INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 7, Special Issue 1, 2016: 357-366 www.ijcs.uaic.ro

ADVANTAGES AND IMPORTANCE OF NATURAL DYES IN THE RESTORATION OF TEXTILE CULTURAL HERITAGE

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Abstract

*Identification of an art object material of cultural heritage had received significant attention, because of its importance for the development of appropriate restoration and conservation strategies. In this paper, optical microscopy, CIE L*a*b* spectrophotometer/colorimeter, scanning electron microscopy (SEM) coupled to energy dispersive X-ray (EDX) spectroscopy and high performance liquid chromatography coupled to diode-array-detection (HPLC-DAD) are used to investigate many historical textiles samples in some museums.*

Keywords: *Natural dyes; Restoration; Cultural heritage; HPLC-DAD; SEM-EDX; Colour measurements*

Introduction

Historical textiles in museums are primary evidence for the production, trade and use of clothing, furnishings, decoration, etc. across all social levels. Aspects of a nation's past economic, social and cultural history can be revealed through the dyes used for the textiles. Natural dyes have advantages since their production requires renewable resources causing minimum environmental pollution and has a low risk factor in relation to human health.

Analyses are very important for restoration and conservation of historical textiles. Samples are analyzed with non-destructive and microanalysis methods. The most widely used methods are HPLC-PDA (high performance liquid chromatography with diode array detection), SEM-EDX (scanning electron microscopy with energy dispersive X-ray), colour measurements and technical analysis [1].

The identification of dyes is one of the most important targets aimed for in the scientific examination of paintings, textiles, illuminated manuscripts and other historic and archaeological materials. Thus, several analytical techniques have been used, for example thin layer chromatography, high performance liquid chromatography [2-13] gas chromatography/mass spectrometry, UV-visible spectrometry [14] reversed phase liquid chromatography and capillary electrophoresis with electrospray mass spectrometric detection, FTIR spectroscopy and Raman spectroscopy [15]. Of these techniques, high performance liquid chromatography (HPLC) using a diode-array detection (DAD) is ideally suited to the identification of dyes sampled from museum collections especially [16-17]. The CIE L*a*b* system (1976) was introduced to describe colour as a result of these three factors [18- 21].

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Obtained dataset at the end of the analyses are used in the restoration and conservation. Natural dye sources were used in the historical textiles until end of the 19th century. In this case, used fabrics or yarns can be restored with the same dye stuffs used originally. The most important reason is so the materials used for the restoration and the dye in the historical textile will change at the same rate.

The development of multi-analytical strategies, which include the use of complementary techniques, to identify dyes, metal treads, colour and structure in historical findings ~~is~~ are important for many reasons. Thorough strategies can be implemented to study different types of objects where colourants were applied in different ways paints, textiles etc. Multi-analytical strategies can provide a better understanding on the identity and moreover the ancient application process of a dye or pigment.

Non-destructive techniques (NDT) have an inherent advantage which is the preservation of samples removed from an archaeological or historical object. Furthermore, NDT techniques can, in principle, be used to characterize both inorganic and organic colourants and other materials, thus providing a thorough understanding of ancient and historical painting and dyeing recipes. However, if an organic colourant is present in the historical sample, then the application of separation, chromatographic methods is usually necessary to achieve a detailed characterization. Chromatography can easily provide quantitative results for the compounds detected in an archaeological or historical sample. This can be extremely important to identify the exact biological source of an organic colourant, as it was shown, for instance, for cochineal, madder, dragon’s blood and Tyrian purple species weld, gall oak, etc. [22].

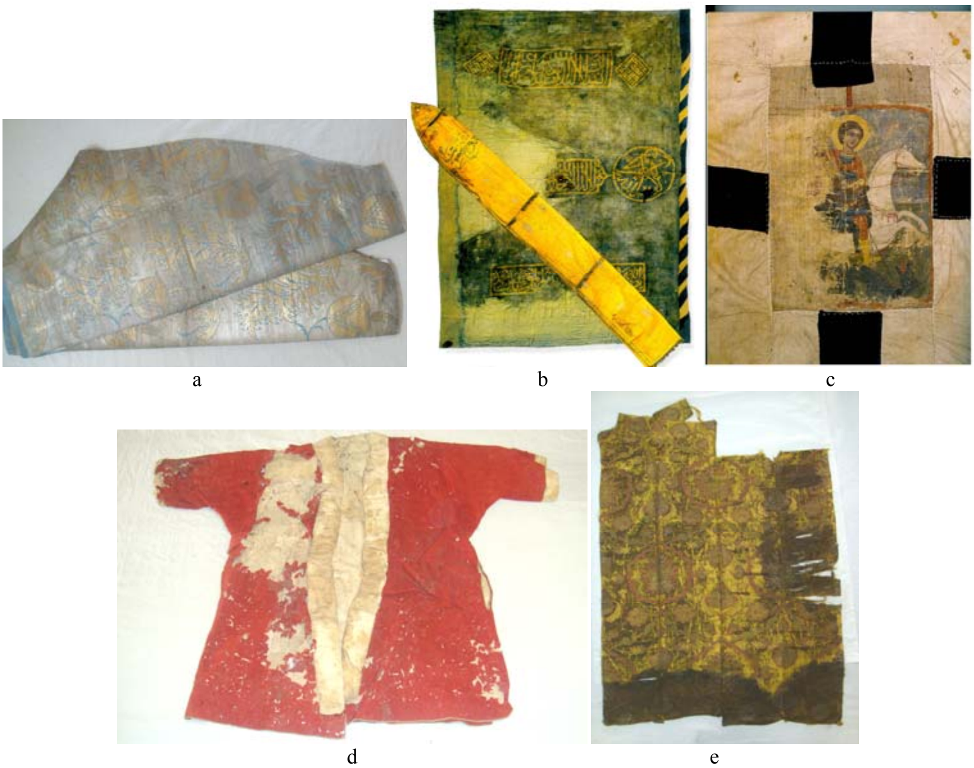

Fig. 1. Images of the historical textiles: a - Sultan shalwar (Inv. No. 13/1898) Topkapi Palace Museum; b - Kosova Banner (Inv. No: 351-362) Military Museum; c - Byzantine Flag (Inv. No: 353-97) Military Museum;; d - Prince caftan (Inv. No. 13/874) Tokapi Palace Museum; E- Silk brocade fabric (Inv. No. 13/1748) Topkapi Palace Museum.

The study presented here in aims at characterising the materials contained in many samples removed from different museums in Turkey (Fig. 1). The Choosen textile samples were 14-15th century flag and banner in Harbiye Military Museum and 16-17th century Ottoman silk brocades in Topkapi Palace Museum (Fig. 1). The objects have been damaged and they need to restoration and conservation. For this reason, samples from chosen historical textiles were analyzed and in accordance with analyses results, restoration and conservation methods are decided.

Experimental

HPLC Analysis

Extraction Procedure for HPLC Analysis of Historical Textiles

Historical textiles were chosen for dyestuff analyses from Topkapi Palace Museum collection (Table 1).

Table 1. Identified colouring compounds by HPCL-DAD and dye source of the selected textiles

Inv. No.	Museum	Sample colour	Detected components	Identified dye sources
13/124	Topkapi Palace	purple	Kermesic acid and indigotin	*Kermes vermilio* Planchon + *Indigofera tinctoria* L. or *Isatis tinctoria* L.
13/156	Topkapi Palace	red	Carminic acid	*Dactylopius coccus* Costa
		purple	Laccain acid and indigotin	*Kerria lacca* Kerr + *Indigofera tinctoria* L. or *Isatis tinctoria* L.
13/1005	Topkapi Palace	yellow	Luteolin, apigenin, indigotin and indirubin	*Reseda luteola* L. + *Indigofera tinctoria* L. or *Isatis tinctoria* L.
		red	Carminic acid, ellagic acid and flavokermesic acid	*Dactylopius coccus* Costa + *Quercus infectoria* Olivier or *Quercus ithaburensis* Decaisne
		blue	indigotin	*Indigofera tinctoria* L. or *Isatis tinctoria* L.
13/1455	Topkapi Palace	blue	ellagic acid and indigotin	*Quercus infectoria* Olivier or *Quercus ithaburensis* Decaisne
		red	Carminic acid, flavokermesic acid and ellagic acid	*Dactylopius coccus* Costa + *Quercus infectoria* Olivier or *Quercus ithaburensis* Decaisne
13/1900	Topkapi Palace	red yellow	Fuchsine Picric acid	Synthetic dyes Synthetic dyes
13/874	Topkapi Palace	red	Alizarin, purpurin and xhantopurpurin	*Rubia tinctorum* L.
351-362	Military Museum	yellow	Luteolin and apigenin	*Reseda luteola* L.
353-97	Military Museum	Blue	Indigotin and indirunin	*Indigofera tinctoria* L. *or Isatis tinctoria* L.

The extraction of historical textile samples (flag, banner and silk brocades) (Fig. 2-3) were performed with a solution mixture of 37% HCl:$MeOH$:H_2O; 2:1:1; v:v:v) for 8 minutes at 100ºC in open small tubes to extract dyestuffs. After cooling under running cold tap water, the solution was evaporated just to dryness in a water bath at 65ºC under a gently stream of nitrogen. The dry residue was dissolved in 200µL of the mixture of $MeOH$:H_2O (2:1; v:v) or

200µL DMF and was centrifuged at 4000 rpm for 10 min. 50 to 100µL supernatant was injected into the HPLC apparatus.

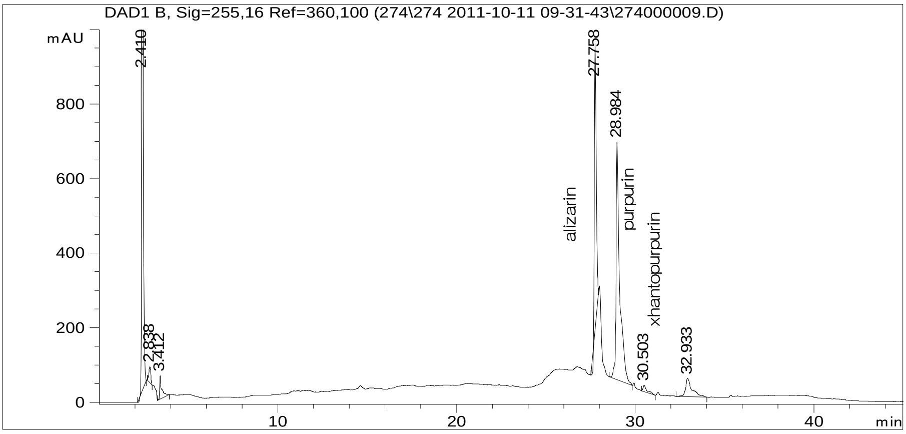

Fig. 2. HPLC chromatogram of historical art object (Inventory number 13/874, red sample from Topkapi Palace Museum)

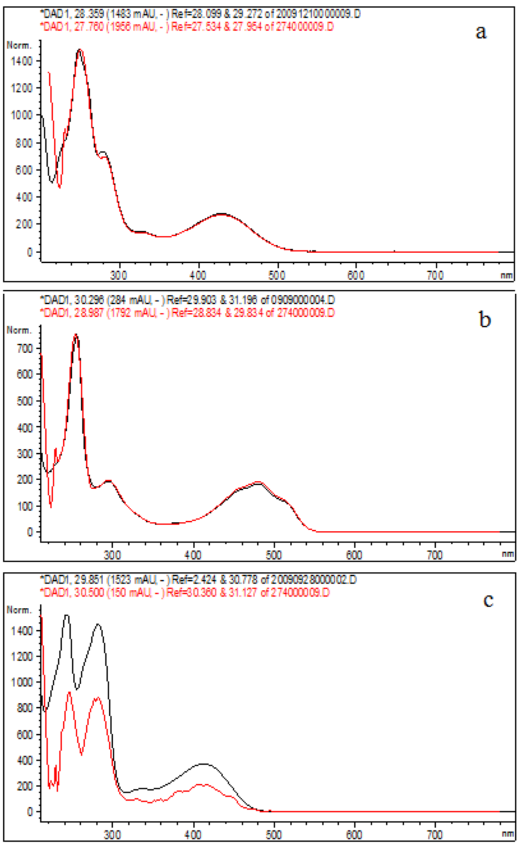

Fig. 3. Spectrum of red sample (Inventory number 13/874; from Topkapi Palace Museum). (a) spectra of sample together with alizarin standard; (b) spectra of sample together with purpurin standard; (c) spectra of sample together with xhantopurpurin standard

HPLC Instrumentation

Chromatographic measurements were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including G1322A Degasser, G1311A Quat pump, G1329A autosample, G13166 TCC, and G1315D Diode Array Detector. PDA detection is performed by scanning from 191 to 799nm with a resolution of 2nm, and the chromatographic peaks were monitored at 255, 268, 276, 350, 491, 520, 580 and 620nm. Column: A Nova Pak C18 analytical column (39×150mm, 4µm, Part No WAT 086344, Waters) was used. Analytical and guard columns were maintained at 30°C and data station was the Agilent Chemstation. Two solvents were utilized for chromatographic separations of the hydrolyzed samples. Solvent A: H_2O - 0.1% TFA and solvent B: CH_3CN - 0.1% TFA. The flow rate was 0.5mL/min. and following elution program was applied in Table 2.

Table 2. HPLC analysis is performed using the following gradient elution

Time (min.)	Flow rate (ml/min)	H_2O-0,1% TFA (v/v)	CH_3CN-0,1% TFA (v/v)
0.0	0.5	95	5
1.0	0.5	95	5
20	0.5	70	30
25	0.5	40	60
28	0.5	40	60
33	0.5	5	95
35	0.5	5	95
40	0.5	95	5
45	0.5	95	5

Colour Measurements of Historical Textiles

L*, a* and b* values for historical textiles and reproduced silk brocades were measured with Konica Minolta CM-2300d Software Spectra Magic NX (6500 K, 45°). CIELAB graph belong to an art object and of chosen art object L*, a* and b* values were shown (Fig. 4). The colour values and colour values of restoration material must be same values or very close values. The colour values are very important for selection of restoration materials [23-29].

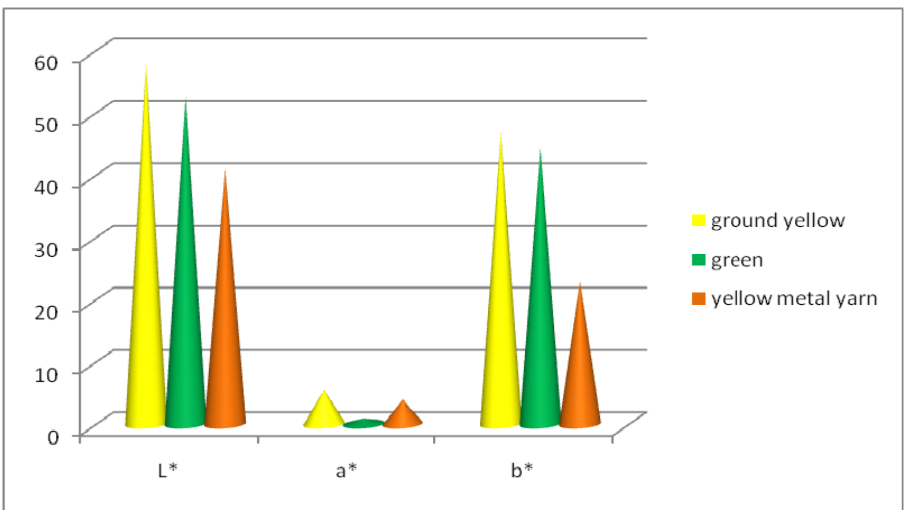

Fig. 4. CIEL*a*b* graph of historical art object
(Inventory number 13/1748, from Topkapı Palace Museum collection)

Table 3. Colorimetric values of chosen historical textiles

Inventory number	Part of historical object	L*	a*	b*
13/8	Yellow (inside different part)	61.91	11.07	68.43
	Orange (lining)	57.45	26.96	25.52
13/20	blue	65.61	-4.76	8.08
13/470	green	58.87	-9.99	25.71
13/817	yellow	65.01	13.92	57.03

SEM-EDX Analysis

Characterization of metal threads on historical textiles is important for preservation of valuable cultural heritage. In this work the samples were investigated using a TESCAN VEGA3 EasyProbe Scanning Electron Microscope (SEM) equipped with energy dispersion spectroscopy (EDX with detector Bruker 410-M, software: Esprit 1.9). In this work some metal fibres collected from historical textile materials were characterized. SEM image and EDX result were shown in Fig. 5 and Table 4 and 5.

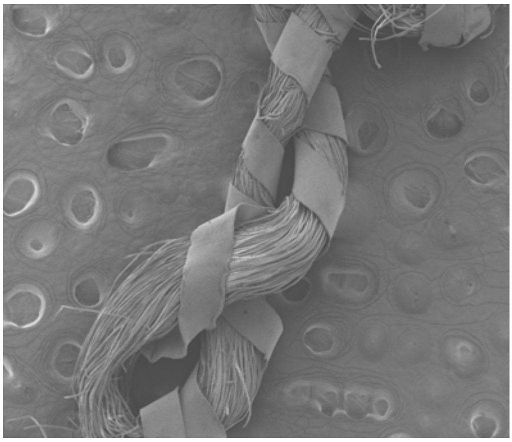

Fig. 5. SEM- EDX image of historical textile.
(Inventory number 13/1898, from the Topkapi Palace Museum collection)

Table 4. Elemental analyses results (Inv. No. 13/1898, from the Topkapi Palace Museum)

Identified Element Name	Wt%	At%
Carbon (K series)	06.07	34.96
Oxygen (K series)	02.86	12.36
Sulphure (K series)	00.38	00.83
Cloride (K series)	00.27	00.53
Silver (L series)	67.44	43.26
Gold (L series)	22.97	08.07

Table 5. SEM-EDX results of the surface elements expressed in mass percentages (wt %)

Inventory number	Identified elements and their Wt%.						
	C	O	S	Cl	Ag	Au	Cu
13/8	7.57	4.15	-	0.72	38.43	43.77	5.36
13/1060	4.37	2.13	5.11	0.39	85.52	-	2.47
13/1909	9.67	2.45	3.71	12.15	71.61	-	0.42
13/2253	11.57	3.14	-	-	3.60	-	81.69

Technical Analysis

Optical microscope is used for yarn or fibre characterization of historical textiles. In this study the historical samples were investigated using a OLYMPUS SZ61 (SZ2-ILST, camera C18U). Optical microscope images in Fig. 6 and technical analyses results of the chosen historical textiles were shown in Table 6.

Fig. 6. Optical microscope images of the Inventory number 13/1524 historical textile, from the Topkapi Palace Museum collection)

Table 6. Technical analyses results of the chosen historical textiles

Inventory number	Spun direction		Number of yarn/per cm	
	weft	warp	weft	warp
13/968	Z	S	23	96
13/268	Z	S	24	96
13/1421	Z	Z	18	96
13/1894	Z	S	26	96

Mordanting and Dyeing for Restoration Materials

Mordanting

Three important methods were used for mordanting. Textile materials (silk, wool, cotton and linen yarns or fabrics) in the first method were dyed after mordanting process for red and yellow colours. The other one, vat dyeing with natural indigo for blue colour and textile materials in the last method were dyed with natural indigo before mordanting then it was mordanted with alum and it was dyed with yellow dyes for green colour. The most commonly used mordants such as alum (potassium aluminium sulphate), iron (ferrous II sulphate) and tin (stannous II chloride) were chosen. Textiles materials were submerged in hot water (about 60ºC) for 60 min. to relax the textile materials. The mordanting process was carried out according to the historical mordanting recipes.

Dyeing

The dyeing procedures were performed in accordance with the historical dyeing method. A ratio of dyestuff to yarns or fabrics from 1:10 to 1:100 was chosen based on the weight of fresh natural dyes extracted to the silk fabrics used in the experiment ~~except~~. The yarns and fabrics were immersed in a dye bath composed of 100% aqueous solution of the dye. The temperature of the dye-bath was then gradually raised to about 60-65ºC and was kept at this temperature for about 10-20 min. The temperature of the dye-bath was then allowed to cool about 30ºC; then the dyed yarn or fabrics were squeezed, rinsed thoroughly with water and open air-dried.

Weld, dyer's sumac, oak and gall oak plants in the yellow and green colours dyeing, madder roots and cochineal insect for red colour dyeing and indigo plant was used for blue and green colours dyeing. Especially for green colour dyeing, the yarns and fabrics were mordanted after indigo dyeing and were carried out yellow dyeing recipes.

Results and Discussions

In accordance with the analyses results, textile material which will use for restoration was dyed with same dyestuff resource in the historical textile. The dyed restoration materials have got same characteristic or very closed with historical art objects. It is important that art object and restoration materials have got same characteristic (same colour value, same dye, same metal, same yarn, etc). Restored historical art object has been effected depend on many factors such as, time, humidity, temperature, dust, environmental conditions, etc. In spite of same or very closed of the colours on the restoration material (yarn or fabric) and historical art object in the past, there have been many bad changes in the course of time. We can give examples of bad restored two banners or flag in Military Museum in Istanbul. One of them is Kosova Banner (inv. no: 351-362) (Fig. 6-A) which belongs in 14th century (June 15, 1389) and the other one is Byzantine Flag (inv. no: 353-97) (Fig. 6-B) which belongs in 15th century.

Thus flags or banners were restored twenty five years ago. Due to the flags very fragile, back side of the flags were supported with same colour fabrics in the restoration. But all the flags were badly affected with colour (dyestuff) of the supported fabrics. Both sides of flags were affected with dyestuff of supported fabrics. Because, colouring compounds of flags and supported fabrics are different dyestuffs group. Therefore, restoration works have failed in the flags. The flags were damaged. Anymore, it is impossible that the flags go back to original state. If natural dyes and same colouring compounds group had been used in the restoration materials, the flags would not have destroyed.

Conclusion

Structure of historical textiles with non-destructive or micro analysis methods can be identified. Analyses results help for restoration works. Chemical and physical properties of the dyes on the historical textiles are identified. Accurate dating of textiles can be enabled. Geographical region of the historical textiles and their production centers can be identified. Such as, an object (inv.no.13/1900) was dated as 16^{th} century, but the object was analyzed and synthetic dyes (fuchsine and picric acid) were found in the object. According to the dye analysis results, the object is not 16^{th} century. Because, fuchsine and picric acid were not exist in the 16^{th} century Proper restoration methods are detected based on the chemical and physical properties of the identified dyes in historical textiles. Same biological resources and colouring compounds can be used for restoration material. Ratio of elements in metal yarns are identified. Worthless metals (Cu, Zn, Cd, etc.) can be identified in textiles. Moreover, air pollutants (Cl, Mg, S, C, O, etc.) can be detected in metal yarns. Metal yarns were identified as alloys or gild. Thickness and wideness of metal threads can be identified. Same metal thickness and wideness can be used in re-productions.

The sustainable and diverse using of natural resources is significant in the development of environmentally beginning processes and products in the future. Utilization of renewable natural resources has significance. Identifying the weaving structure, colour value, twist and spinning of yarns, chemical compositions of metal yarns, dyestuffs and dye sources of art objects is made possible by this work for accurate and non-destructive restoration, conservation and cleaning methods of objects.

Acknowledgements

Support from the Turkish Cultural Foundation and Armaggan company are gratefully acknowledged (www.turkishculturalfoundation.org; www.tcfdatu.org; www.armaggan.com)

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Received: September, 24, 2015
Accepted: February, 25, 2016