

IDENTIFICATION OF DYES APPLIED TO OTTOMAN TEXTILES

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Abstract

Representative samples of textiles taken from Ottoman costumes were chemically analyzed for dyes identification purpose. The collection dates from the 19th century and belongs to the Museum of Jordanian Heritage. The chemical analyses were carried out using HPLC, FT-IR and two samples with EDX. Indigo, Madder, Prussian blue, Scheele's green, synthetic alizarin and tannin additives were successfully identified. Relative production dates have been approximately determined. Such information is very helpful for future conservation. It also enriches our knowledge about these costumes in specific and costumes of the late Ottoman period in general.

Keywords: *Dyes, Ottoman textiles, Jordanian Heritage, HPLC, FTIR, EDX.*

Introduction

The Ottoman dyes and dyeing industry are considered the natural and continued progress in the thousands-years use of dyes. It was handed down from father to son through generations as trade secrets, and it reached us almost without significant changes, keeping the primary production stages as they have been since antiquity. The painstaking production process made the dyestuffs of great commercial importance. Some dyes or dyed textiles were even used to pay taxes, where the dyes workshops paid part of their production or the harvest to the government instead of cash.

In present days, the knowledge of the production of natural dyes and the ways of using them on textiles has almost disappeared. Yet modern scientific research of ancient dyes can help in decipher the secrets associated with ancient dyeing practices and thus to regain the lost art related to this technology. The results of such an investigation would open a historical window to the understanding of the development of culture and technology in history.

Several analysis methods are widely used for identifying the dyes used in historical and archaeological textiles and can provide information as to where, when and how the textiles were dyed [1-10]. Tens of papers have studied the extraction of dyes from textiles, followed by analysis using HPLC systems equipped with a diode array detector (DAD). They have proven to be useful for identifying single and multiple coloured components of many dyes [11-13]. FT-IR is another method for the analysis of dyes, and mainly used to avoid the extraction step when there is no sufficient amount of textiles understudied [14-16]. EDX detector has been used to detect metallic mordants used in the dyeing process [17, 18]. Although the literature about

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chemical examination of historical textiles is quite extensive, very little attention was paid to Ottoman textiles [19, 20].

The aim of this study was to identify dyes from small fragments of different colours taken from the collection of Ottoman costumes from the 19th century and held by the Museum of Jordanian Heritage. Furthermore, the information that will be obtained by such methods, will lead to a better understanding of the dyeing techniques used in the 19th century by the Ottomans. In addition, identification of some kinds of dyes and chemical components on Ottoman textiles can be helpful in their dating or establishing their biological sources. For example, Prussian blue was first discovered in 1704, but it was not used for dyeing textiles in the region until 1810 [21], while cultivated madder can be inferred from the high intensity signal of alizarin, which is the main chemical marker comparing with other chemical components [22-24].

Historical context of Ottoman dyes

In the Ottoman period, the dyestuffs trading was one of the main economic activities that the state depended on. It witnessed variable levels of dyeing production and importing. Private merchants controlled the dyestuff trade, but occasionally the government entered the market, directly as a seller, and imposed taxes on the dyers farms. In general, there was prosperity in the production of dyestuffs and textiles manufacture in the 16th and 17th century [25].

One of the most important and available dyestuff was madder root, the source of the famed "Turkey-red" colour. It was so valued by European and Ottoman consumers. Indigo was another important dye for the region consumers, many women were everyday dressing of indigo blue, but the dye was also used for the men's clothing and head veils. The plant was grown in the "Ghor", the area of the Jordan valley, but stocks were later supplemented with imports from India. Saffron was cultivated in villages. Other red colours were obtained from cochineal or kermes insects mixed with pomegranate. Oak bark or natural linen was the source of black colour [26].

Material and methods

Samples

Unfortunately, because the number of the textiles collection is limited, few samples were available for analysis. Taking into account this limitation, nine samples consisting of small portions or few fibres taken from costumes dated to the late Ottoman period "19th century" and belonging to the museum of Jordanian heritage were studied. The samples were taken from already damaged parts and selected to represent the whole group (Table 1). For identification purposes, new dyed samples corresponded to the historical review were prepared to be used as reference samples. The dyeing process was done according to [27], and mordanted with alun (potassium and aluminum disulfate), and iron (ferrous sulfate) salts.

Experimental

The identification procedure was carried out in two stages. Firstly, chemical analysis was carried out for historical and contemporary samples. The recorded data were qualitatively compared and matched. Energy Dispersive X-ray diffraction (EDX), Fourier Transform Infrared spectroscopy (FT-IR) and High Performance Liquid Chromatography (HPLC) techniques were used for elemental and chemical analysis as an integrated techniques.

Chromatographic identification was carried out through two criteria, retention time and UV-Vis spectra (Table 2), using a simple isocratic system consists 40:60 acetonitrile: water, and 0.1% trifluoroamine (TFA), Column RP 18 pure sphere star (125*4.6mm) and fixed at wavelength 275nm. The extraction process was achieved by using 200µL of dimethyl

formamide (DMF) for samples containing blue dyestuffs component and μL of formic acid/methanol 5:95 (v/v) for the rest of samples.

Table 1. The identified dyes of the examined samples

Sample no.	Sample description	Colour	Compounds identified
1	Fibres from man cloak	Black	Indigo, Tannins
2	Lining of the black cloak	Red	Synthetic alizarin
3	Fibres from a man cloak	Brown	Natural wool
4	Chest decoration fibres of the brown cloak	Brown-yellowish	Madder
5	Fragment of a woman dress	Blue	Prussian blue
6	Lining of the blue dress	Green	Chrome green
7	Fragment of a woman dress	Green	Indigo, Scheele's green. Cobalt and Chrome Yellow, saffron
8	Lining fragment of the green dress	Red	Madder
9	Lining fragment of a child cloth	Green	Indigo, yellow dye?

The FT-IR measurement was undertaken mainly to avoid the extraction process due to the small size of samples or when it failed to give any useful information. Typical samples area ranges from 2mm to 3mm in diameter. Each spectrum reflects the ratio of 100 scans. Band positions were determined from 1st derivative spectra of the samples.

Though EDX is used generally to detect metallic mordants, it was used in this case to determine other inorganic elements that might have served as dyes compounds. The samples were analyzed without washing or cleaning; they appeared to be clean, unsoiled, unstained, and none were badly faded.

Results

Dyes were successfully identified in all of the samples except of the yellow dye in sample 9 (Table 2). Indigo were detected in three of the nine samples 1, 7 and 9.

Table 2. Chromatographic results and maximum absorption for ancient examined dyes

Natural source	Major chemical compound	Peak no.	Retention time (min)	Absorption maximum (nm)
Indigo	Indigotin	1	20.08	240, 285, 609
Madder	Alizarin	2	10.77	245, 285 (sh) *, 425
Tannins	Ellagic acid	3	8.82	258, 369
Saffron	Crocin	4	5.71	519

*Sh: peak shoulder

The reason of the black shade of sample 1 is due to the presence of tannin additives (Fig. 1). Tannins are believed to play as organic mordant that increases the fastness of the light towards light and impart deeper shade. The other two samples containing indigo were mixed with yellow dyes to impart the green colour (Fig. 2). The yellow dye saffron was detected in sample 7 in small amounts, it also appeared to contain chrome (Cr), cobalt (Co), copper (Cu) and arsenic (As) elements in appreciable amounts (Fig. 1-4). The presence of Cr and Co suggests that chrome and cobalt yellow pigments might have been added, while the recognition of Cu and As indicated the use of copper-arsenic based green pigment. One of the main and earliest copper-arsenic pigments that were used to dye textiles in the 19th century is called "Scheele's Green". "Scheele's Green" was discovered in 1775, which is chemically cupric

hydrogen arsenide CuHAsO_3 . It was used in some paints, as a colour for paper, and sometimes used to dye cotton and linen.

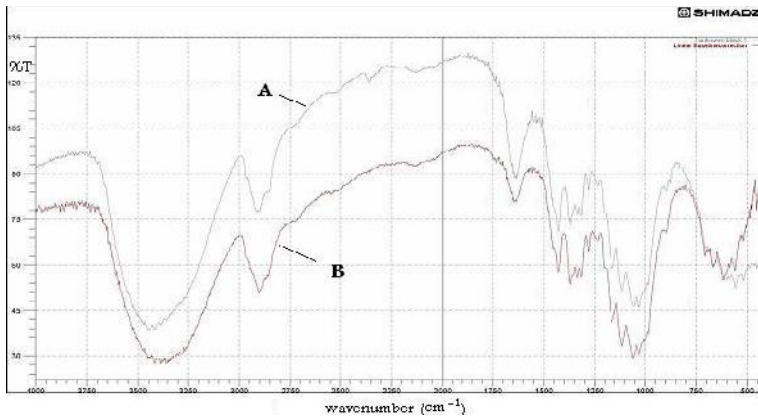


Fig. 1. IR spectra: A - sample 1a; B - new prepared indigo – tannin sample

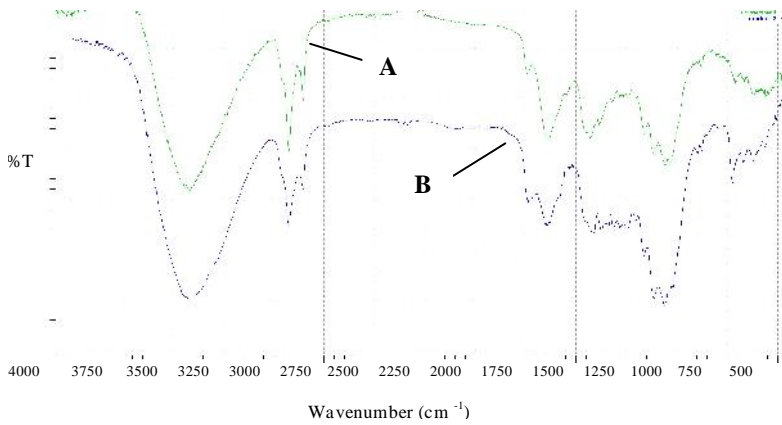


Fig. 2. IR Spectrums: A - sample 8; B - new cotton sample dyed with madder

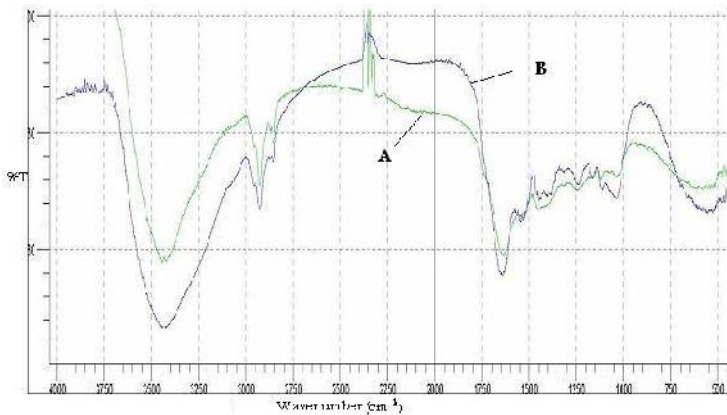


Fig. 3. IR Spectrums: A - natural brown wool; B - sample 3.

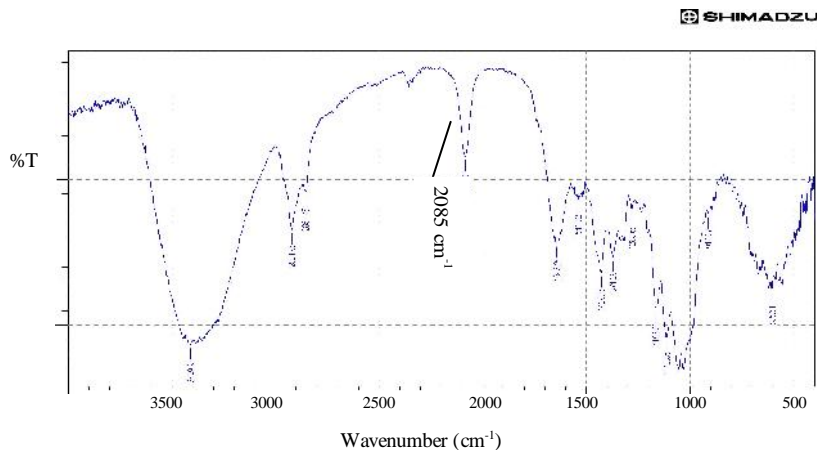


Fig. 4. IR Spectrum for sample 5

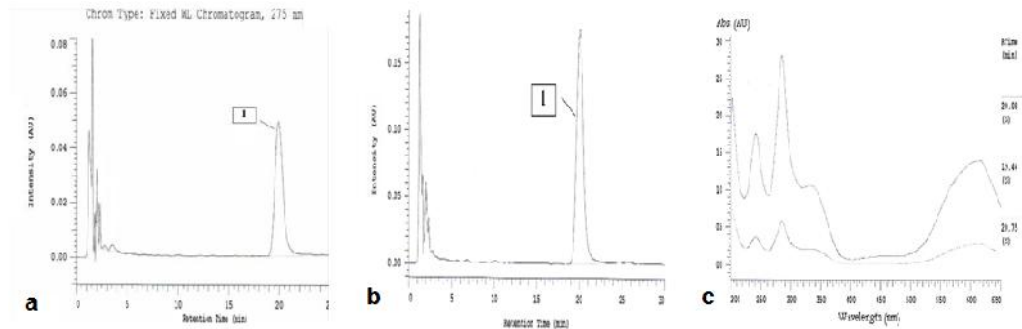


Fig. 5. Chromatograms: a - new indigo dye extract; b - sample 7; c, UV-vis spectrum of indigo

Madder was characterized in the extracts of samples 4 and 8, though they have two different colorus (Fig. 6), this is due to mordant effect where the yellowish brown hue of sample 4 can be achieved by adding ferrous salts as mordant to the red madder dye. It can be concluded from the high intensity signal of the chromatographic result of sample 8 that cultivated madder has been used (Fig. 6b).

Synthetic alizarin was detected from the extract of sample 1 (Fig. 7). For further verification wet chemical method was carried out, by warming the dyed fibres in 1% ammonium solution, the colour ran considerably. When adding few drops of concentrated sulfuric acid, the colour changed to deep violet, which is a cut evidence for the presence of a synthetic dye [28]. Synthetic alizarin (1,2-dihydroxyanthraquinone) was first made in 1868, by Carl Laiberman, from anthracene, which is a coal tar product [21].

The IR spectrum of sample 3 showed it to be made of protein fibres, in specific sheep wool (Fig. 2). This result was obtained after comparison with five different reference samples, but the overall degree was insufficient to reach conclusive identification. However, the positive identification was based on literature [29, 30], the built-in library spectra, and by comparison with natural brown sheep wool.

The analysis of sample 5 showed to contain Prussian blue. This dye has a characteristic fingerprint at about 2085cm^{-1} (Fig. 4). It contains cyanide group (a carbon-nitrogen triple bond "C N"), which unmistakably absorbs in the infrared at about 2080cm^{-1} . Lead and chrome were detected by EDX in sample 9 in proportion of 0.1 and 5.55 (wt %) respectively (Fig. 7b); this is may be to the presence of the pigment lead white (PbCrO_4). Mixing lead white with Prussian blue can yield a green colour called "Chrome green".

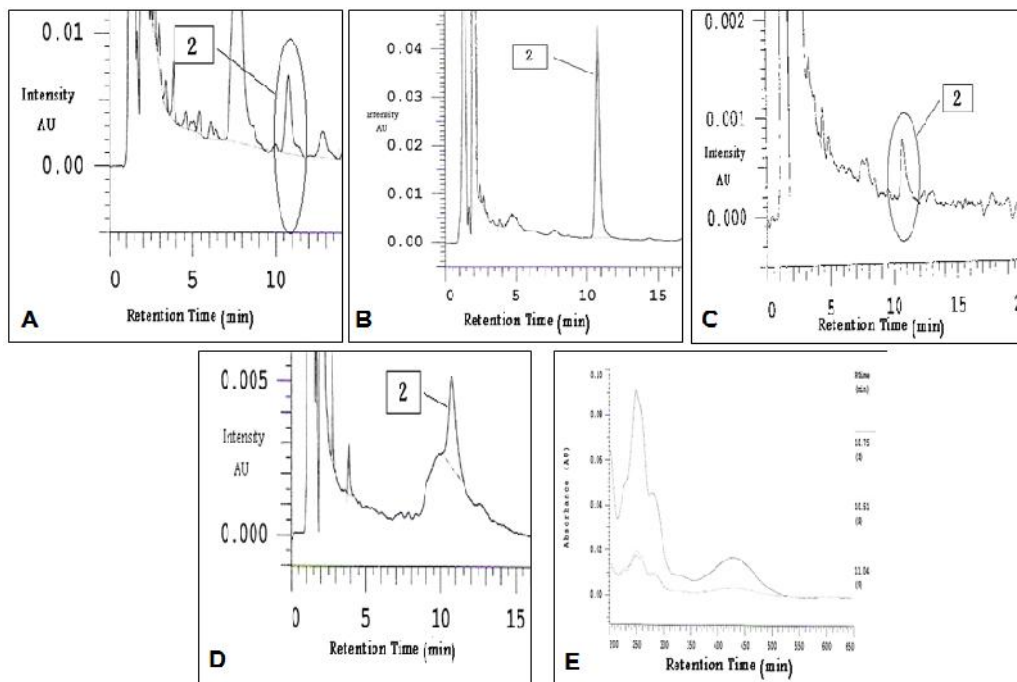


Fig. 6. Chromatograms of the samples: A - new madder extract; B - sample 8; C - sample 4; D - sample 2; E - UV-vis spectrum of alizarin

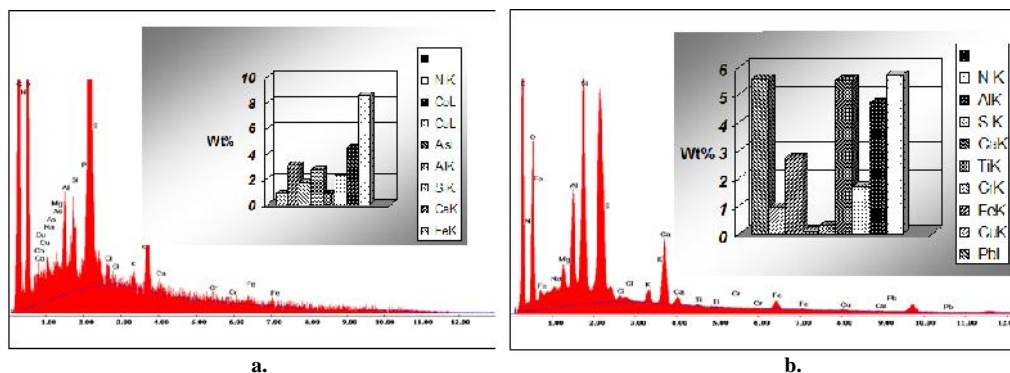


Fig. 7. EDX results: a – sample 7, b – sample 6

Discussion

Indigo, madder and synthetic alizarin dyes were common in the 19th century, while Prussian blue and green Scheele’s weren’t mentioned in the historical context of the Ottoman sources. The local production of Prussian blue, Scheele’s green and synthetic alizarin was not common; these dyes were rather imported from Europe and used locally, since it was a way to avoid increased expenses. The failure of detecting the yellow matter in sample 9 was due to low concentration in the sample or chemical alteration of the dye components as a result of weak stability towards ageing or photochemical reactions.

Some of the identified dyes have a known production or discovery time, which lead to narrow the manufacturing date, based on this alizarin was not commercially produced until 1868, Prussian blue was first to use on textiles around 1810, while Scheele's green or its similar copper based pigments started to be used in the 19th century [21].

From technical point of view, the use of multidisciplinary devices is considered an important factor for a successful investigation of historical textiles dyes that belong to a period of transformation during which the dyeing industry witnessed dramatic changes towards the use of synthetic dyes instead of natural ones. For instance, FT-IR was effective in characterizing Prussian blue, while HPLC could not. In addition, HPLC proved a very high detection signals for minor compounds. If chemical references would be available, the exact biological sources could be determined. It is worthwhile to mention that the improved extraction procedure proved a high efficiency than the routine extraction procedure.

Finally, such results obtained from dye analysis could help in the reconstruction of destroyed textiles with threads dyed by same natural dyes as the identified ones. This could assure that further ageing of the textile would be uniform, and there would be no differences between supplements and historical materials.

Conclusion

The results obtained from the analysis of the Ottoman textiles dyes suggest that it was made around the fifties of the 19th century. It can also shed important light on the dyeing techniques used during that period. Further studies of the kinds of mordants and fibres will make the picture clearer.

The varieties of dyes used like Prussian blue from Europe, indigo from India, and locally cultivated madder, points to the international trade network that the Ottoman state was part of.

The results of the green woman dress, which appears to contain arsenic-based pigment, has immediate health and safety implications, specifically with respect to the handling of the costume by the museum staff.

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