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## Analyses of Dye, Weaving and Metal Thread in Ottoman Silk Brocades and their Reproduction

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### Introduction

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. Natural dyes have advantages since their production implies renewable resources causing minimum environmental pollution and has a low risk factor in relation to human health. Some of natural dyes are used by pharmaceutical industry as a basis for drug products and by the food industry [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 [4,14] 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 [3,16,17].

The CIEL\*a\*b\* (1976)-system was introduced to describe colour as a result of these three factors. This system is a three-dimensional space, with coordinate axes L\*, a\* and b\*. L\* denotes the brightness of the colour (L\*=0: black, L\*=100: white), a\* represents the green-red axis (a\* negative: green, a\* positive: red) and b\* represents the blue-yellow axis (b\* negative: blue, b\* positive: yellow). Each colour can be represented as a set of values for L\*, a\* and b\*, and consequently as a point in this colour space [18].

### Experimental

#### *Dye Plants, Dye Insect and Chemicals*

Weld (*Reseda luteola* L.), dyer's sumac (*Cotinus coggygria* SCOP), madder (*Rubia tinctorum* L.) and natural indigo (*Indigofera tinctoria*) were provided from Turkish Cultural Foundation Natural Dyes Research and Development Laboratory. Cochineal insect (*Dactylopius coccus* Costa) was obtained from Kremer Pigmente GmbH & Co. KG.. Hydrochloric acid, methyl alcohol and DMF (dimethylformamide) were obtained from Merck (Darmstadt, Germany, [www.merck.de](http://www.merck.de)). Alum [KAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O], sodium hydroxide (NaOH) and sodium hydrosulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) were obtained from Sigma.

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### ***Extraction Procedure for HPLC Analysis of Historical Textiles***

The extraction of historical textile samples were performed with a solution mixture of %37 HCl:MeOH:H<sub>2</sub>O 2:1:1; v:v:v) for 8 minutes at 100 °C 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 65 °C under a gently stream of nitrogen. The dry residue was dissolved in 200 µl of the mixture of MeOH:H<sub>2</sub>O (2:1; v:v) or 200 µl DMF and was centrifuged at 4000 rpm for 10 min. 50 to 100 µl supernatant was injected into the HPLC apparatus.

### ***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, G1315D Diode Array Detector. PDA detection is performed by scanning from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 235, 255, 268, 276, 350, 491, 520 and 580. Column: A Nova Pak C18 analytical column (3,9 x 150 mm, 4 µm, Part No WAT 086344, Waters). Analytical and guard columns were maintained at 30 °C and data station was a Agilent Chemstation. Two solvents were utilized for chromatographic separations of the hydrolyzed samples. Solvent A: H<sub>2</sub>O - 0.1% TFA and solvent B: CH<sub>3</sub>CN- 0.1 % TFA. The flow rate was 0.5 mL/min. and following elution program was applied (Table 1).

Time (min.)	Flow rate (ml/min)	H <sub>2</sub> O-0,1% TFA (v/v)	CH <sub>3</sub> CN-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

***Table 1. HPLC analysis is performed using the above gradient elution.***

### ***Mordanting and Dyeing for Reproduction Silk Brocades***

#### ***Mordanting***

Three methods were used for mordanting that the first method silk yarns were dyed after mordanting for red and yellow colours. The other one, vat dyeing with natural indigo for blue colour and the last method silk yarns were dyed with natural indigo before mordanting then was mordanted with alum and 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. The silk yarns were submerged in hot water (about 60 °C) for 60 min to relax the silk fibres. The mordanting process was carried out according to the historical mordanting recipes.

## ***Dyeing***

### ***Dyeing for Red and Yellow Colours***

The dyeing procedures were performed in accordance with the historical dyeing method. A ratio of dyestuff to silk yarn 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 yarn was 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 °C and was kept at this temperature for about 10-20 min. The temperature of the dye-bath was then allowed to cool about 30 °C; then the dyed silk fabric was squeezed, rinsed thoroughly with water and open air-dried.

### ***Dyeing for Green Colour***

The silk yarns were mordanted after indigo dyeing and were carried out yellow dyeing recipes.

### ***Colour measurements of Historical Textiles and Reproduced Silk Brocades***

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 graphs and L\*, a\* and b\* values were shown (Figures 8-13).

### ***FESEM-EDAX Analysis***

Characterization of metal threads on historical textile materials is important for preservation of valuable cultural heritage. In this study the samples were investigated using a ZEISS ULTRA PLUS Field Emission Scanning Electron Microscope (FESEM) equipped with energy dispersion spectroscopy (EDAX with detector Bruker AXS, software: Genesis). In this work some metal fibers collected from historical textile materials were characterized (Figures 16-17). The results were shown in Table 3.

### ***Technical Analysis***

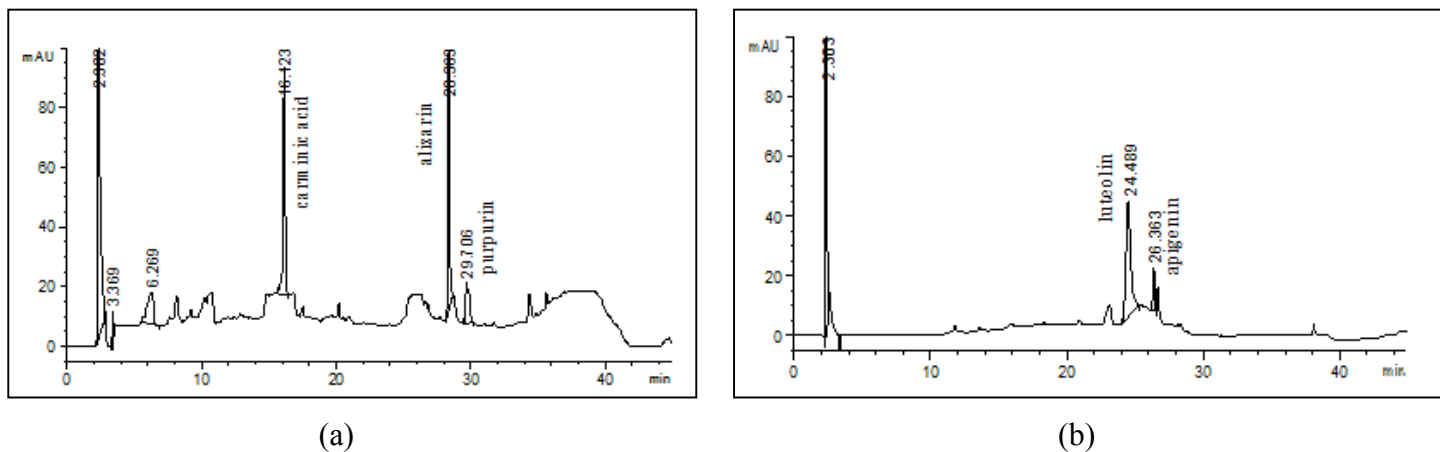
Optical microscope is used for yarn or fibre characterization of historical textiles. In this study the historical samples were investigated using a OLYMPUS SZ61 (SZ2-ILST, camera C18U). The microscope images were shown in Figures 14-15.

## **Results**

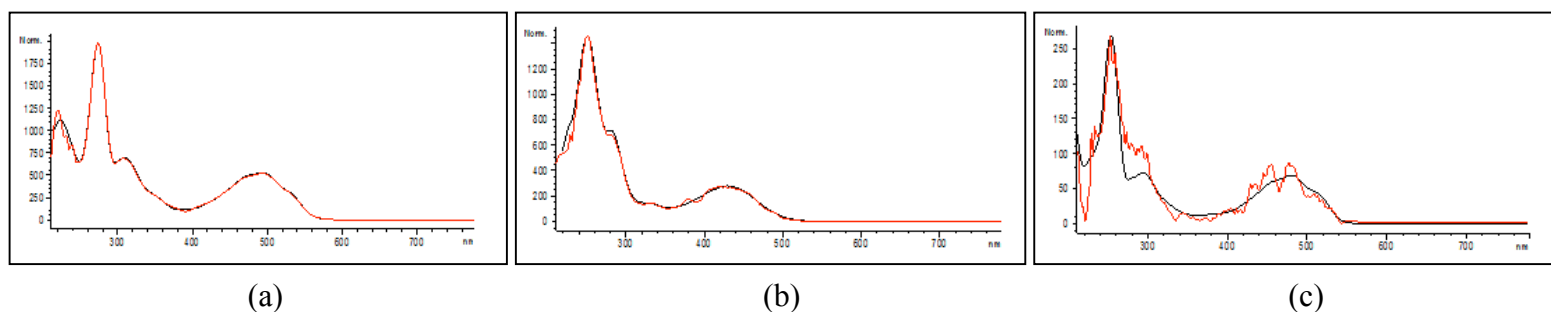
Identifying the weaving structure, color value, twist and spinning of yarns, chemical compositions of metal threads, dyestuffs and dye sources of the art objects for accurate and non-destructive restoration, conservation and cleaning methods.

The yarns of the new brocades were dyed and weaved with the same material, under the same conditions, same techniques and same dye sources. This has led to one-on-one characteristics of the reproduction silk brocades and Ottoman silk brocades.

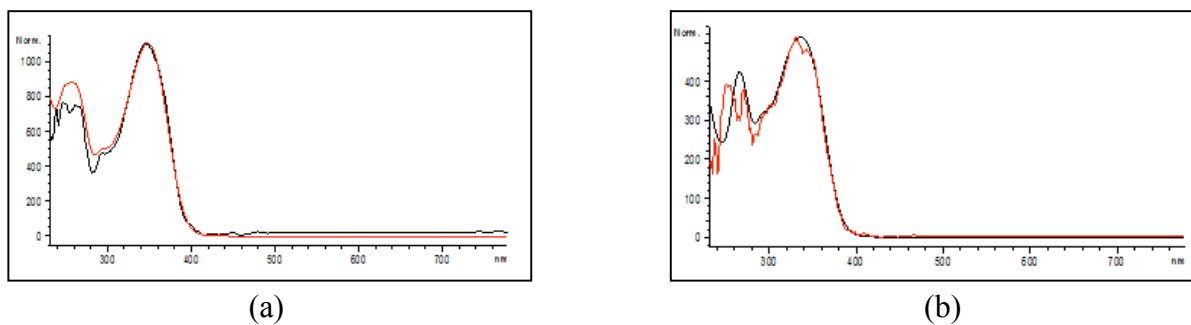
Historical textiles in museums are exposed to many challenges such as humidity, changing temperature, effect of light, effect of air pollution, non-standard storage and display methods.



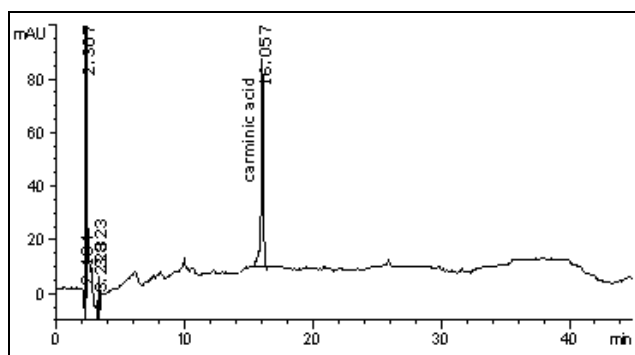
**Figure 1. HPLC chromatograms of historical art object (Inventory number 13/46). (a) red sample and (b) yellow sample.**



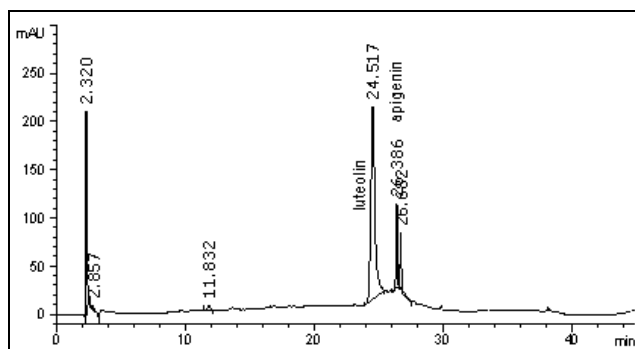
**Figure 2. Spectrum of red sample (Inventory number 13/46). (a) spectra of sample together with carminic acid standard, (b) spectra of sample together with alizarin standard and (c) spectra of sample together with purpurin standard.**



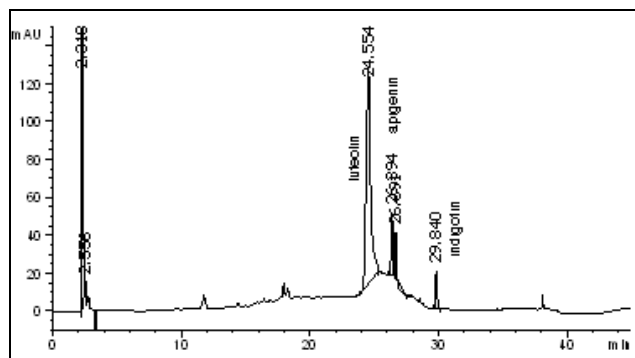
**Figure 3. Spectrum of yellow sample (Inventory number 13/46). (a) spectra of sample together with luteolin standard and (b) spectra of sample together with apigenin standard.**



(a)

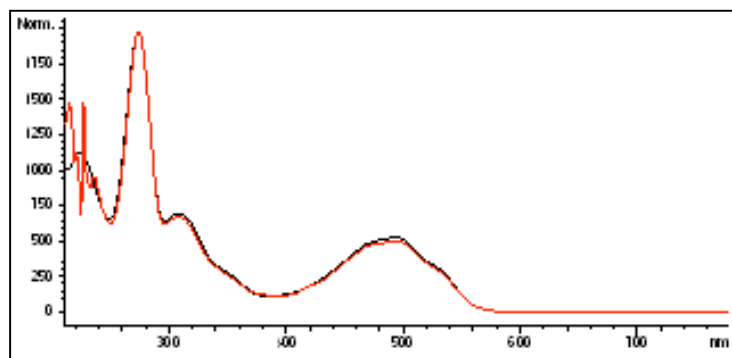


(b)

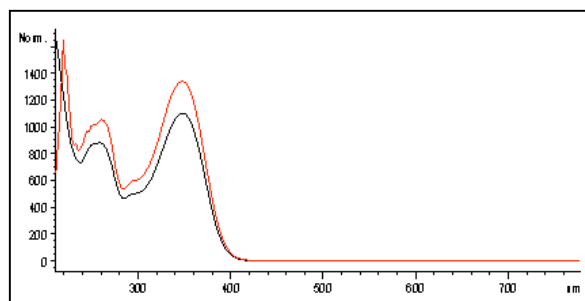


(c)

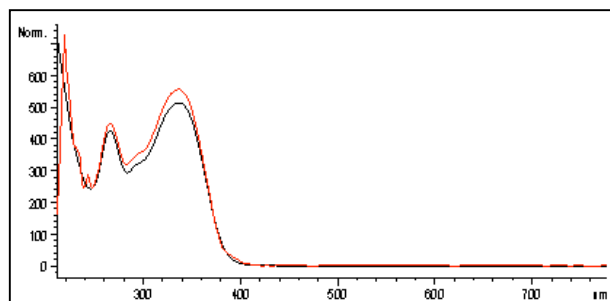
**Figure 4. HPLC chromatograms of historical art object (Inventory number 17624-D.261).  
(a) red sample, (b) yellow sample and (c) green sample.**



**Figure 5. Spectrum of red sample (Inventory number 13/46). spectra of sample together with carminic acid standard.**

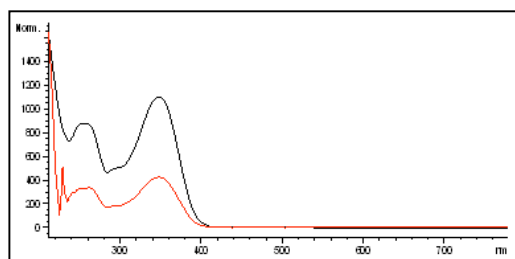


(a)

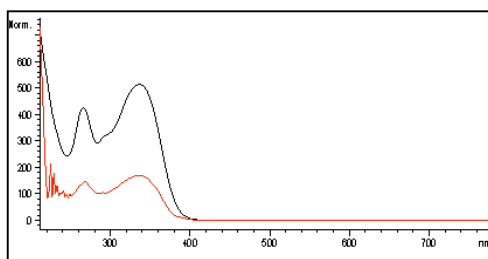


(b)

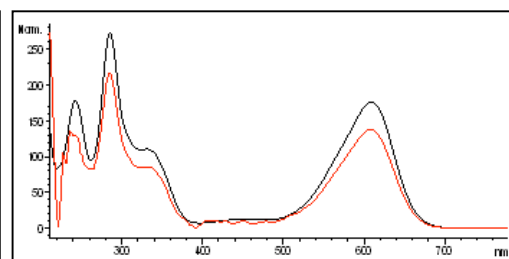
**Figure 6. Spectrum of yellow sample (Inventory number 17624-D.261 ).  
(a) spectra of sample together with luteolin standard and  
(b) spectra of sample together with apigenin standard.**



(a)



(b)

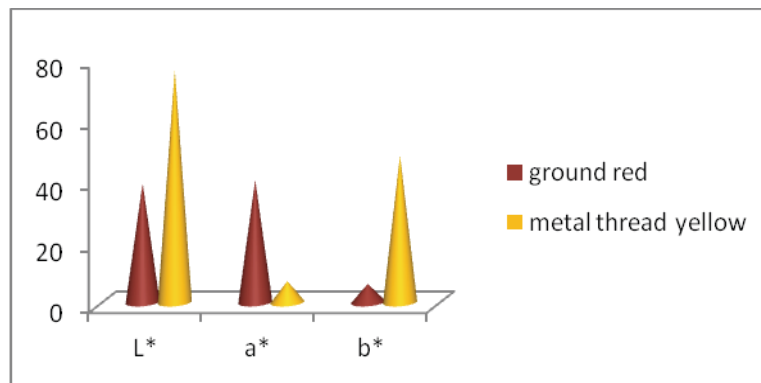


(c)

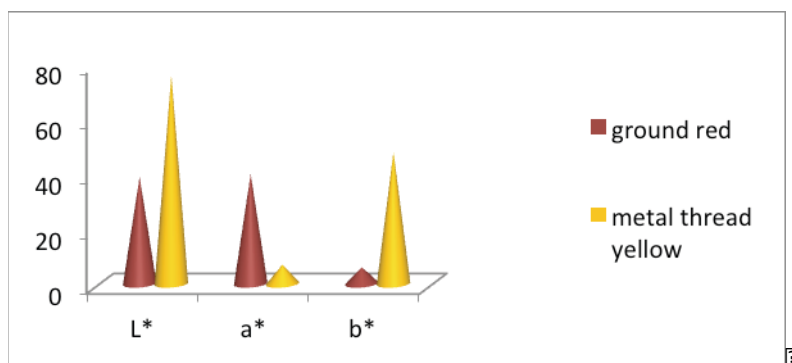
**Figure 7. Spectrum of green sample (Inventory number 17624-D.261).  
(a) spectra of sample together with luteolin standard,  
(b) spectra of sample together with apigenin standard and  
(c) spectra of sample together with indigotin standard.**

Inventory Number of 16 <sup>th</sup> historical textiles	Sample Color	Identified Dyestuffs	Biological Source
13/46	red	Carminic acid Alizarin, purpurin	<i>Dactylopius coccus</i> Costa + <i>Rubia tinctorum</i> L.
	yellow	Luteolin, apigenin	<i>Reseda luteola</i>
17624-D.261	red	Carminic acid	<i>Dactylopius coccus</i> Costa
	yellow	Luteolin, apigenin	<i>Reseda luteola</i>
	green	Luteolin, apigenin indigotin	<i>Reseda luteola</i> + <i>Indigofera tinctoria</i> or <i>Isatis tinctoria</i>

**Table 2. Dyestuff analysis result table of some historical art objects.**

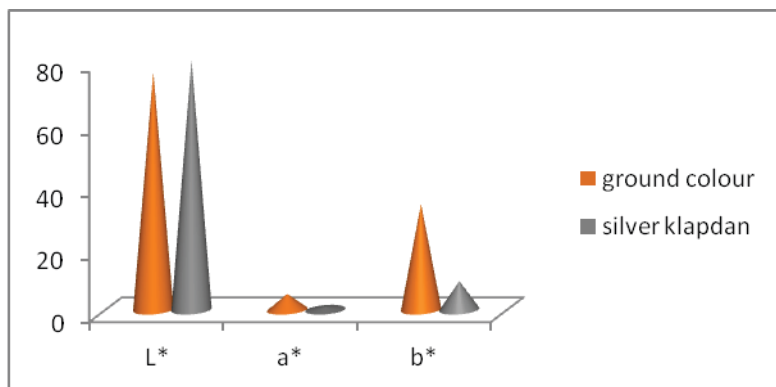


**Figure 8. The CIEL\*a\*b\* graph of historical art object (Inventory number 13/46, from the Topkapi Palace Museum collection).**

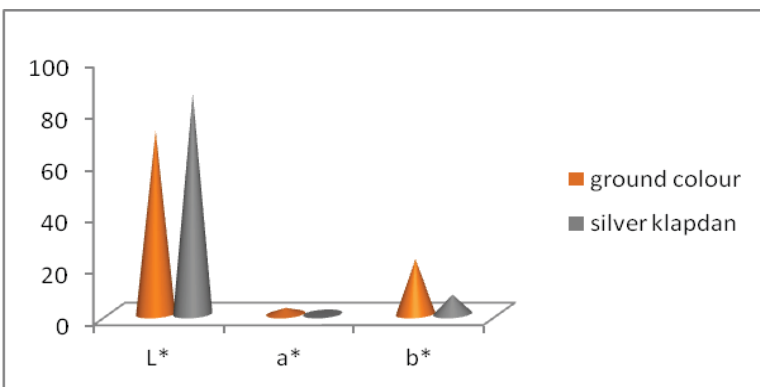


**Figure 9. The CIEL\*a\*b\* graph of reproduced new silk brocade.**

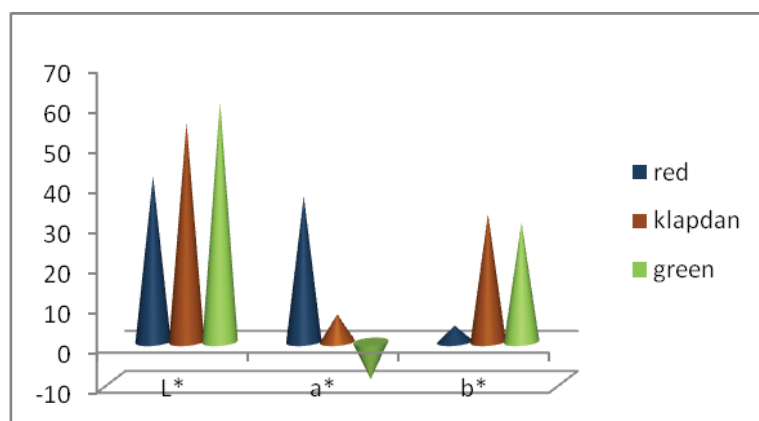




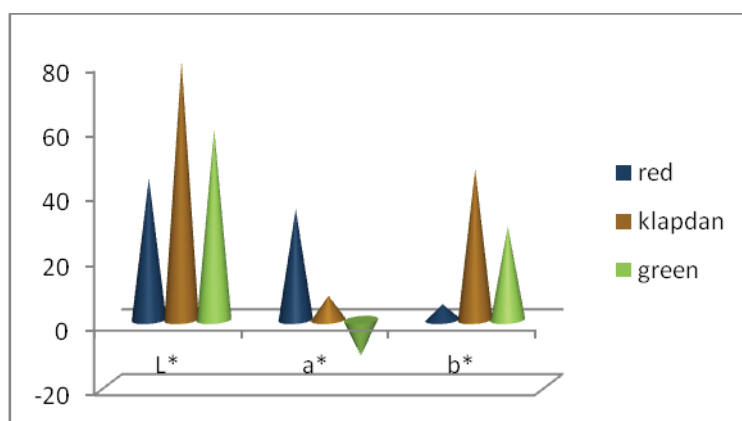
**Figure 10, left. The CIEL\*a\*b\* graph of historical art object (Inventory number 13/665, from Topkapı Palace Museum collection).**



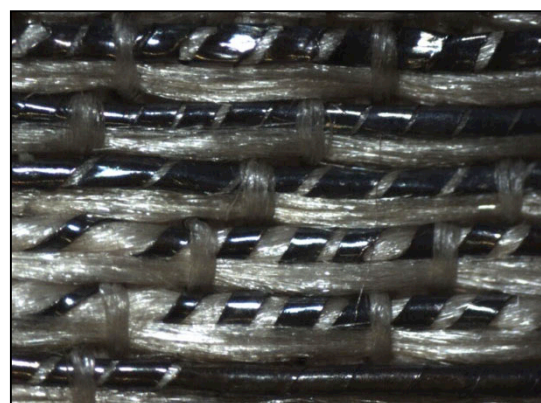
**Figure 11, right. The CIEL\*a\*b\* graph of reproduced new silk brocade.**



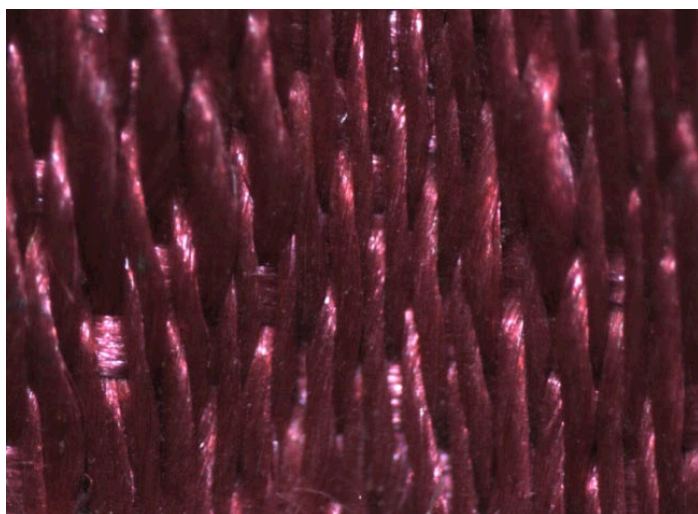
**Figure 12, right. The CIEL\*a\*b\* graph of historical art object (Inventory number 17624-D.261, from Sadberk Hanım Museum collection).**



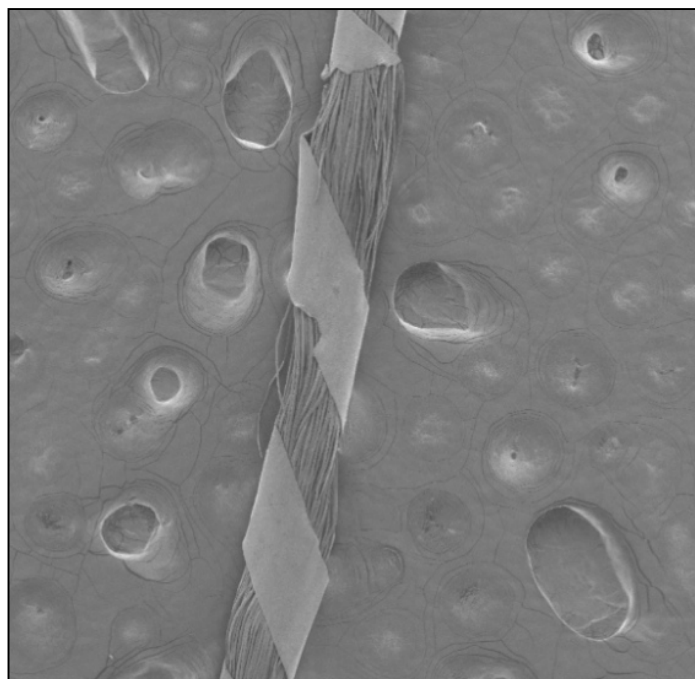
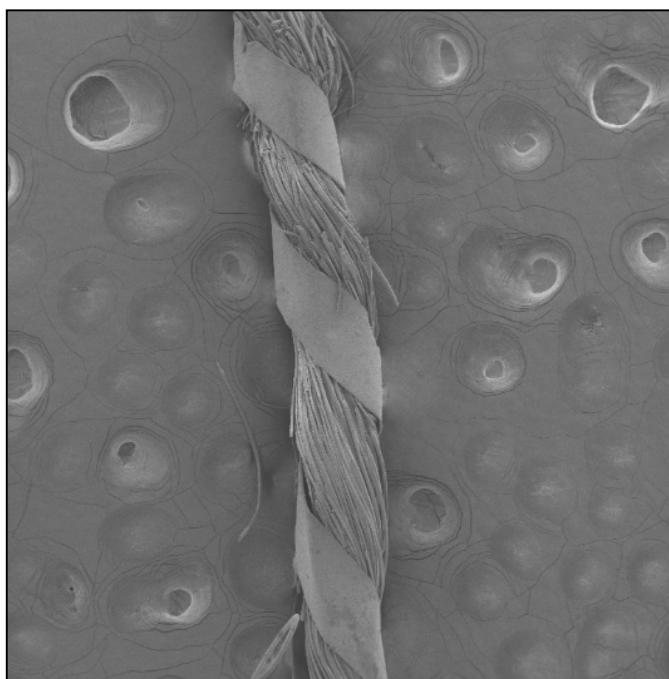
**Figure 13, left. The CIEL\*a\*b\* graph of reproduced new silk brocade.**



**Figure 14. The microscope images of historical textile (Inventory number 13/665, From the Topkapı Palace Museum collection).**



*Figure 15. The microscope images of historical textile (Inventory number 13/46, from the Topkapi Palace Museum collection).*



*Figure 16. The FESEM- EDAX images of historical textile (Inventory number 13/1891, from the Topkapi Palace Museum collection).*

*Figure 17. The FESEM- EDAX images of historical textile (Inventory number 13/1662, from the Topkapi Palace Museum collection).*



Inventory Number of 16 <sup>th</sup> historical textiles	Elemental percentage				
	Au (%Wt)	Ag (%Wt)	S (%Wt)	O (%Wt)	C (%Wt)
13/1891	7.78	79.83	1.84	4.30	6.25
13/1662	24.02	67.74	-	2.42	5.82

**Table 3. The metal analysis results of some 16<sup>th</sup> historical textiles (from the Topkapi Palace Museum collection).**

## Conclusion

According to the results of dye analysis and technical analysis, yarns of the new brocades were dyed and weaved with the same material, same conditions, same techniques and same dye sources.

Reproduced silk brocades were compared with 16<sup>th</sup> Ottoman silk brocades. Both of the new production and 16<sup>th</sup> century Ottoman silk brocades are same characteristically. The images of originals and reproduction brocades can be compared in Figures18-23, below.



**Figure 18, left. # 13-665, Topkapi Palace Museum (N. Atasoy, Silk 2001)**



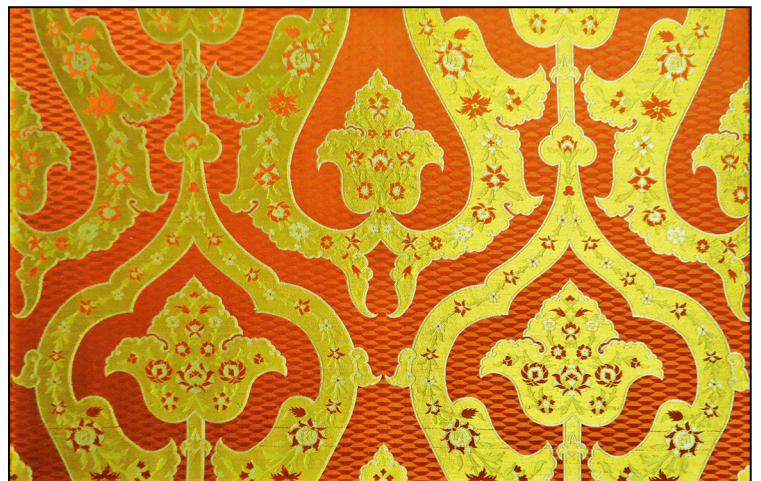
**Figure 19, right. Reproduction.**





*Figure 20, right. Sadberk Hanim Museum.*

*Figure 21, right. Reproduction.*



*Figure 22, left. # 13-46, Topkapi Palace Museum ( N.Atasoy, Silk, 2001).*

*Figure 23, right. Reproduction.*

## Acknowledgements

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