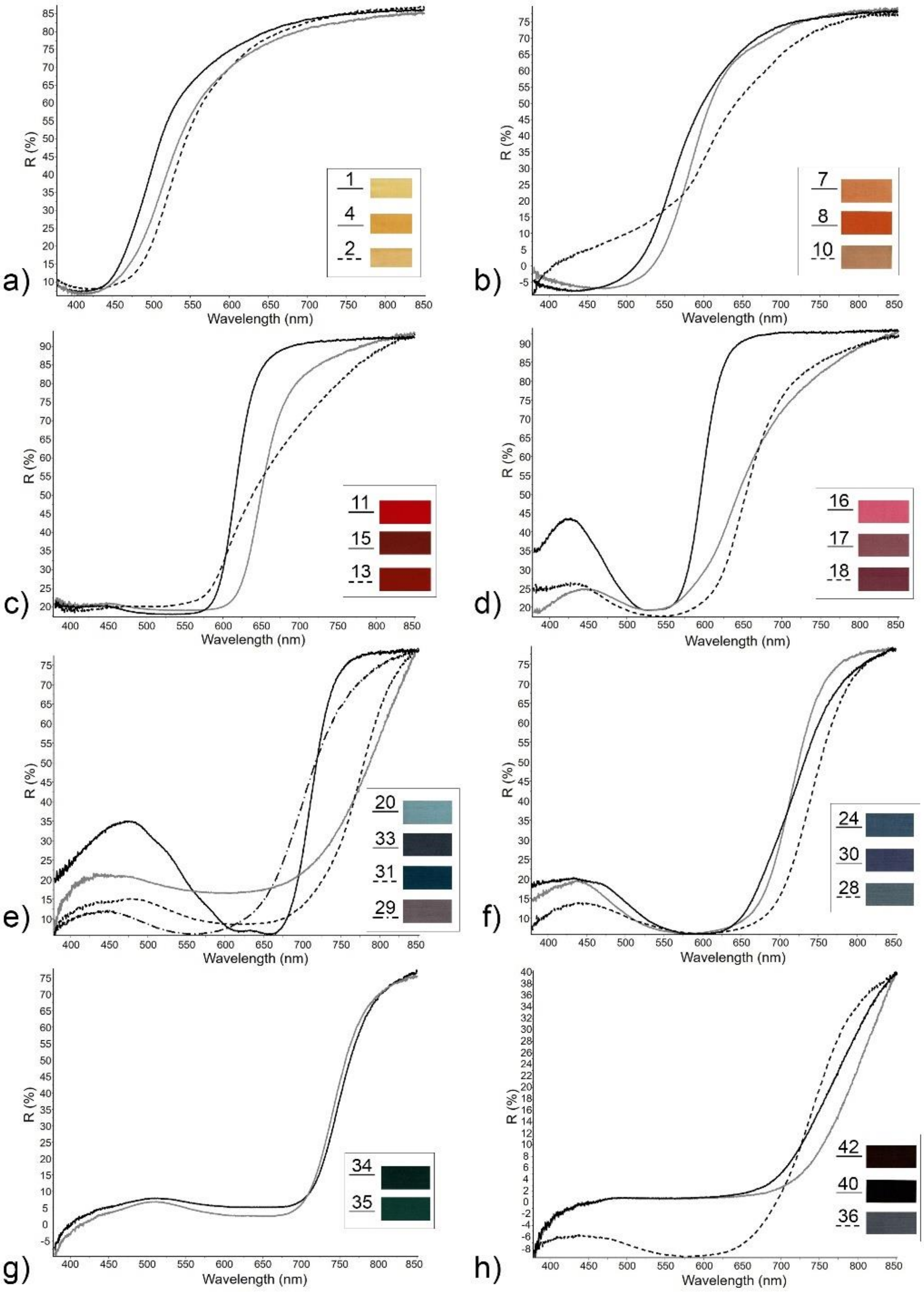


Fig. 1. Reflectance spectra of samples of silk-cotton blend colored with a) yellow, b) orange, c) red, d) pink and violet, e), f) blue, g) green, h) black dyes. The codes of the dyes are reported in Table 2.

Red and violet colors

The red colors appear quite varied in their definitions distinguishing “roth” (red), “echtroth” (fast red), “scarlach” (scarlet) and “bordeaux”, generating reflectance spectra with differentiated profiles within the typical sigmoidal curve of red colors [43]. In the spectrum of *Diaminechtroth F (13)* it was 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.3c). The *Diaminechtroth F* dye showed a different structure with respect to “rot” *Diaminrot 10B*, namely the substituents are not symmetrical, i.e. the amine was not used for the two diazo-copulations (Table 1) [32].

The *Diaminscharlach 3B (11)* spectrum was 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.2c). It is a bis-azo compound not symmetrical, that is in the second step of the reaction the phenol was used, while in case of *Diaminechtroth F* salicylic acid was employed. The *Diaminbordeaux S (15)* spectrum exhibited 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.1,c,d): the inflection points were very close in both cases, while the *Diaminviolet N* (17) dye is better differentiated for its absorbance maximum position (Fig.1d, Table 3).

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* (16) reflectance spectrum (Fig. 1d).

Blue colors

The blue colors were 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* (20) 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* (33) whose spectrum is indeed much less structured and typical of dark colors, where the correct features positions are difficult to be read [9] (Fig.1e). The *Diaminsthalblau L* (31) color is slightly lighter, with an analogous profile, but more easily readable features (Fig.2e). The *Diaminazoblau 2R* (29) dye is peculiar and not much blue-like, it can be differentiated by the combination of its features (Fig.1e). Finally, *Diaminblau RW* (22), *Diaminblau 3B* (23), *Diaminblau 2B* (24) and *Diamineralblau R* (28) 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* (23), *Diaminblau BG* (25), *Diaminblau 3R* (26) and *Diaminbrillantblau G* (34) have the same position of the reflectance maximum (440 nm) and a tight interval of inflection points (690-715 nm) (SM2, Fig.1f).

Green colors

The FORS spectra of the only two green dyes were almost overlapped (except for more marked features of *Diamingrun G* (39)), mirroring the high similarity of molecular structures (Fig.1g). Both dyes were obtained starting from benzidine which reacted with one mole of phenol (*Diamingrun B* (38)) or salicilic acid (*Diamingrun G*) and one mole of H acid (8-amino-1-naphtol-3,6-disulfonic acid) which in turn was coupled with p-nitroaniline [32].

Black colors

Many dyes defined as “black” are rather brownish or greyish like *Diaminschwarz BH* (36) (Fig.1h), the darkest shades such as *Oxydiaminschwarz D* (42) and *Halbwollschwarz S* (40) (Fig.1h) show reflectance spectra with a flat profile between 450 and 650 nm.

3.2.2 Diamine dyes on wool-cotton blend.

The reflectance spectra are presented in SM3.

The two yellow colors show two completely different spectra patterns, depending on their corresponding structural formulas (Table 2). 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* (23) is identified by its double reflectance maximum at about 440 and 470 nm.

4 Variability of the Diamine Colors reflectance spectra

Since visible spectra were taken into account, with their features positions and colorimetric coordinates, it seems 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 [9], such as the supporting fibers [47] or the concentration [48], and to what extent these variations can hinder the dyes identification. Therefore, these aspects will be discussed in the following paragraphs.

Other important parameters not to be neglected are also mordants and ageing phenomenon. Nevertheless, as already clarified, textiles showed up in perfect conservation conditions. In addition, 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 [9].

Furthermore, as regards salts, sodium phosphate, sodium sulphate or sea salt, and sodium carbonate 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 effect of salts on the final color and which one that of the fiber.

3.4.1 Same dye on different fibers: silk-cotton and wool-cotton blends comparison.

Taking into account the pattern book displaying the Cassella dyes applied to the wool-cotton blend, and comparing their reflectance spectra to those of the same dyes on silk-cotton blend, the existence of two cases must be considered. The great part of the dyes uniformly color wool and cotton at, while the remaining five color cotton more intensely than wool: in the latter, color results not uniform but performing stripes. Therefore, considering that the collection spot of the instrument is of about 4 mm^2, it must be noted that differently colored adjacent yarns could be analyzed at the same time, since each stripe measures about 1.5 mm. A still recognizable reflectance spectrum is generated, but it could be possibly misleading in the perspective of the discussion here carried out.

Sticking to uniformly-coloring dyes, a different behavior was noted in the comparison of the two blends for darker dyes and lighter ones if applied in the same concentration (2% w:w).

The darker dyes (30, 34, 35: L*= between 15 and 26 for wool and between 19 and 25 for silk) displayed almost superimposable spectra for silk-cotton and wool-cotton blends in the visible region, slight differences can be seen in the spectrum 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 of the supporting fiber characterization [10].

All other dyes applied to wool, though maintaining the same spectral shape, showed a blue-shift of their reflectance maximum and/or a red-shift of their inflection point (Fig. 2e,g).

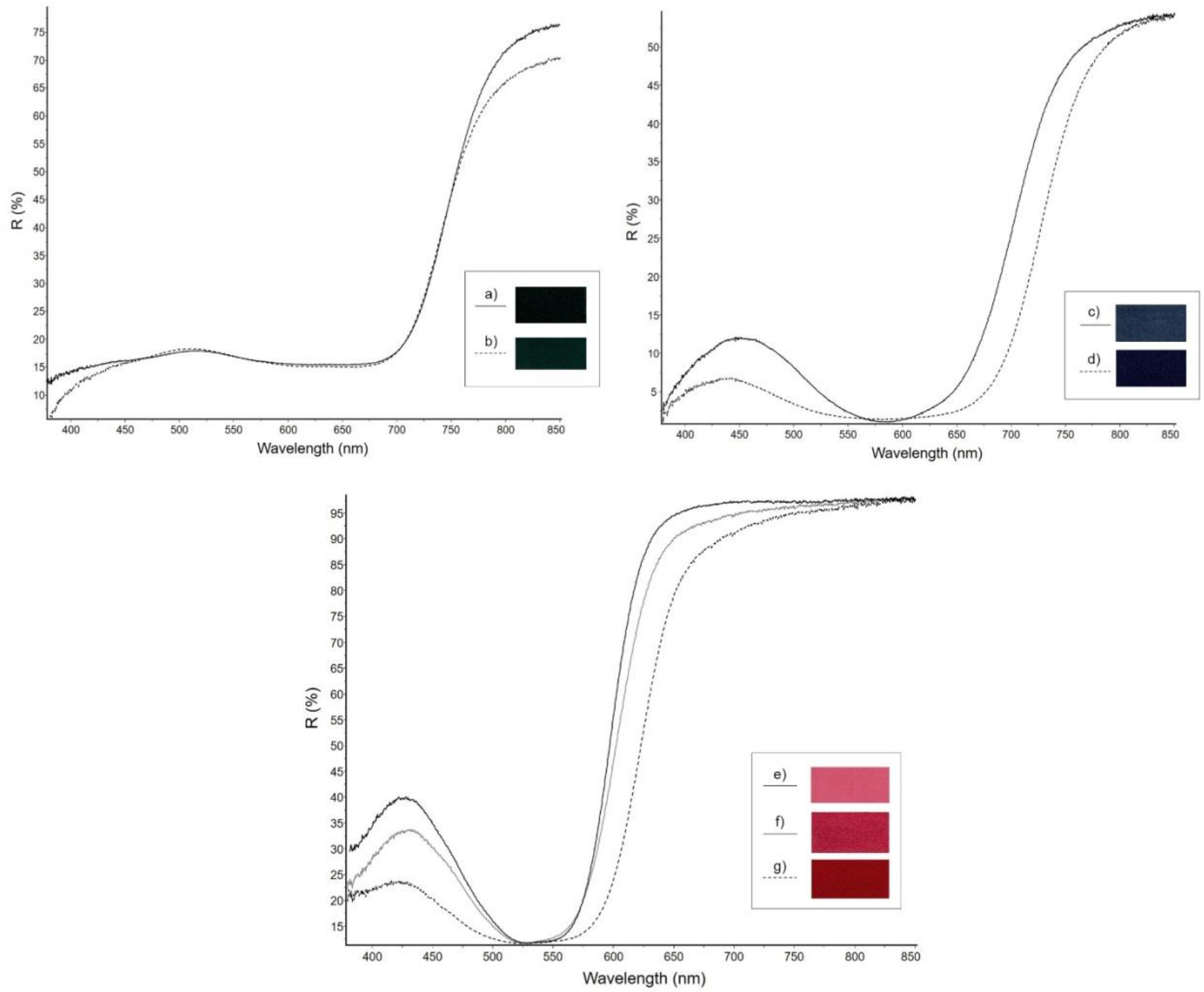


Fig. 2 Reflectance spectra comparing: same dark-coloured dye and same concentration (2%) on two different blends (Diamingrun B on a) wool-cotton and b) silk-cotton); same dye on the same blend (wool-cotton) in different concentrations (Diaminbrillanblau G in c) 0.75% and d) 2%); same bright-coloured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

3.4.2 Same dye in different concentrations: wool-cotton blend examples

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, once again 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 [11].

3.5 Chemometric treatment

Some multivariate statistical treatments have been applied to the set of spectra and colorimetric parameters and accordingly some remarks on molecular structures have been reported.

The silk-cotton and wool-cotton blends items all together were treated by PCA (Fig. 3). Colors' labels represent the corresponding color dye. The first 3 PCs contain respectively 56.3, 22.7 and 12.8% of the total explained variance. The generated 3D score plot highlighted an overall trend based on the discrimination between colors. No further pattern was observed in the distribution of objects. This led to hypothesize that FORS and colorimetric parameters linked to the dye composition are more significant in the statistical treatment than the textile and dye concentration.

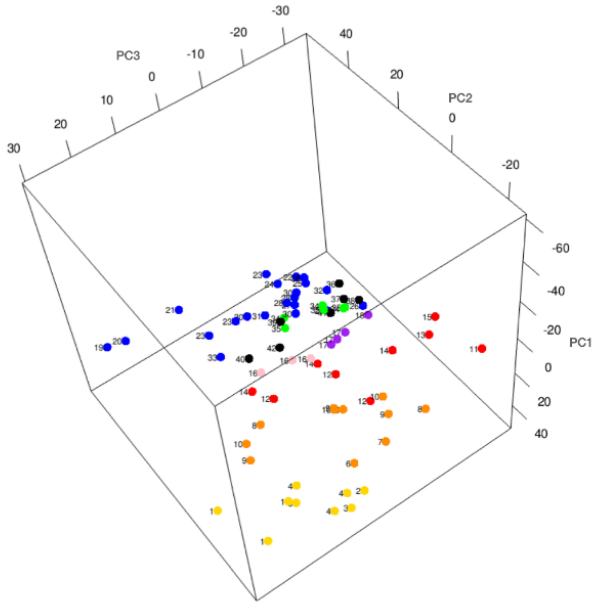


Fig. 3 Score plot (3D) considering all samples analyzed (silk-cotton and wool- cotton blend).

A PCA model formed by silk-cotton samples with red, yellow, and blue colors (the RYB model) has been computed (Fig. 4a and 4b).

The first three PCs explain respectively 53.9, 27.2, and 15.0% of the total variance.

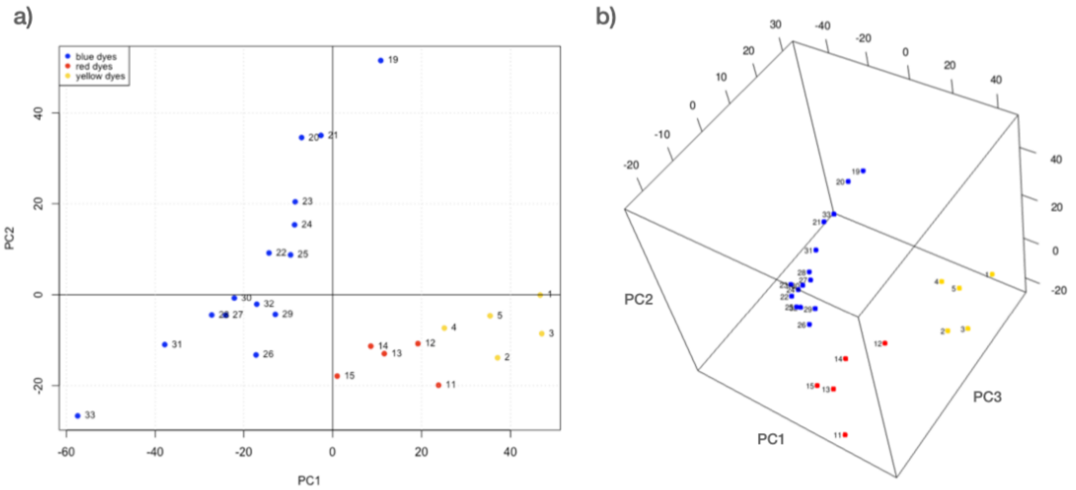
Results highlight a good distinction of RYB primary colors: red and yellow samples are closer (all in second quarter, PC1 positive and PC2 negative) with respect to blue ones. Blue samples 18 and 33 are located farther respect to blue grouping. The blue dye closer to *Diaminreinblau* (19) is *Diaminreinblau FF* (20): they differ from each other by the different position of two pairs of sulphonic groups on the double naphthalenic system. *Diaminblau CB* (21) refers to two possible molecular structures, one very similar to *Diaminreinblau FF* (20) and the other quite different. Hence, the proximity between items 20 and 21, allows us to hypothesize as more likely the molecular structure containing six aromatic rings. *Diaminschwarzblau B* (33) refers to two possible molecular structures too, one quite different from the other blue ones and the other more similar to a black dye (*Oxydiaminschwarz D* (42)) (Table1).

Diaminrot 10B (12), *Diaminechtrot F* (13) and *Diaminbordeaux B* (14) show some similarities in the molecular structures unlike items *Diamineschارlach 3B* (11) and *Diaminbordeaux S* (15). This consideration perfectly reflects the score plot.

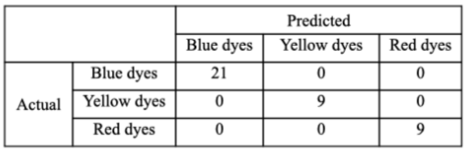
Lastly, the 2D score plot showed yellow samples quite distant from each other, a not unexpected finding since the group of yellow dyes is represented by the more heterogeneous molecular structures: this can be useful to differentiate yellow dyes, which highlighted the most difficult spectra to be distinguished.

A classification method, the PLS-DA, was applied to the data to evaluate if the three primary colors of the dataset, red, yellow and blue, could be discriminated regardless of the textile material or dye concentration (Fig 4c).

Thus, the *a priori* classes were the colors red, yellow and blue., the cross validation Leave-One-Out method was used in order to validate the model. The cumulative explained variance in X and in Y were, respectively, of 97.3% and 86.5%. The optimal number of latent variables was chosen as the number associated to the minimum error (ER) and at the same time to the minimum number of not assigned samples. The percentage of correctly classified objects (Non-error rate, NER) was excellent: 100%. The values of specificity and sensitivity were always 1 for all the classes. These results confirmed the good performance of the classification model.



c)



		Predicted		
		Blue dyes	Yellow dyes	Red dyes
Actual	Blue dyes	21	0	0
	Yellow dyes	0	9	0
	Red dyes	0	0	9

Fig. 4 a) 2D score plots of the RYB model.; b) 3D scores plot of the RYB model; c) PLS-DA Confusion matrix obtained with the three classes of the RYB model as a priori classes.

The orange, violet, pink, green and black items have been projected on the RYB model (Fig. 5). The projecting set highlights further noteworthy considerations. Black items are located close to blue ones. *Diaminschwarz BO* (37) and *Diaminschwarz RO* (38) differ very little in their molecular structures (presence or absence of an ethoxy group) and are located very close to each other. On the other hand, *Diaminschwarz BH* (36) and *Diaminschwarz RO* (38) differ in the position of an amino group and the presence of a sulphonic group in *Diaminschwarz BH* (36).

Not surprisingly, PCA shows black dyes as well integrated in the blue group. Black *Halbwollschwarz S* (40) is very close to blue dye *Diaminschwarzblau B* (33), supporting the hypothesis of a blue dye similar to a black one. *Diaminschwarz BH* (36) is close to *Diaminblau 3B* (23) and *Diaminblau BG* (25), all endorsed by similar structures.

The similarity (the only difference is the presence of a carboxylic group) of the two molecular structures of green dyes (*Diamingrun B* and *G*) can be observed also in their PCA position where the two items are nearby.

Diaminorange B and pink dye *Diaminrosa BD* are located close to each other, both containing thiazole groups.

Diaminviolet N (17) and *Diaminbordeaux B* (14) are located very close to each other, showing very similar molecular structures. *Oxydiaminviolet B* (18) and *Diaminechtrot F* (13) too have comparable molecular structures and are close in the score plot; on the other hand, also *Diaminbordeaux S* (15), characterized by a different molecular structure, is rather near to them.

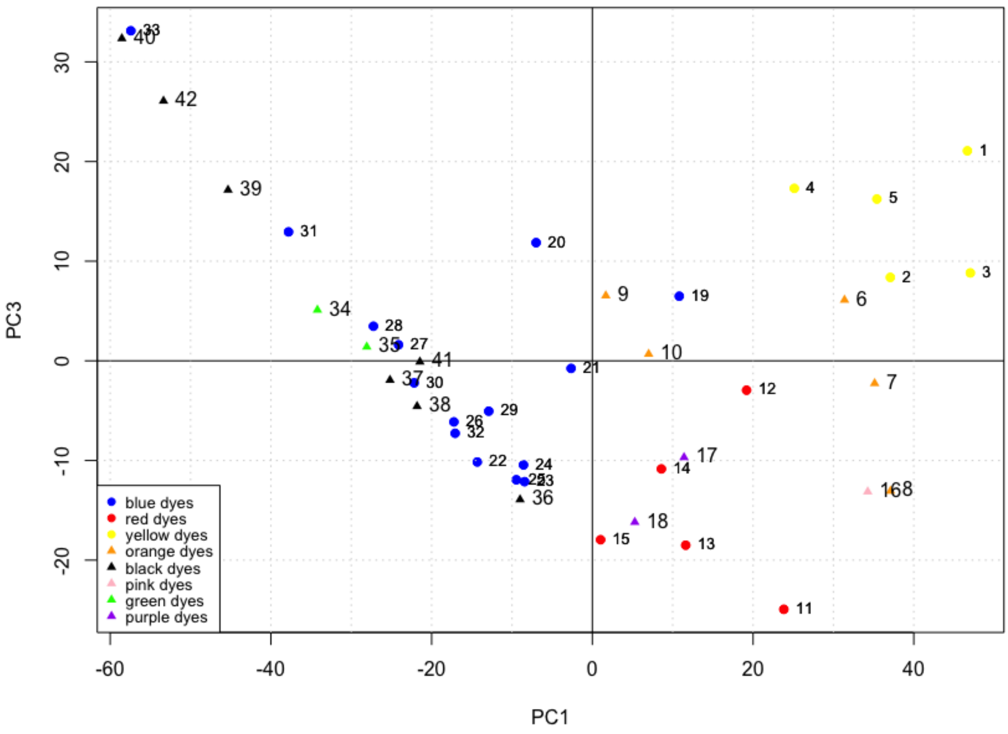


Fig. 5 Score plot (PC1 and PC3) of the control model.

4. Conclusions

A scientific storytelling about an exceptional historical period (late 19th - early 20th century) was investigated, when different areas of expertise stood out and intersected: synthetic chemistry, multinational firms, intellectual properties, research and industrial scale-up.

on the study was focused on the first synthetic azo dyes proposed by Leopold Cassella & Co. considering silk-cotton and wool-cotton blends pattern books. Within the process of study and recovery of data concerning these colorants, a first attempt to spectroscopic characterization was carried out on the textiles dyed with Cassella diamine colors, assisted by their molecular structures.

The collected colorimetric and spectral information treated by PCA are the first about this class of historical synthetic dyes in the literature 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. Three macro groups differed considerably: blue, red and yellow dyes. A PLS-DA analysis was applied to the data in order to further highlight the discrimination between the three clusters, obtaining a percentage of correctly classified objects of 100%.

Most of the analyzed dyes could be well differentiated, while others, especially those with similar molecular structures (often implying the same name but with a different alphanumeric code as in the case of Diamingrun B and G) can be hardly distinguished with the proposed techniques, becoming more differentiable by the use of multivariate statistical treatments. Also, the PCA graphs obtained, made it possible to prefer a molecular structure instead of another when the bibliographic search had not led to unambiguous results.

Furthermore, the application of the same dyes on different blends and with different concentrations in the two considered pattern books, offered the opportunity to compare in detail the obtained data. The results showed that the changing variables did not hinder the recognizability of these dyes, since the spectral variations in position and intensity generally follow specific, predictable rules.

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