Investigation of Metal Wired Coloured Historical Textile Using Scanning Electron Microscopy and HPLC-DAD

Turkan Yurdun\textsuperscript{1*}, Seher Karsli-Ceppioglu\textsuperscript{1} and R. Gurcan Oraltay\textsuperscript{2}

\textsuperscript{1} Faculty of Pharmacy, Department of Pharmaceutical Toxicology, Marmara University, Haydarpasa-Istanbul 34668, Turkey
\textsuperscript{2} Marmara University, Engineering Faculty, Environmental Engineering Dept. Goztepe-Istanbul 34722, Turkey

Received: June 13, 2012 / Accepted: July 05, 2012 / Published: July 25, 2012.

Abstract: SEM-EDS (scanning electron microscopy-energy dispersive spectrometry) and HPLC (high performance liquid chromatography) with DAD (diode array detection) were used to examine metal-wrapped coloured textiles. The sample was provided from Azerbaijan History Museum. Material included silk and thin wire. SEM micrographs showed that the metal strip had 250 µm width and 6 µm thickness. SEM-EDS results indicated elemental composition of the wrapping: the presence of gold, silver as the components of the gilt metals. Furthermore, sulphur and chlorine were determined as contaminants. EDS analysis also revealed that both sides were gildered. Colouring compounds in the same sample were identified by HPLC-DAD. The major colouring compound found in the red fibre sample in large quantity was carminic acid and fuchsin components. The presence of fuchsin, which is a synthetic dye, dates the sample between the end of 19th and beginning of 20th century. Fisetin, which is a natural dye, was detected in the yellow fibre.

Key words: Textile; dye; HPLC; SEM.

1. Introduction

Identification of the natural dyestuff and metal threads on historical textile fragments is important information source for the restoration and preservation of the cultural heritage artifacts. Inappropriate methods for preservation and cleaning would cause irreversible damage to the historical objects.

The knowledge of the composition of the natural dye mixtures gives hints on appropriate procedures for restoration strategies. Identification of the dyes used, the establishment of their biological source, how they have been prepared, how these historical textiles were made, can provide important information. The dyestuffs used up to 19th century were either of plant (weld, madder, indigo, etc.) or animal origin (insects, molluscs, etc.) and belonged to various chemical types, such as anthraquinones (red), flavonoids (yellow), indigoids (blue and violet) and tannins (yellow, black, brown etc). Red dyes identified were dyer’s madder (\textit{Rubia tinctorum} L) with alizarin and purpurin as mainly colourants, cochineal, an insect (\textit{Dactylopius coccus} Costa, \textit{Porphyrophora polonica} L., \textit{Porphyrophora hameli} Brandt) with carminic acid, kermes (\textit{Kermes vermilio} Planchon) with kermesic acid and flavokermesic acid and lac dye (\textit{Kerria lacca} Kerr) with lacaic acid. Weld (\textit{Reseda luteola} L.) appears to be the most commonly used yellow dye with luteolin and apigenin. The blue dyes woad (\textit{Isatis tinctoria} L. and \textit{Indigofera tinctoria} L.) was identified which is the principal colourant of indigoid dyes [1].

The problems of identification of colouring materials in the historical textiles are directly linked to their chemical stability, fading, degradation, extensive use, microbiological attack, radiation, moisture and other properties. Many analytical methods are available for the identification of natural dyestuffs. Dyestuffs have been analyzed, initially by TLC (thin...
layer chromatography) [2-4] and more recently by HPLC (high performance liquid chromatography) with DAD (diode array detection) and MS (mass spectrometric detection) [5-14]. HPLC-DAD and HPLC-MS method was utilized for the identification of organic colouring ingredients in historic yarns, textiles fibres [15-20], historic maps [21], paintings [22] and icons [23, 24].

The HPLC techniques provide qualitative and quantitative analyses of compounds of natural dyes. Before HPLC analysis the sample should be hydrolysis from the material of textile fibres. Acid hydrolysis has been suggested for mordant dyes. The acidic hydrolysis procedures are composed of HCl/methanol/water (widely used extraction method) [2, 7, 14], HCl/ethanol [10], formic acid/methanol [25], DMSO (dimethyl sulfoxide)/HCl [16], oxalic acid [20, 26], or citric acid [26], TFA (trifluoroacetic acid) [15, 26], EDTA-acetonitrile-methanol [25], formic acid-EDTA [26], for extraction from textile samples. After hydrolysis, many natural dyestuffs are soluble in mixture of water-organic solvent (e.g., methanol, acetonitrile), but indigotin is insoluble in methanol-water solvents therefore, soluble with N,N-dimethylformamide (only for blue and green samples) [20, 27] or DMSO [28]. In addition to indigotin and other dyes are extracted from historical samples by basic hydrolysis with pyridine [10].

SEM-EDS analysis has also been widely applied at determination of the content of the metals, although its drawbacks of being an average measurement [34], a large amount of data have been accumulated over decades [30, 33-36]. The penetration of the electron beam through most of the time very thin gilt layer may also be used as an indicator of the underlying metal. Furthermore, it may lead to determination of the thickness of the gilt layer after careful calibration procedures [31, 37]. Investigation of the cross sectional area of the metal threads has been proved to give further information on the thickness, type and manufacturing methods [38, 39].

In the work presented, SEM-EDS was utilized to investigate metal threads and HPLC-DAD (high performance liquid chromatography with a diode-array-detector) was performed to describe some dyestuff colored textile proved from Azerbaijan History Museum textile collection.

2. Experimental Section

2.1. Chemicals

All reagents were analytical grade, unless stated otherwise. High purity water was obtained with a Milli-Q water purification system (Millipore, Bedford, MA, USA) and the HPLC mobile phase was prepared using Milli-Q water.

Dried insects (36040 cochineal Coccus cacti, C.I. Natural Red 4 Kremer Pigmente GmbH) were finely ground in a glass mortar and then extracted with HCl extraction method as described below. Fisetin 7383 employed as reference standard material was obtained from Roth, trifluoroacetic acid was from Riedel-de-Haën. All solvents used were HPLC grade.

2.2. Historical Sample

Textile sample was obtained from Azerbaijan History Museum (inventory number EF 1974; dimension: 30.5 × 25 cm) (Fig. 1.). The metal embroidered textile object that is dated between the end of 19th and at the beginning of 20th century was
investigated. This study presents approaches that can be used in analysis of historical textile decorated with thread and silk fibre.

2.3. HCl Extraction Method

Dyestuff extraction was performed according to previously described methods [2, 3, 14]. Historical textile microsamples (0.5-2.0 mg) were hydrolyzed in 400 µL of H₂O-MeOH-37% HCl (1:1:2; v/v/v;) in conical glass tubes for precisely at 100 °C, for 10 min in a water bath to extract the organic dyes. After rapid cooling under running cold water, the solution was evaporated just to dryness in a water bath at 50-65 °C under a gentle stream of nitrogen flow. The dry residues were dissolved in 200 µL of a mixture of MeOH:H₂O (2:1; v/v) and was centrifuged to separate the particulate matter (2500 rpm for 10 min.). Then 25 µL and/or 50 µL of the supernatant were injected into the HPLC instrument.

2.4. Chromatographic Analysis with Diode-array Detection

Chromatographic experiments were performed using an Agilent 1100 series system (Agilent Technologies, Germany), which included a G1311A quaternary pump, a Rheodyne 7725i injector with 50 µL sample loop, a G1315A Diode-Array Detector, a G1322A vacuum degasser and a G1316A thermostatted column compartment. The data station was an Agilent Chemstation. The chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm. The wavelengths selected for routine monitoring and dyestuff identification were performed at 255, 268, 276, and 491 nm. Separations were carried out on a reversed-phase Nova-Pak C 18 analytical column (4 µm particle size, 150 mm × 3.9 mm, Part No. WAT 086344, Waters, Ireland), protected by a guard column filled with the same material. Analytical and guard columns were maintained at a stable temperature of 30 °C.

For HPLC-DAD studies, gradient elution was performed using two solvent consisting of A: 0.1% (v/v) TFA in H₂O and B: 0.1% (v/v) TFA in CH₃CN and the applied elution program is described in Table 1 [14, 40]. The flow rate was 0.5 mL/min.

2.5. SEM-EDS Instrumentation

SEM (scanning electron microscope) Model JEOL 5910 LV coupled with EDS (energy dispersive spectrometry) was applied to examine the surface of

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>H₂O-0.1% TFA (v/v)</th>
<th>CH₃CN-0.1% TFA (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>1.0</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>20.0</td>
<td>70.0</td>
<td>30.0</td>
</tr>
<tr>
<td>25.0</td>
<td>40.0</td>
<td>60.0</td>
</tr>
<tr>
<td>28.0</td>
<td>40.0</td>
<td>60.0</td>
</tr>
<tr>
<td>33.0</td>
<td>5.0</td>
<td>95.0</td>
</tr>
<tr>
<td>35.0</td>
<td>5.0</td>
<td>95.0</td>
</tr>
<tr>
<td>45.0</td>
<td>95.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>
metal thread with accelerating voltage 20 KV, magnification up to 10,000×. The sample was investigated directly without any coating layer.

3. Results and Discussion

In the present study, HPLC-DAD was used to identify individual chemical components of dyes in extracts from fibres of different colours taken from Azerbaijan History Museum textile collection. Elemental analysis using SEM-EDS technique was performed to identify metal on threads from textile sample.

The typical metal thread consisting of metal strip wound around the textile yarn is shown in Fig. 2. SEM micrographs showed that metal strip had approximately 250 µm width and 6 µm thickness, as shown in Fig. 3. SEM-EDS results indicated elemental composition of the wrapping: the presence of gold and silver as the components of the gilt metals. EDS analysis also revealed that both sides were gilt in Fig. 4. Furthermore, sulphur and chlorine determined as contaminants, as seen in Fig. 5.

In the same sample were identified colouring compounds by HPLC-DAD. The major colouring compound found in the red fibre sample in large quantity was carminic acid and fuchsin components (Fig. 6). The most common pigment obtained from cochineal is carminic acid. Spectral properties of the solution obtained from red sample were coincided with data obtained for extract of Dactylopius coccus Costa (American cochineal). Carminic acid is one of the additives approved by legislation as a natural colourant for the pharmaceutical industry as a basis for drug products and by the food industry [41].

Presence of fuchsin components, which is semi-synthetic dye, dates the sample between the end of 19th and at the beginning of 20th century. Fuchsin (early synthetic dyes) reference compound is a mixture of four fuchsin homologues (Fig. 6). In the yellow fibre, fisetin (Cotinus coggyria Scop., Anacardiaceae) was detected, which is a natural dye (Fig. 6). Identification of dyestuffs is based on comparison of the dye absorption...
Investigation of Metal Wired Coloured Historical Textile Using Scanning Electron Microscopy and HPLC-DAD

Fig. 4 The typical SEM-EDS spectra of the gilt surface (point 2) and sides (point 1).

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Cl</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>4.32</td>
<td>0.91</td>
<td>85.68</td>
<td>9.09</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

Point 2

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
<th>Ag</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>5.23</td>
<td>2.96</td>
<td>0.86</td>
<td>1.32</td>
<td>89.64</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Fig. 5 SEM microphotograph of the surface contamination.

4. Conclusions

Characterization of dyestuff and metal items on historical textile samples is important part in preservation and conservation of historical and cultural heritage. This work showed that HPLC-DAD and SEM-EDS may be easily applied in this purpose.

Silk microsamples provided from Azerbaijan History
Investigation of Metal Wired Coloured Historical Textile Using Scanning Electron Microscopy and HPLC-DAD

Museum (inventory number EF 1974; dimension: 30.5 × 25 cm) were treated with HCl (acidified methanol), a method which is extensively used to extract dyes from historical textile fibres and then investigated using HPLC-DAD for dyestuff identification. The organic colorants were identified: carminic acid, fuchsin and fisetin (\textit{Cotinus coggygria} Scop.).

Metal threads were investigated using SEM-EDX. The composition of the outer and inner surfaces of the metal threads, gold and silver were found. Furthermore, sulphur and chlorine determined as contaminants.

Acknowledgments

The authors would like to thank Mrs. Gulzade Abdulova from Azerbaijan History Museum for supplying the sample and Eng. Mustafa Ilhan for SEM analysis.

References


Investigation of Metal Wired Coloured Historical Textile Using Scanning Electron Microscopy and HPLC-DAD


[28] Clementi, C.; Nowik, W.; Romani, A.; Cibin, F.;


