

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

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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 gilded. 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 (*Rubia tinctorum* L) with alizarin and purpurin as mainly colourants, cochineal, an insect (*Dactylopius coccus* Costa, *Porphyrophora polonica* L., *Porphyrophora hameli* Brandt) with carminic acid, kermes (*Kermes vermilio* Planchon) with kermesic acid and flavokermesic acid and lac dye (*Kerria lacca* Kerr) with laccaic acid. Weld (*Reseda luteola* L.) appears to be the most commonly used yellow dye with luteolin and apigenin. The blue dyes woad (*Isatis tinctoria* L. and *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

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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 (scanning electron microscopy- energy dispersive spectrometry) has been widely used to characterize historical objects for conservation/restoration purposes as a non-destructive tool because of its simplicity to provide high resolution images at high magnifications and analytical data on the elemental composition [29]. Among the historical objects, textiles with metal threads are of great importance [30, 31]. Valuable information on the surface conditions of the textiles-level of degradation and corrosion, type of the threads used and manufacturing methods can be obtained by this investigation [32, 33].

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



Fig. 1 Fragment of silk sample from Azerbaijan History Museum.

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 H_2O -MeOH-37% HCl (1:1:2; v/v/v) in conical glass tubes for precisely at 100 $^\circ\text{C}$, 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 $^\circ\text{C}$ under a gentle stream of nitrogen flow. The dry residues were dissolved in 200 μL of a mixture of MeOH: H_2O (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 \times 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 $^\circ\text{C}$.

For HPLC-DAD studies, gradient elution was performed using two solvent consisting of A: 0.1% (v/v) TFA in H_2O and B: 0.1% (v/v) TFA in CH_3CN 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 1 Profile of gradient elution program for HPLC.

Time (min)	H_2O -0.1% TFA (v/v)	CH_3CN -0.1% TFA (v/v)
0.0	95.0	5.0
1.0	95.0	5.0
20.0	70.0	30.0
25.0	40.0	60.0
28.0	40.0	60.0
33.0	5.0	95.0
35.0	5.0	95.0
45.0	95.0	5.0

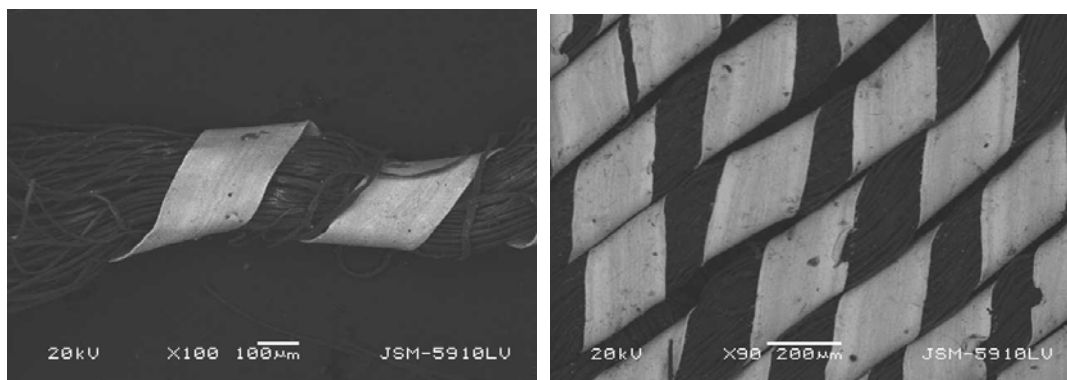


Fig. 2 BEI (backscattering electron image) microphotographs of the textile sample at $\times 90$ magnification.

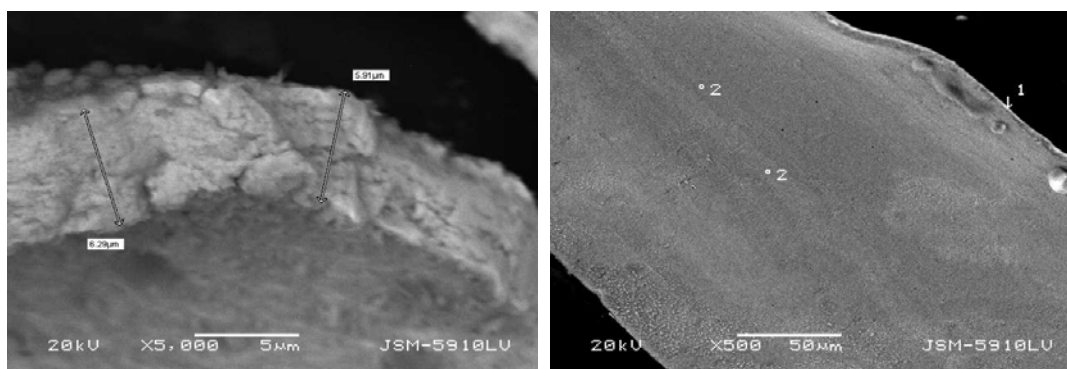


Fig. 3 SEM microphotograph of the cross section of the metal strip.

metal thread with accelerating voltage 20 KV, magnification up to 10,000 \times . The sample was investigated directly without any coating layer.

3. Results and Discussion

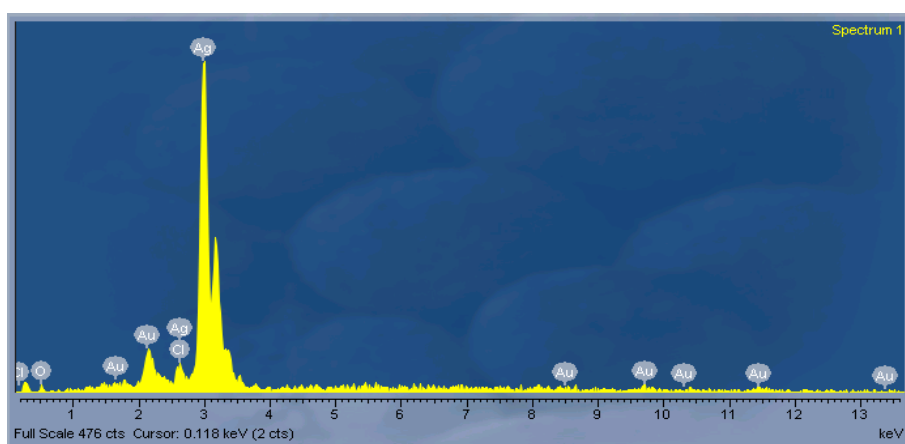
In the present study, HPLC-DAD was used to identify individual chemical components of dyes in extracts from fibres of different colours taken from Azerbaijan History Museum textile collection. Elemental analysis using SEM-EDS technique was performed to identify metal on threads from textile sample.

The typical metal thread consisting of metal strip wounded 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.

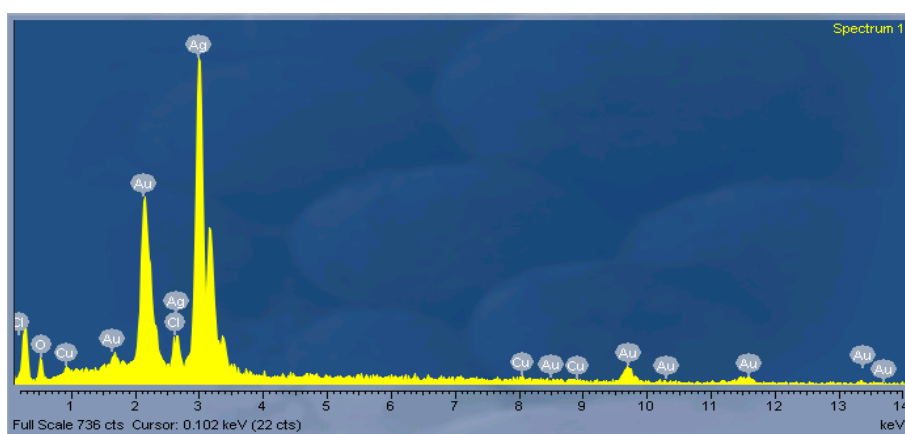
In the same sample were identified colouring compounds by HPLC-DAD. The major colouring compound found in the red fibre sample in large quantity was carminic acid and fuchsin components (Fig. 6). The most common pigment obtained from cochineal is carminic acid. Spectral properties of the solution obtained 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 coggygia* Scop., Anacardiaceae) was detected, which is a natural dye (Fig. 6). Identification of dyestuffs is based on comparison of the dye absorption



Point 1

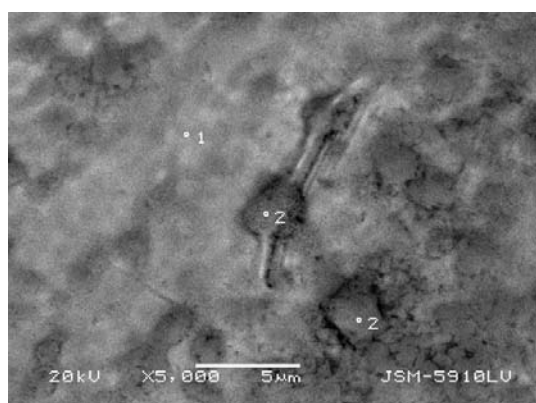
Elements	O	Cl	Ag	Au	Total
%	4.32	0.91	85.68	9.09	100



Point 2

Elements	O	Cl	Cu	Ag	Au	Total
%	8.53	2.04	0.85	61.23	27.34	100.00

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



Point 2

Elements	C	O	S	Cl	Ag	Total
%	5.23	2.96	0.86	1.32	89.64	100.00

Fig. 5 SEM microphotograph of the surface contamination.

spectrum, retention time and reference standards (Fig. 7).

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

Point 1

Elements	C	O	Cl	Ag	Au	Total
%	7.57	4.29	0.77	67.87	19.50	100.00

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

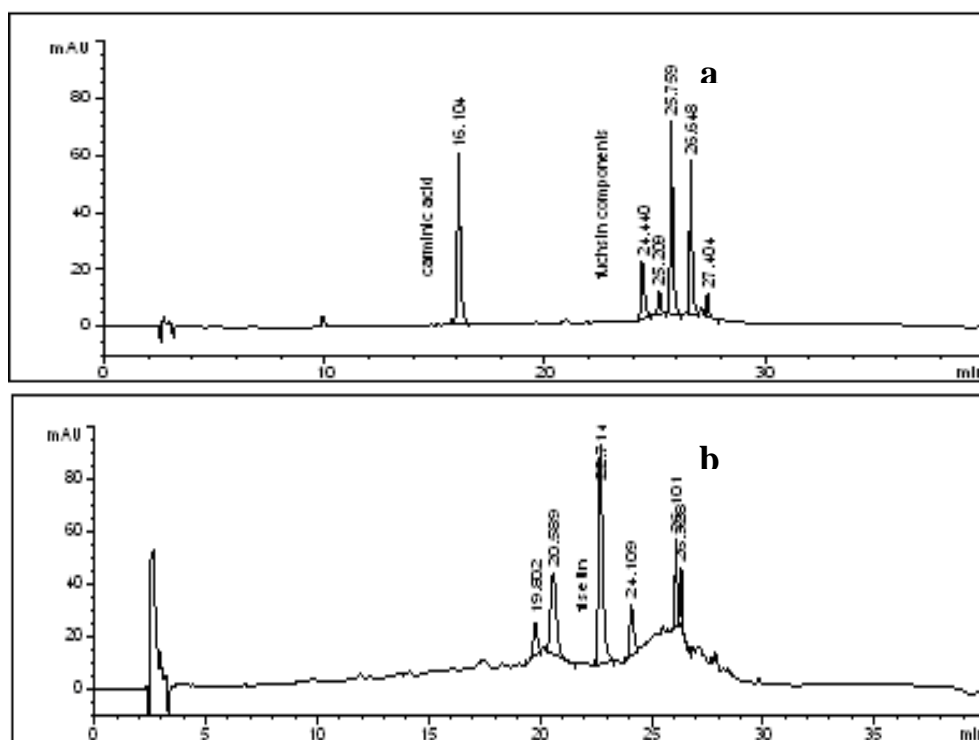


Fig. 6 Chromatograms obtained at 491 nm from (a) red fibre and (b) at 350 nm from yellow fibre.

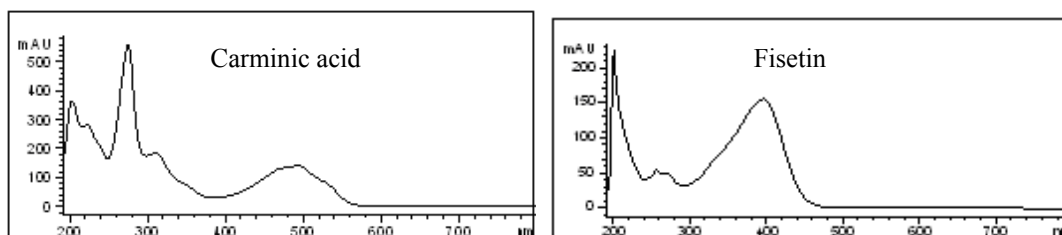


Fig. 7 DAD spectra of the natural dyestuffs.

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 (*Cotinus coggygia* 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

- [1] Trojanowicz, M.; Orska-Gawryś, J.; Surowiec, I.; Szostek, B.; Urbaniak-Walczak, K.; Kehl, J.; et al. Chromatographic Investigation of Dyes Extracted from Coptic Textiles from the National Museum in Warsaw. *Stud. Conserv.* **2004**, *49*(2), 115-130.
- [2] Wouters, J. High-Performance Liquid Chromatography Anthraquinones: Analysis of Plant and Insect Extracts and Dyed Textiles. *Stud. Conserv.* **1985**, *30*, 119-128.
- [3] Wouters, J.; Verhecken, A. The Coccid Insect Dyes: HPLC and Computerized Diode-Array Analysis of Dyed Yarn. *Stud. Conserv.* **1989**, *34*, 189-200.
- [4] Schweppe, H. Identification of Dyes on Old Textiles. *J. Am. Inst. Conserv.* **1979**, *19*(1), 14-23.
- [5] Serrano, A.; Sousa, M. M.; Hallett, J.; Lopes, J. A.;

- Oliveira, M. C. Analysis of Natural Red Dyes (Cochineal) in Textiles of Historical Importance using HPLC and Multivariate Data Analysis. *Anal. Bioanal. Chem.* **2011**, *401*(2), 735-743.
- [6] Novotná, P.; Pacáková, V.; Bosáková, Z.; Stulík, K. High-Performance Liquid Chromatographic Determination of Some Anthraquinone and Naphthoquinone Dyes Occurring in Historical Textiles. *J. Chromatogr. A* **1999**, *863*(2), 235-241.
- [7] Wouters, J.; Rosario-Chirinos, N. Dye Analysis of Pre-Columbian Peruvian Textiles with High-Performance Liquid Chromatography and Diode-Array Detection. *J. Am. Inst. Conserv* **1992**, *31*, 237-255.
- [8] Koren, Z. C. An Efficient HPLC Analysis Scheme for Plant and Animal Red, Blue and Purple Dyes. *Dyes History Archaeol.* **1995**, *13*, 27-37.
- [9] Surowiec, I.; Quye, A.; Trojanowicz, M.; Liquid Chromatography Determination of Natural Dyes in Extracts from Historical Scottish Textiles Excavated from Peat Bogs. *J. Chromatogr. A* **2006**, *1112*, 209-217.
- [10] Surowiec, I.; Orska-Gawry, J.; Biesaga, M.; Trojanowicz, M.; Hutta, M.; Halko, R. Identification of Natural Dyestuff in Archeological Coptic Textiles by HPLC with Fluorescence Detection. *Anal. Lett.* **2003**, *36*(6), 1211-1229.
- [11] Karapanagiotis, I.; Mantzouris, D.; Chryssoulakis, Y.; Saadeh, H. A.; Alawi, M. A.; Mubarek, M. S. et al. Inter-Laboratory Chemical Study of Natural Materials from the Historical Wiesner Collection. *Jordan Journal of Chemistry* **2009**, *4*(2), 195-208.
- [12] Karapanagiotis, I.; Lakka, A.; Valianou, L.; Chryssoulakis, Y. High-Performance Liquid Chromatographic Determination of Colouring Matters in Historical Garments from the Holy Mountain of Athos. *Microchim. Acta.* **2008**, *160*(4), 477-483.
- [13] Petrovicu, I.; Albu, F.; Medvedovici, A. LC/MS and LC/MS/MS Based Protocol for Identification of Dyes in Historic Textiles. *Microchem. J.* **2010**, *95*, 247-254.
- [14] Yurdun, T.; Karadag, R.; Dolen, E.; Mubarak, M. S. Identification of Natural Yellow, Blue, Green and Black Dyes in 15th-17th Centuries Ottoman Silk and Wool Textiles by HPLC with Diode Array Detection. *Rev. Anal. Chem.* **2011**, *30*, 153-164.
- [15] Mantzouris, D.; Karapanagiotis, I.; Valianou, L.; Panayiotou, C. HPLC-DAD-MS Analysis of Dyes Identified in Textiles from Mount Athos. *Anal. Bioanal. Chem.* **2011**, *399*(9), 3065-3079.
- [16] Puchalska, M.; Połec-Pawlak, K.; Zadrozna, I.; Hryszko, H.; Jarosz, M. Identification of Indigoid Dyes in Natural Organic Pigments Used in Historical Art Objects by High-Performance Liquid Chromatography Coupled to Electrospray Ionization Mass Spectrometry. *J. Mass Spectrom.* **2004**, *39*(12), 1441-1449.
- [17] Zhang, X.; Good, I.; Laursen, R. Characterization of Dyes in Ancient Textiles from Xinjiang. *J. Arch. Sci.* **2008**, *35*, 1095-1103.
- [18] Szostek, B.; Orska-Gawryś, J.; Surowiec, I.; Trojanowicz, M. Investigation of Natural Dyes Occurring in Historical Coptic Textiles by High-Performance Liquid Chromatography with UV-vis and Mass Spectrometric Detection. *J. Chromatogr. A* **2003**, *1012*, 179-192.
- [19] Balakina, G. G.; Vasiliev, V. G.; Karpova, E. V.; Mamatyuk, V. I. HPLC and Molecular Spectroscopic Investigations of the Red Dye Obtained from an Ancient Pazyryk Textile. *Dyes Pigments* **2006**, *71*, 54-60.
- [20] Marques, R.; Sousa, M. M.; Oliveira, M. C.; Melo, M. J. Characterization of Weld (*Reseda luteola* L.) and Spurge Flax (*Daphne gnidium* L.) by High-Performance Liquid Chromatography-Diode Array Detection-Mass Spectrometry in Arraiolos Historical Textiles. *J. Chromatogr. A* **2009**, *1216*(9), 1395-1402.
- [21] Blanc, R.; Espejo, T.; López-Montes, A.; Torres, D.; Crovetto, G.; Navalón, A. et al. Sampling and Identification of Natural Dyes in Historical Maps and Drawings by Liquid Chromatography with Diode-Array Detection. *J. Chromatogr. A* **2006**, *1122*, 105-113.
- [22] Daniilia, S.; Minopoulou, E.; Andrikopoulos, K. S.; Karapanagiotis, I.; Kourouklis, G. A. Evaluating a *Cumaean Sibyl*: Domenichino or Later? A Multi Analytical Approach. *Anal. Chim. Acta.* **2008**, *611*, 239-249.
- [23] Karapanagiotis, I.; Daniilia, S.; Tsakalof, A.; Chryssoulakis, Y. Identification of Red Natural Dyes in Post- Byzantine Icons by HPLC. *J. Liq. Chromatogr. R. T.* **2005**, *28*, 739-749.
- [24] Karapanagiotis, I.; Valianou, Y.; Daniilia, S.; Chryssoulakis, Y. Organic Dyes in Byzantine and Post-Byzantine Icons from Chalkidiki (Greece). *J. Cult. Herit* **2007**, *8*, 294-298.
- [25] Zhang, X.; Laursen, R. A. Development of Mild Extraction Methods for the Analysis of Natural Dyes in Textiles of Historical Interest using LC-Diode Array Detector-MS. *Anal. Chem.* **2005**, *77*(7), 2022-2025.
- [26] Valianou, L.; Karapanagiotis, I.; Chryssoulakis, Y. Comparison of Extraction Methods for the Analysis of Natural Dyes in Historical Textiles by High-Performance Liquid Chromatography. *Anal. Bioanal. Chem.* **2009**, *395*(7), 2175-2189.
- [27] Karapanagiotis, I.; Lakka, A.; Valianou, L.; Chryssoulakis, Y. High-Performance Liquid Chromatographic Determination of Colouring Matters in Historical Garments from the Holy Mountain of Athos. *Microchim. Acta.* **2008**, *160*(4), 477-483.
- [28] Clementi, C.; Nowik, W.; Romani, A.; Cibir, F.;

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

- Favaro, G. A Spectrometric and Chromatographic Approach to the Study of Ageing of Madder (Rubia Tinctorum L.) Dyestuff on Wool. *Anal. Chim. Acta.* **2007**, *596(1)*, 46-54.
- [29] Sandu, I. C. A.; Sade, M. H.; Pereira, M. C. Ancient "Gilded" Art Objects from European Cultural Heritage: A Review on Different Scales of Characterization. *Surf. Interface Anal.* **2011**, *43*, 1134-1151.
- [30] Jaro, M. Gold Embroidery and Fabrics in Europe: XI-XIV Centuries. *Gold Bull* **1990**, *23*, 119-128.
- [31] Tronner, K.; Nord, A. G.; Sjostedt, J.; Hydman, H. Extremely Thin Gold Layers on Gilded Silver Threads. *Stud. Conserv.* **2002**, *47*, 109-116.
- [32] Hacke, A. M.; Carr, C. M.; Brown, A.; Howel, D. Investigation into the Nature of Metal Threads in Renaissance Tapestry and Cleaning of Tarnished Silver By UV/Ozone (UVO) Treatment. *J. Mater. Sci.* **2003**, *38*, 3307-3314.
- [33] Cakır, A. F.; Simsek, G.; Tezcan, H. Characterization of Gold Gilt Silver Wires from Five Embroidered Silk Qaaba Curtains Dated Between the 16th and 19th Centuries. *Appl. Phys. A* **2006**, *83*, 503-511.
- [34] Rezic, I.; Curkovic, L.; Ujevic, M. Simple Methods for Characterization of Metals in Historical Textile Threads. *Talanta* **2010**, *82*, 237-244.
- [35] Hacke, A. M.; Carr, C. M.; Brown, A. In *Characterization of Metal Threads in Renaissance Tapestries*, Proceedings of Metal 2004 National Museum of Australia Canberra ACT ABN 70 592 297 967, 2004.
- [36] Jaro, M.; Gal, T.; Toth, A. The Characterization and Determination of Modern Metallic Threads. *Stud. Conserv.* **2000**, *45*, 95-105.
- [37] Nord, A. G.; Tronner, K. A Note on the Analysis of Gilded Metal Embroidery Threads. *Stud. Conserv.* **2000**, *45*, 274-279.
- [38] Karatzani, A.; Rehren, T. The Use of Metal Threads and Decorations in Byzantine-Greek Orthodox Ecclesiastical Textiles. *Journal of the Minerals, Metals and Materials Society* **2006**, *58*, 34-37.
- [39] Karatzani, A. Study and Analytical Investigation of Metal Threads from Byzantine/Greek Orthodox Ecclesiastical Textiles. *X-Ray Spectrom.* **2008**, *37*, 410-417.
- [40] Halpine, S. M. An Improved Dye and Lake Pigment Analysis Method for High Performance Liquid Chromatography and Diode-Array Detector. *Stud. Conserv.* **1996**, *41*, 76-94.
- [41] European Union (1994). European Parliament and Council Directive 94/36/EC of 30 June 1994 on colours for use in foodstuffs., Official Journal of the European Communities, No. L 237/13-29.