

Examination of Historical Textiles With Dyestuff Analyses by TLC and Derivative Spectrophotometry

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A group of historical textiles in the Topkapı Museum, i.e., silk brocades classified as 16th century pieces by art historians, were investigated by TLC and spectrophotometric analyses of their dyestuffs for the purpose of dating these pieces. The dyestuffs contained in textile fibers were extracted with acid solutions of varying strength, and the acid extracts were analyzed by both TLC and spectrophotometry, either directly or after an organic solvent extraction step. The first derivative spectra proved to provide more information than the main spectra. In order to eliminate possible interferences in spectrophotometry arising from impurities in the fibers, e.g., compounds containing amino- and carboxyl-groups or mordant metals, the uncoloured fibers which had been prepared for dyeing were subjected to the same type of extraction, and the aqueous or organic extracts obtained were used as a reference. Thus, first derivative spectrophotometry with the developed reference and blank emerges as a new tool for analyzing the extracts of historical textiles as an indispensable aid to dating efforts.

Introduction

The aim of this work was to date some historical textiles kept in the Topkapı Palace Museum by the way of analyzing their dyestuffs. Thus the real age of a group of silk brocades classified as 16th century pieces by art historians would be found by modern destructive instrumental techniques utilizing minute amounts of textile samples.

For the identification of the ingredients and sources of dyestuffs contained in historical textiles, basic chromatographic methods were used¹⁻¹⁴. The majority of these chromatographic techniques are associated with TLC analysis¹⁻¹⁰. Recent advances involve the use of HPLC^{6,11-14}. HPLC separation in a suitable solvent using an UV detector, followed by spectral characterization along each peak, is a recently established method for the analysis of mordant dyes¹⁵. A highly sophisticated but expensive version of HPLC is its combination with diode array detection and data manipulation in order to quantify the minor components of insect red dyes¹³. Reflectance spectroscopy of the solid samples¹⁶ or visible spectroscopy in solution are not preferred to a large extent. Because dyes absorb in the visible region of the spectrum, absorption

spectroscopy is naturally a powerful tool in dye identification¹⁷. This technique is based on the scission of the bonds between the dye and the fiber, extraction of the freed dye and its spectrophotometric determination in the extract¹⁸. Absorption spectrometry alone may, in some cases, identify the colorant, but TLC is essential to distinguish among certain closely related dyes¹⁷.

The basic reference of comparison of spectrophotometric methods up to date⁵⁻²² has been either pure commercial dyes of dyestuffs extracted from plant and insect sources¹⁸⁻²². An interesting point here recognized by the authors is the during the dyeing procedure of textile fibers, some dyestuffs of plant or insect origin are not retained by the fibers. This fact complicates analytical results and introduces uncertainty to conclusions. If this interference could be removed, both dyestuffs and their sources could be identified more precisely. The accurate removal of this reported interference necessarily involves the adaptation of identical conditions used in dyeing historical textiles (in terms of dyeing procedure and dyestuff sources) and in extracting dyes from the fibers.

It is also interesting to note that literature identification of dyestuffs has been primarily based on the main spectra of these dyes, and neither first nor higher derivative spectra have been considered. The authors believe that derivative spectroscopy enabling better resolution of normally overlapped peaks provides easier identification of dyes and dyestuff sources. These identification efforts aid the dating of historical textiles. The dyes obtained from a limited number of dyestuff sources have been used over certain historical periods, a brief outline of which is given below.

Dyeing began in 5000 B.C., but the use of natural dyes began at the early periods of the bronze age^{23,27}. For blue colour *Indigofera tinctori* L. and *Isatis tinctoria* L.^{23,26,27}, for purple *Murex trunculus* and *Murex brandaris*^{3,23,27}, for red in 1727 B.C. *Kermes ilicis* L. and later Lac insects (*Karria lacca* Kerr) were used. In the early years of A.D. *Alkanna tinctoria* Tausch and *Rubia tinctoria* L.^{1,23} and later *Porphyrophora hamalii* Brand were used⁵. For the colour yellow *Reseda luteola* L.²⁷, *Corcus sativus* L., and *Curcuma long* L. plants were used^{23,27}. After the 16th century, an insect called *Dactylopius cocus* Costa from South America and *Rubia tinctorum* L. plants were used commonly²³. In the 14th century A.D., the first synthetic dye orchil and later in 1740 indigo sulfonic acid, in 18th A.D. picric acid, in the years 1853-1865 murexide, in 1856 aniline purple, 1859 aniline red, later fuchsine, in 1909 aniline blue and later synthetic alizarin were utilized.

Experimental

Chemicals and Solutions

Ethylacetate, isoamylalchol, HCl, H₂SO₄, acetone, uranylacetate, picric acid, formic acid, methyl ethyl ketone, methanol, fuchsin and chloroform were purchased from E. Merck; luteolin, apigenin, quercetine, rhamnetin, daticetin, carminic acid, laccaic acid, kermesic acid, alizarin, pseudopurpurin, munjistin, indigo, and indigo sulfonic acid were provided by Roth. All chemicals were of analytical reagent grade.

Instruments

Schleicher & Schuell (S&S) F1700 DC-Mikropolyamidfolien plates with a conventional chromatographic tank were used for TLC analysis.

A Shimadzu-UV-2100 S UV-Vis double beam recording spectrophotometer was used for obtaining the main and derivative spectra of the dye ingredients.

Procedures

For obtaining the sample and reagent blank solutions, the historical textile samples taken from the brocades and the undyed fibers (used as reference) were separately incubated in 1:1 (v/v) diluted hydrochloric acid solutions (37% HCl +water) at 20°C for 6 hours. Thus the diffusion of the contained dyestuffs into the acid solution was practically complete. The final aqueous solutions were extracted with organic solvents (isoamylalcohol for red and ethylacetate for different coloured solutions) at an organic-to-aqueous volume ratio of 1:1. After the removal of the raffinate, the organic extracts (the upper phases in the separation funnels) were rinsed 3 times with distilled water, recovered and separated into two portions.

The first portion of the extracts, reserved for TLC analyses, were evaporated in a water bath to leave behind the dyestuffs. The residues were dissolved in pure acetone or an acetone mixture (acetone + 37%HCl) (99/1,v/v) and applied to TLC plates utilizing the mobile phases of methanol-formic acid (7/3, v/v), methyl ethyl ketone-formic acid (95/5, v/v), and chloroform-methanol-methyl ethyl ketone-formic acid (6/2/1/1,/v/v/v/v), as required.

After the evaporation of the mobile phases, the spots on the plates were developed with dilute uranylacetate solution in methanol to observe the colour changes and to record the R_f values.

The UV-visible as well as the first derivative spectra (in 5 nm intervals) of the second portion of the extracts produced from red coloured solutions were taken against the reagent blanks. The different coloured extracts (other than red) were first evaporated, and the residual dyestuffs were dissolved in concentrated H_2SO_4 and diluted ten-fold with water. The spectra of the acidic aqueous extracts were recorded against reagent blanks produced from the sulfuric acid extracts of undyed fibers under identical conditions.

Results and Discussion

For achieving reliable results, the undyed fibers used as reference should be treated in the same manner as the historical textiles so as to obtain the true spectra of the dyestuffs against the reagent blanks produced from the extraction of the former under identical conditions. (See Figures 1-12 for the 1st derivative spectra). Derivative spectrophotometry used in this work proved to be more efficient than conventional spectrophotometry, e.g., as used by Whiting (1985), for obtaining inconclusive spectra of laccaic acids and carminic acid.

Thus possible interferences arising from impurities in the fibers, e.g., compounds containing amino- and carboxyl-groups or mordant metals, should have been eliminated. Moreover, once the dyes used in the dyeing of historical textile samples are identified, pure commercial products of these dyestuffs may be utilized for treating reference textiles so as to confirm the analytical results obtained by both TLC and spectrophotometry. When using pure commercial dyestuffs as reference in TLC, it has been observed that the R_f value is slightly greater than that of the original fibers. This might stem from the blockage of diffusion of dyestuff ingredients during dye resolution and/or acid extraction by amino- and carboxyl-groups of the original fibers. If reference fibers are dyed under identical conditions, as those of the brocades and dye resolution are made in identical manner, the analytical differences are eliminated and the R_f values happen to be the same. The R_f values of the identified dyestuffs as well as their colour change with uranylacetate as the visualization agent⁹ are depicted in Table 1-3.

Table 1. Mobile phase: Methanol/formic acid (7/3, v/v).

Inventory number or dyestuff	R_f	Original colour	The observed colour change on the uranylacetate
13/1449	0.57	Red	Green
13/1626	0.30	Red	Green
	0.43	Red	Green
Laccain acid A	0.30	Red	Green
Laccain acid B	0.43	Red	Green
Carminic acid	0.57	Red	Green
Fuchsin	0.88	Pink	Pink

Table 2. Mobile phase: Methyl ethyl ketone/Formic acid (95/5, v/v).

Inventory number or dyestuff	R_f	Original colour	The observed colour change on the uranylacetate
13/1919	0.15	Red	Blue
	0.18	Yellow	Red
	0.75	Yellow	Yellow
Pseudopurpurin	0.15	Red	Blue
Munjistin	0.18	Yellow	Red
Alizarin	0.75	Yellow	Blue

Table 3. Mobile phase: Chloroform/Methanol/Methyl ethyl ketone/Formic acid, v/v/v/v).

Inventory number or dyestuff	R_f	Original colour	The observed colour change on the uranylacetate
13/1646	0.30	Yellow	Yellow
13/1677	0.51	No colour	Yellow
	0.66	No colour	Red
Picric acid	0.30	Yellow	Yellow
Quercetin	0.32	Yellow	Red
Luteolin	0.51	No colour	Yellow
Apigenin	0.66	No colour	Yellow
Indigo	0.94	Blue	Blue

One important reason for using reference fibers treated with pure commercial dyestuffs is that the dyestuff contained by the dye plant or insect can not be sorbed. totally by the fiber. Thus, when reference fibers dyed under conditions identical to those of historical samples are run together in TLC or spectrophotometric analyses, the dyestuff source utilized in historical dyeing can be identified. The spectral overlap of extracts obtained from original brocades and synthetically dyed fibers confirmed the presence of the dyestuff source in historical textiles. When proper solution of the peaks in the main spectra of the historical and reference samples was not able to be made, a better identification of the original dyestuff (and its sources) was achieved by inspection of the first derivative spectra (See Figures 1-12). For example, the finding of picric acid (synthesized after 1845) in the yellow coloured weft thread of fabric with inventory number 13/1646 (Figure 6) and of the fabric with inventory number 13/1990, and the finding of fuchsin in the red coloured weft thread of the latter sample (Figure 12), are indications that the classification of

these textiles should be corrected from 16th century pieces to 19th century ones. On the other hand, dating confirmations (of the classification provided by art historians) were made, as shown in Table 4.

Table 4. Confirmation of manufacturing date/are, dye-material ingredients and dye sources of the brocades due to the dyestuff analyses results.

Inventory Number text	Colour	Dye Ingredient	Dye Source	Estimated manufacturing date/are	Reference Fig. in
13/1677	Yellow	Luteolin Apigenin	Weld (<i>Reseda luteola</i> L.)	Second half of 16th century and alferwards	7
13/1626	Red	Laccain acids	Lac (<i>Kerria lacca</i> Kerr)	16th century	8
13/1919	Red	Pseudopurpurin Alizarin Munjistin	Madder (<i>Rubia tinctorum</i> L.)	16th century	9
13/1449	Red	Carminic acid	Cochineal (<i>Dactylopius coccus</i> Costa)	Second half of 16th century and afterwards	10

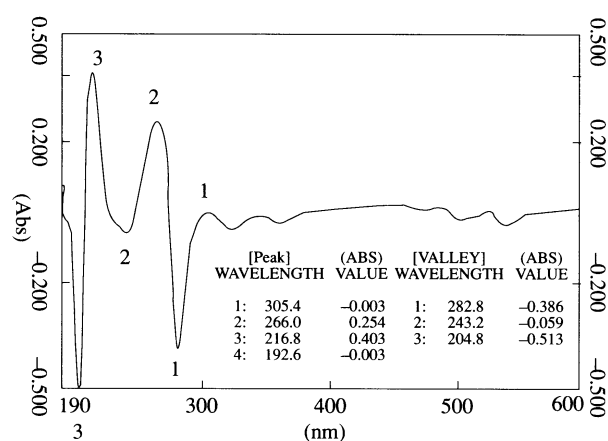


Figure 1. Cochineal (*Dactylopius coccus* Costa), 1st derivative spectrum.

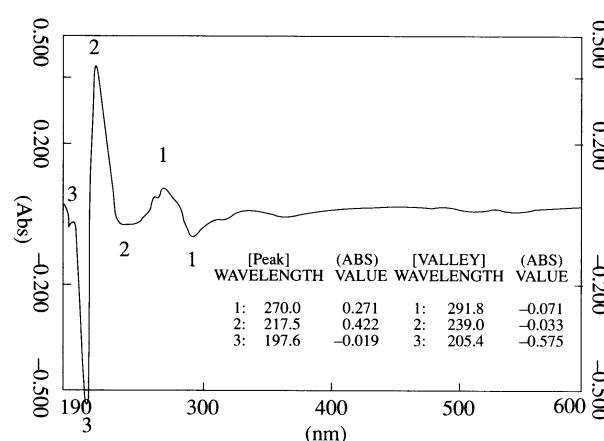


Figure 2. Lac (*Kerria lacca* Kerr), 1st derivative spectrum.

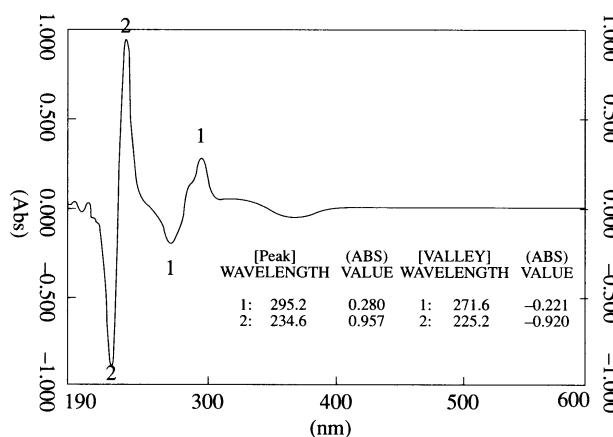


Figure 3. Weld (*Reseda luteola* L.), 1st derivative spectrum.

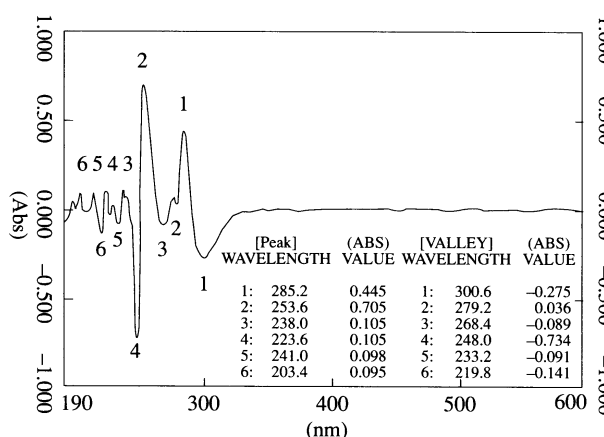


Figure 4. Madder (*Rubia tinctorum* L.), 1st derivative spectrum.

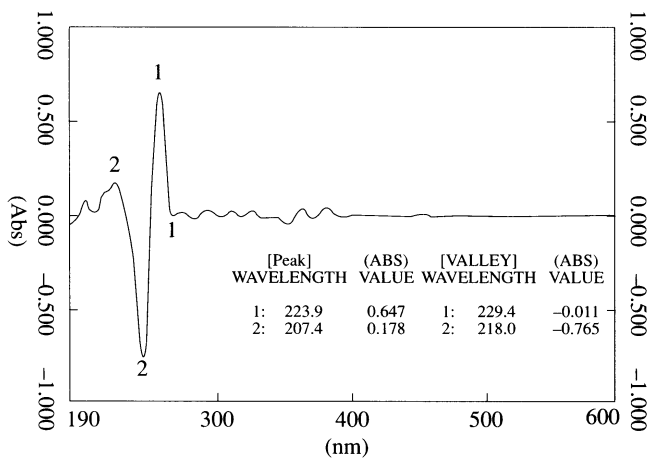


Figure 5. Picric acid, 1st derivative spectrum.

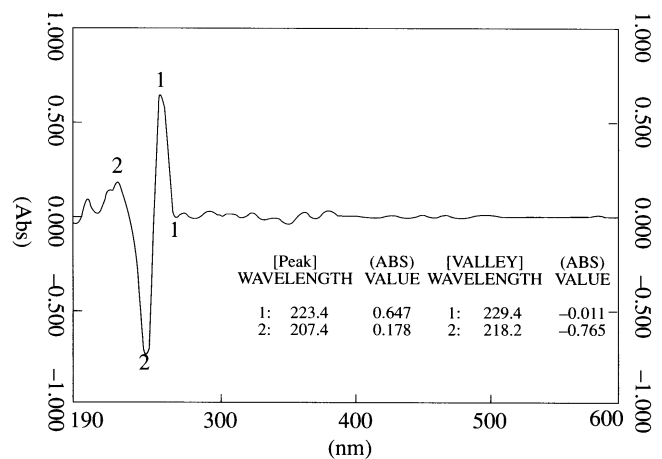


Figure 6. Inventory number 13/1646; yellow weft, 1st derivative spectrum.

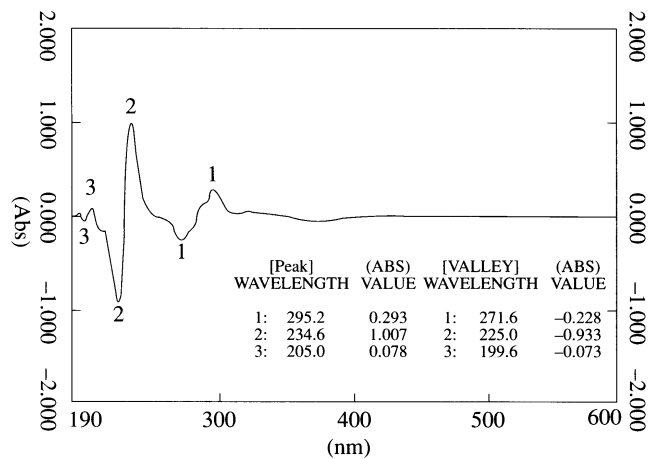


Figure 7. Inventory number 13/1677; yellow weft, 1st derivative spectrum.

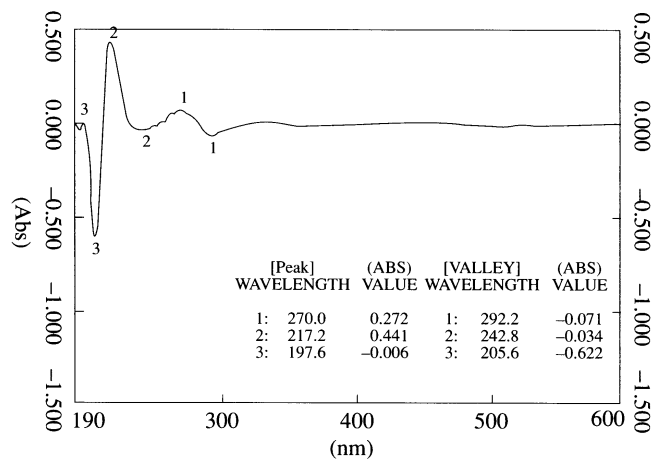


Figure 8. Inventory number 13/1626; red weft, 1st derivative spectrum.

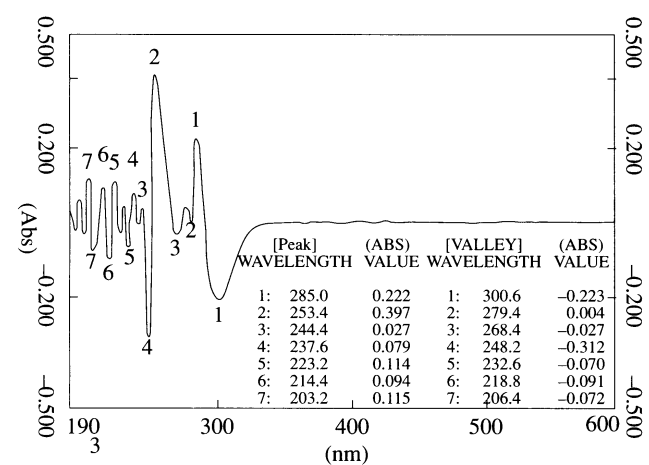


Figure 9. Inventory number 13/1919; red weft, 1st derivative spectrum.

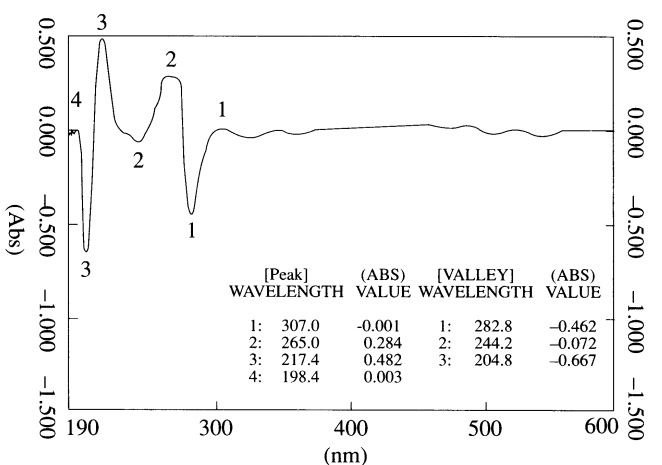


Figure 10. Inventory number 13/1449; red warp, 1st derivative spectrum.

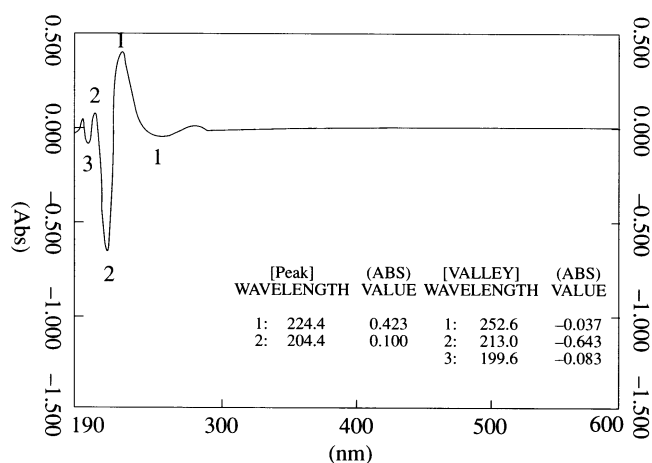


Figure 11. Fuchsine, 1st derivative spectrum.

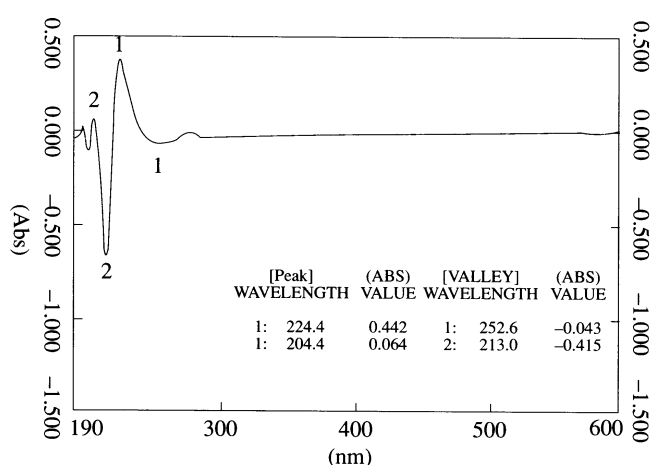


Figure 12. Inventory number 13/1990; red weft, 1st derivative spectrum.

Conclusion

The development of the combination of instrumental analytical techniques applied to dye extracts of historical textiles in the Topkapı Palace Museum as derivative important contribution to the dating of these historical pieces. The removal of spectral interferences by changing the reference and blank is a novel technique.

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