Understanding and Conserving the Past and Recreating Natural Dyes for Today

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Abstract

We aim to use the natural dyeing of textiles from the past as a basis of modern dye natural dyeing of textiles. The natural dyes and methods used in the historical textiles were determined. We adapt these to the recent natural dyes in modern textiles by using different analysis techniques.

In this study, the metal thread, dyestuff and technical analysis of historical textiles by micro and nondestructive analysis methods were determined. Historical samples were provided from many museum collection. Optical microscopy for the technical analysis, CIEL*a*b* spectrophotometer/colorimeter for the color measurements, HPLC-PAD for the dyestuff analysis and SEM-EDX for the metal thread analysis were performed. According to the results of this analysis, the fabrics that are made in modern times have the same characteristics as the fabrics analyzed due to the use of the same natural dyes.

Keywords: Historical textiles, reproduction, natural dyes, dyestuff analysis, elemental analysis, color measurement, technical analysis.

1. 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 [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 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].

2. Experimental

2.1. Dye Plants, Dye Insects and Chemicals

Weld (*Reseda luteola* L.), dyer's sumac (*Cotinus coggygria* SCOP), madder (*Rubia tinctorum* L.), oak (*Quercus ithaburensis*), gall oak (*Quercus infectoria*), natural indigo (*Indigofera tinctoria*) and cochineal insect (*Dactylopius coccus* Costa) were provided from Turkish Cultural Foundation Cultural Heritage Preservation and Natural Dyes Laboratory. Hydrochloric acid, methyl alcohol, DMF (dimetil formamide), TFA (trifluoro acetic acid) and acetonitrile were obtained from Merck (Darmstadt,

Germany, www. merck. de). Alum [$KAl(SO_4)_2.12H_2O$], $FeSO_4.7H_2O$, $SnCl_2.2H_2O$, NaOH and sodium hydrosulphite ($Na_2S_2O_4$) were provided from Sigma.

2.2.Mordanting and Dyeing for Reproduction Silk Brocades

Mordanting

Three methods were used for mordanting. Silk yarns 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 the silk yarns in the last method 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 oC) for 60 min to relax

the silk fibres. 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 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 yarns 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 60-65 ^oC and was

kept at this temperature for about 10-20 min. The temperature of the dye-bath was then allowed to cool about 30 ^oC; then the dyed silk fabric was squeezed, rinsed thoroughly with water and open air-dried.

Weld, dyer's sumac, oak and gall oak plants 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 silk yarns were mordanted after indigo dyeing and were carried out yellow dyeing recipes.

2.3.HPLC Analysis

Extraction Procedure for HPLC Analysis of Historical Textiles

The extraction of historical textile samples were performed with a solution mixture of

%37HCl:MeOH:H_2O; 2:1:1; v:v:v) for 8 minutes at 100 ^oC 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 ^oC under a gently stream of nitrogen. The dry residue was dissolved in 200 µl of the mixture of MeOH:H_2O (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. In this work, samples belong to five different art object were analyzed by HPLC-PDA (Figure 1-2).

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 799 nm with a resolution of 2 nm, and the chromatographic peaks were monitored at 255, 268, 276,

350, 491, 520, 580 and 620 nm. Column: A Nova Pak C18 analytical column (39×150 mm, 4 μm, 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 hydrolysed samples. Solvent A: H_2O- 0.1% TFA and solvent B: CH_3CN- 0.1 % TFA. The flow rate was 0.5 mL/min. and following elution program was applied in Table 1.

Table 1. 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

2.4.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^o). CIELAB graphs and L*, a* and b* values were shown (Figures 3-6).

2.5.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).

2.6.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 images 6-7.

Results

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.

Identifying the weaving structure, color value, twist and spinning of yarns, chemical compositions of metal threads, dyestuffs and dye resources of the art objects need to know for accurate and

non-destructive restoration, conservation and cleaning methods.

The yarns of the new silk brocades were dyed and weaved with the same material, under the same conditions, same techniques and same dye resources. Characteristics of the reproduction silk brocades and original silk brocades are very very close.

In this paper, samples from historical textile objects were provided from various museums. These museums are Topkapi Palace Museum, Washington Textile Museum and The State Hermitage Museum. To this study, five silk brocades were determined (Images 1-5).

Firstly, a reversed phase high performance liquid chromatography (RP-HPLC) is used for the identification of dyestuffs (Figures 6-8). L*, a* and b* values for each colour of original silk brocades (*kemha*) were measured. Dyeing process of reproduction silk brocades are done to the analysis results. Dyed silk yarns are weaved by the mechanical Jacquard looms. Reproduction silk brocades and original silk brocade had been in the same techniques, same design, same color and same quality. Metal thread yarns are same twist and spinning in the reproduction and original silk brocades but they have to the different metal percentages.

Another aim of this work, used natural dyeing methods in the past are developed [9] and these methods are applied at the contemporary textiles (Image 8-9).

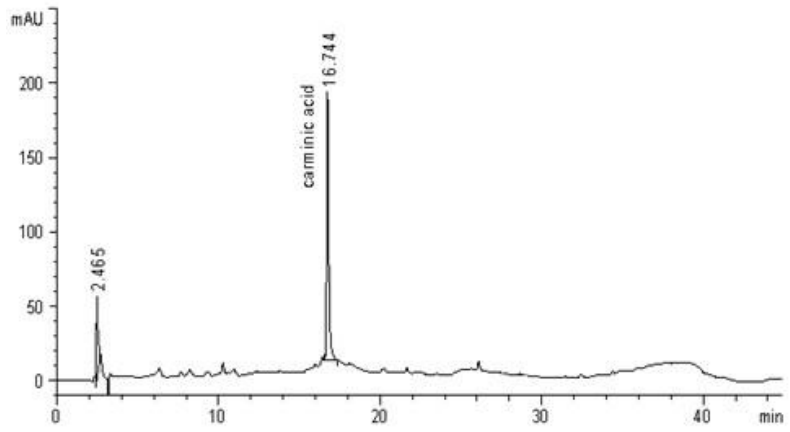
Image 1. *left*: Inventory Number 13/1476 from Topkapi Palace Museum collection (N.Atasoy, Silk, 2001),
right: Reproduction silk brocade from Armaggan company.

Image 2. *left*: Inventory Number 13/408 from Topkapi Palace Museum collection (N.Atasoy, Silk, 2001),
right: Reproduction silk brocade from Armaggan company.

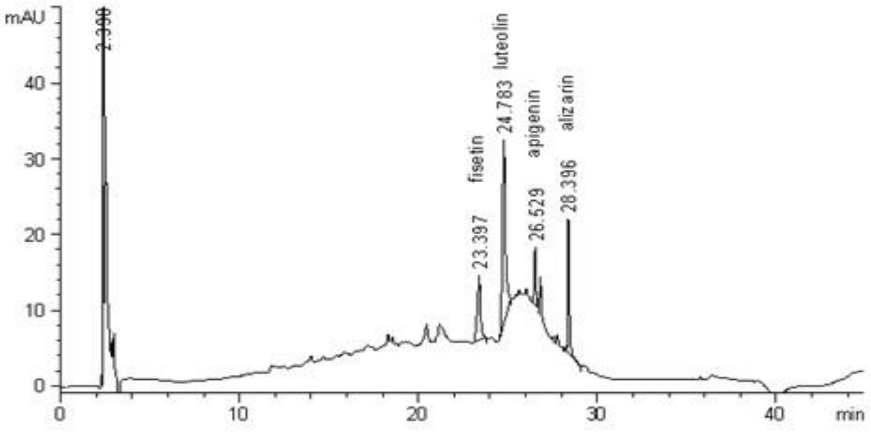
Image 3. *left*: Inventory Number 13/1675 from Topkapi Palace Museum collection (N.Atasoy, Silk, 2001),
right; Reproduction silk brocade from Armaggan company.

Image 4. *left:* Inventory Number OC1.72 from Washington Textile Museum (N.Atasoy, Silk, 2001),
right: Reproduction silk brocade from Armaggan company.

Image 5. *left:* Inventory Number T-357a from The State Hermitage Museum (N.Atasoy, Silk, 2001),
right: Reproduction silk brocade from Armaggan company.



(A)



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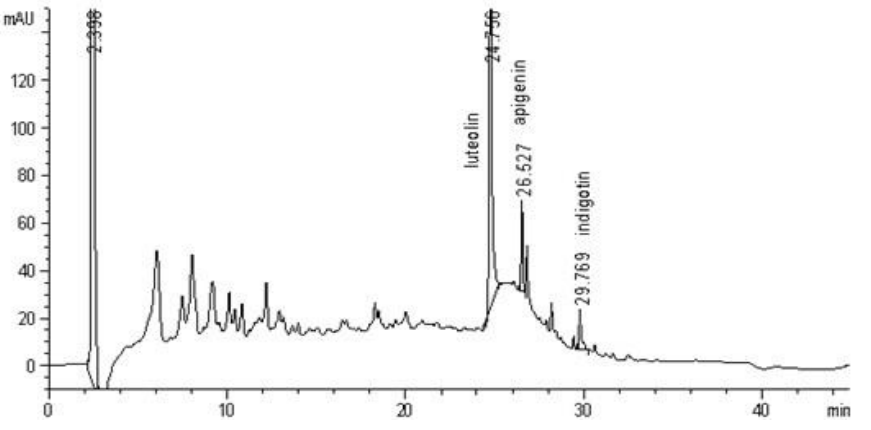


(C)

Figure 1. Chromatograms of the samples belongs to inventory number 13/1675 art object. **A-** red sample, **B-**yellow sample and **C-**green sample.

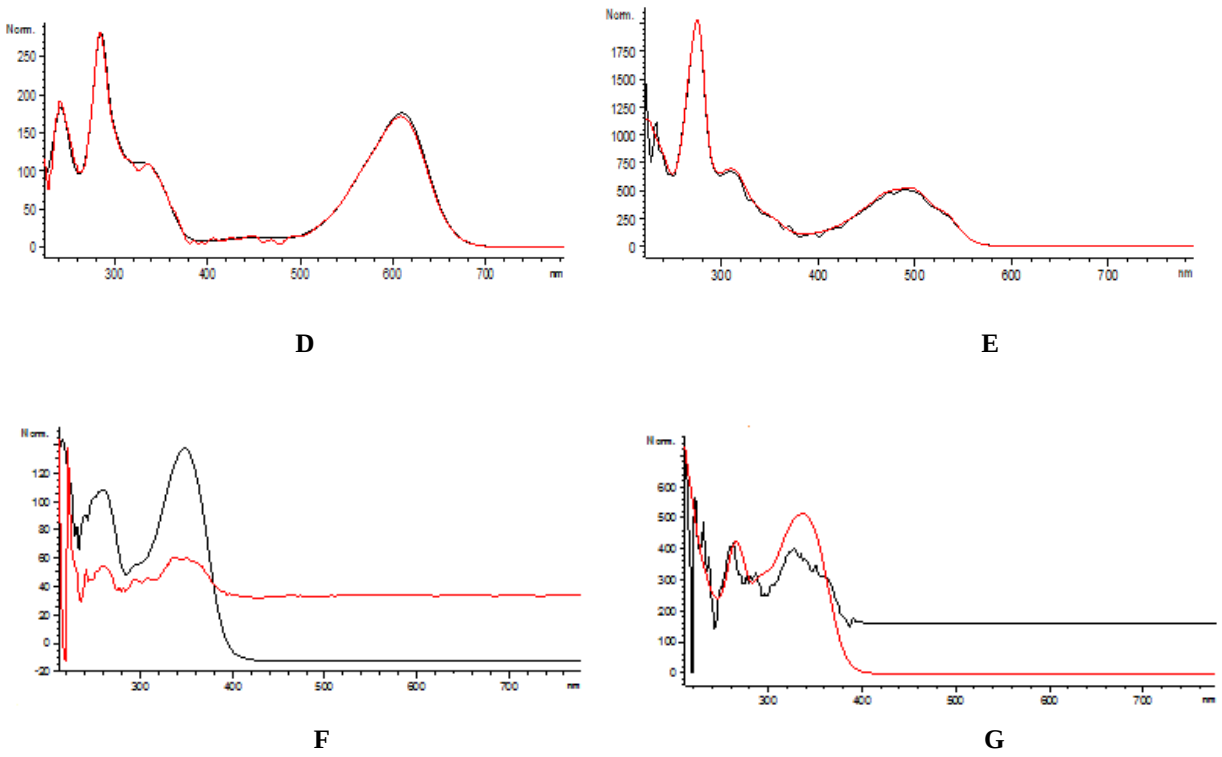


Figure 2. Spectra of the identified dyestuffs in the historical textile samples.
D-indigotin, **E**-carminic acid, **F**-luteolin and **G**-apigenin.

Table 2. Identified dyestuffs and their resources in the historical silk brocades.

Inventory Number	Type of Sample	Colour of Sample	Identified Dyestuffs	Biological Source
13/1476	Silk	red	carminic acid	*Dactylopius coccus* Costa
		yellow	luteolin and apigenin	*Reseda luteola*
		blue	indigotin	*Indigofera tinctoria* or *Isatis tinctoria*
13/408		red	carminic acid	*Dactylopius coccus* Costa
		yellow	luteolin and apigenin	*Reseda luteola*
13/1675		red	carminic acid	*Dactylopius coccus* Costa
		yellow	Fisetin, luteolin, apigenin and alizarin	*Cotinus coggygria* SCOP + *Reseda luteola* + *Rubia tinctorum* L.
		green	luteolin, apigenin and indigotin	*Reseda luteola* + *Indigofera tinctoria* or *Isatis tinctoria*

OC1.72	Silk	blue	indigotin	*Indigofera tinctoria* or *Isatis tinctoria*
		red	carminic acid	*Dactylopius coccus* Costa
		green	luteolin, apigenin and indigotin	*Reseda luteola* + *Indigofera tinctoria* or *Isatis tinctoria*
T-357a		blue	indigotin	*Indigofera tinctoria* or *Isatis tinctoria*
		red	carminic acid	*Dactylopius coccus* Costa
		green	luteolin, apigenin and indigotin	*Reseda luteola* + *Indigofera tinctoria* or *Isatis tinctoria*

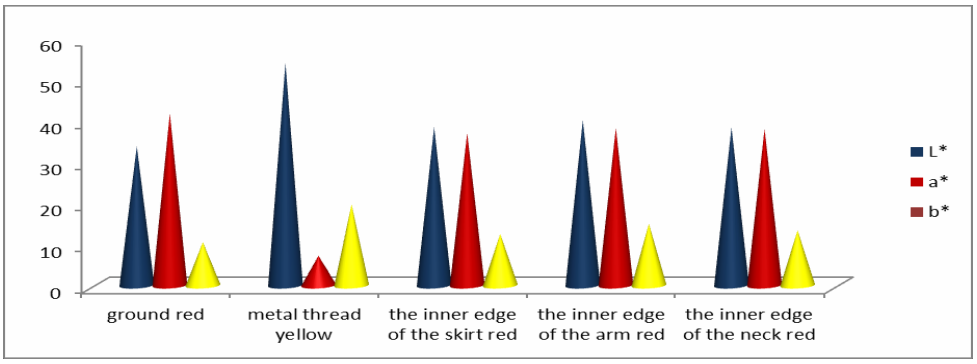


Figure 3. CIEL*a*b graph of historical art object
(Inventory number 13/408, from the Topkapi Palace Museum collection).

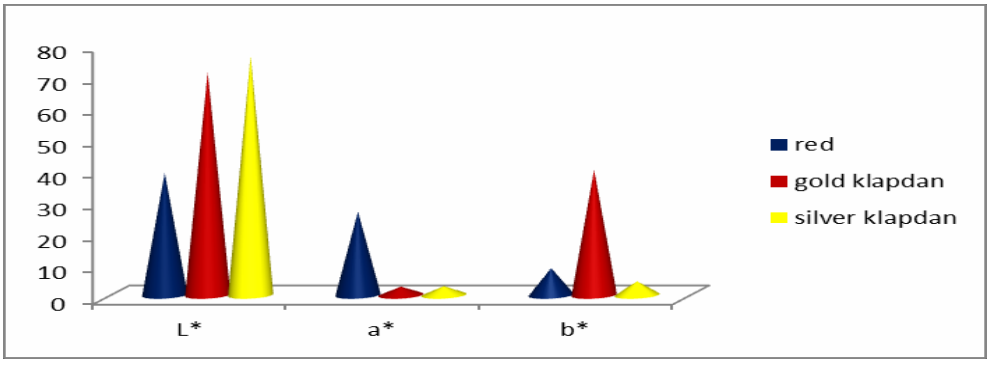


Figure 4. CIEL*a*b graph of reproduction silk brocade (for 13/408).

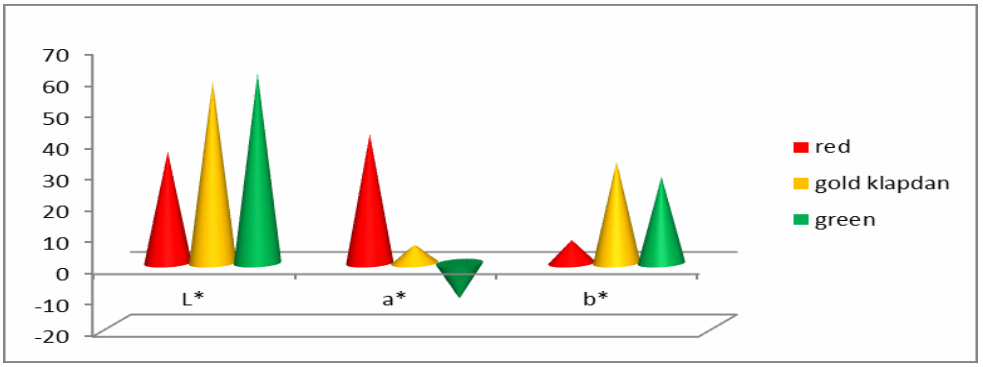


Figure 5. CIEL*a*b graph of reproduction silk brocade.

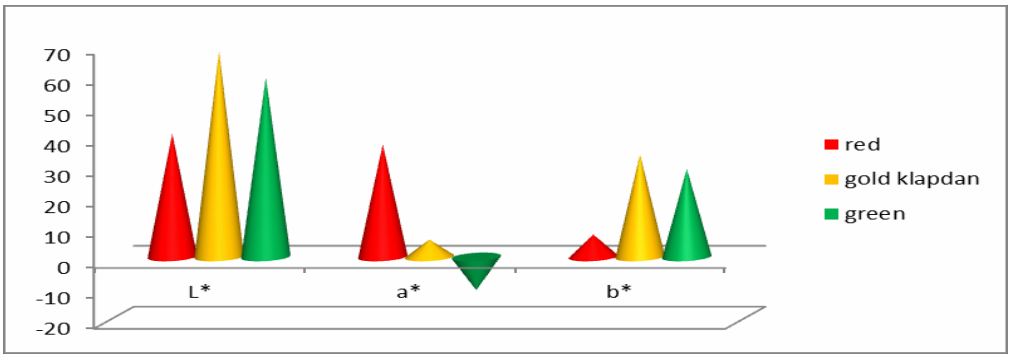
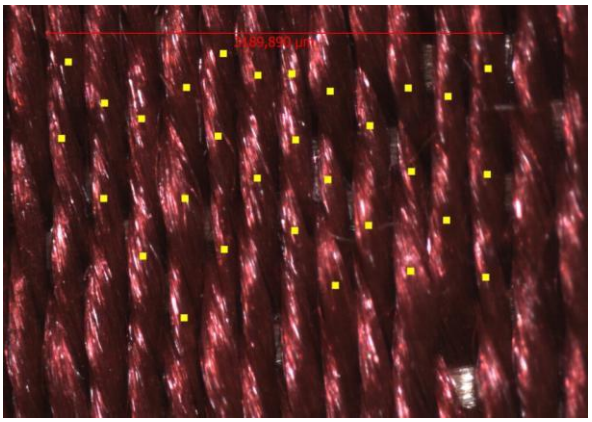
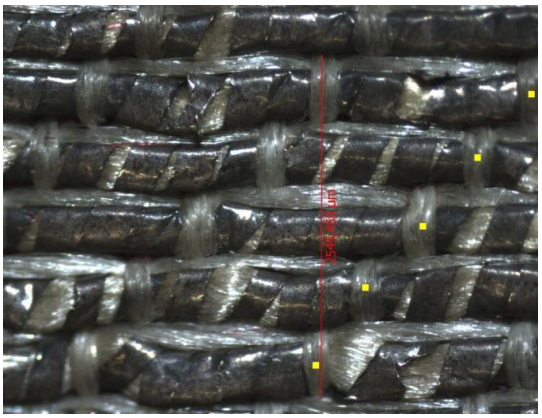


Figure 6. CIEL*a*b graph of reproduction silk brocade (for 13/1675).



(A)



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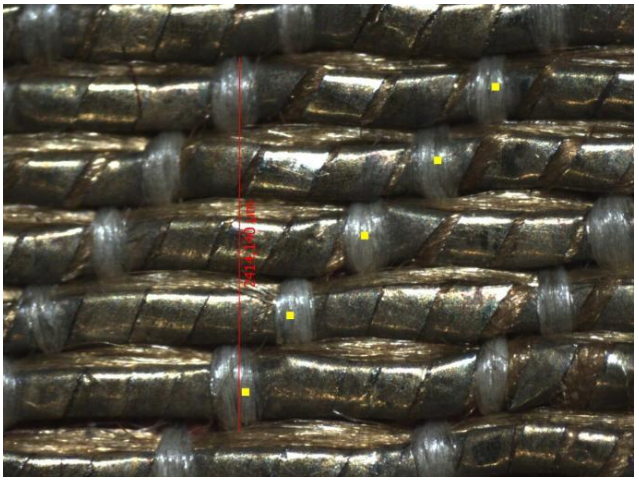
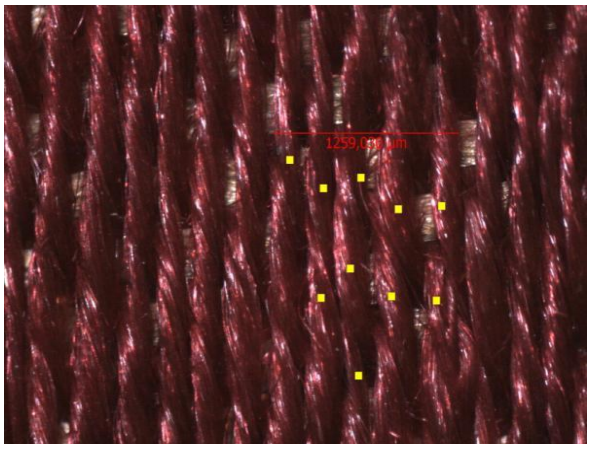
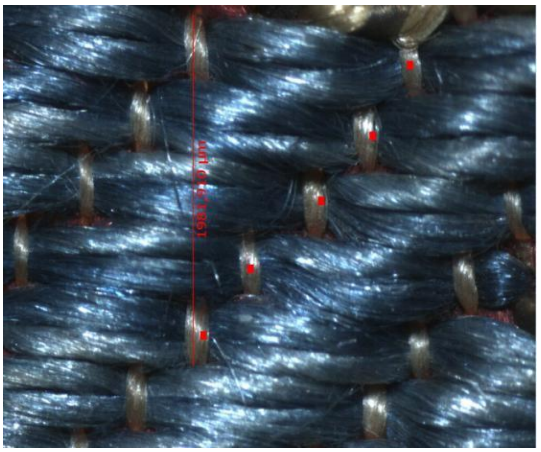


(C)

Image 6. The microscope images of inventory number 13/408 silk brocade.
A-warp, **B**-weft of silver metal thread and **C**- weft of golden metal thread.



D



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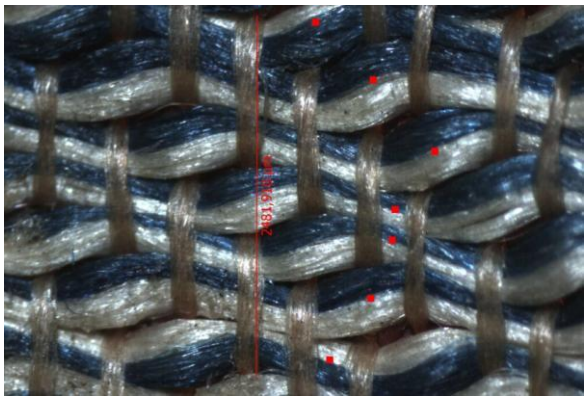

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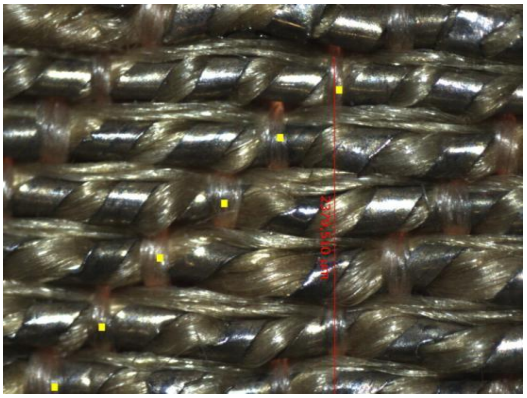

G

Image 7. The microscope images of inventory number 13/1476 silk brocade.
D-warp, **E**-weft (blue colour), **F**- weft (backing side of fabric) and **G**-weft of golden metal thread.

Image 8. Contemporary clothes dyed with natural dyes (Armaggan collection).

Image 9. Silk yarns dyed with natural dyes.

Conclusion

This has led to the identical or very closed reproduction of Ottoman silk brocades. Reproduction of 16th Ottoman silk brocades is proven to be extremely difficult, though not impossible.

The sustainable and diverse use of natural resources is significant in the development of environmentally begin processes and products in the future. Utilization of renewable natural resources has significance when introducing new ways especially in the textile (Image 8-9).

Identifying the weaving structure, color value, twist and spinning of yarns, chemical compositions of metal threads, 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

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