



DYES IN POST-BYZANTINE AND OTTOMAN TEXTILES: A COMPARATIVE HPLC STUDY

Ioannis Karapanagiotis*¹ and Recep Karadag^{2,3}

¹*University Ecclesiastical Academy of Thessaloniki, Department of Management and Conservation of Ecclesiastical Cultural Heritage Objects, Thessaloniki 54250, Greece*

²*Marmara University, Faculty of Fine Arts, Kadikoy, Istanbul 34718, Turkey*

³*TCF-Cultural Heritage Preservation and Natural Days Laboratory, Istanbul 34775, Turkey*

Received: 02/11/2014

Accepted: 03/02/2015

Corresponding author: Ioannis Karapanagiotis (y.karapanagiotis@aeath.gr)

ABSTRACT

The goal of the study is to compare the dyes used in ecclesiastical post-Byzantine (sixteenth to early twentieth century) textiles of Mount Athos, Greece, with the corresponding organic colourants used in Ottoman (sixteenth to eighteenth century) textiles which are preserved in the Topkapi Palace Museum, Turkey. During the historical period of interest, Mount Athos which has been the spiritual centre of Byzantine culture for centuries, was within the borders of the Ottoman Empire (period of Ottoman rule).

Samples extracted from forty-six and fifty post-Byzantine and Ottoman textiles, respectively, were analysed using high performance liquid chromatography with diode array detection (HPLC-DAD). The analysis of a silk velvet (Topkapi Palace Museum) is presented in detail and serves as an example to describe the methodology that was applied throughout the investigation.

More similarities than differences are observed in the results reported for the two textile collections of different cultural identity. The following materials were found in both post-Byzantine and Ottoman textiles: cochineal, madder, lac, young fustic, weld, dyer's broom, buckthorn berries, indigo/woad and tannins. On the other hand, soluble redwood, old fustic and logwood were found only in post-Byzantine textiles while dyer's chamomile and *Rumex* species were detected only in few Ottoman objects.

KEYWORDS: dye, textile, HPLC, Byzantine, Ottoman

1. INTRODUCTION

Identification of dyes in historical and archaeological textiles is usually carried out using high performance liquid chromatography (HPLC) equipped with diode array detector (DAD) (Deveoglu et al. 2012; Deveoglu et al. 2013; Hofenk de Graaff 2004; Karadag and Yurdan 2010; Karapanagiotis et al. 2011; Koren 1999; Nowik et al. 2005; Serrano et al. 2011; Stuart 2007; Wouters 1985; Wouters and Verhecken 1989; Yurdun et al. 2012) mass spectrometry (MS) (Ferreira et al. 2001; Petrović et al. 2010; Petrović et al. 2012a; Rosenbergs 2008; Szostek et al. 2003; Zhang et al. 2007) or fluorimetric detection (Surowiec et al. 2003). Recently, spectroscopic techniques, such as surface-enhanced Raman spectroscopy (SERS) and other non-invasive methods have started gaining a lot of ground in the identification of dyes (Brosseau et al. 2009; Casadio et al. 2010; Gulmini et al. 2013; Leona et al. 2007; Pozzi et al. 2012).

HPLC is the most widely adopted method for dyestuff identification, because it has two major advantages. First, HPLC is a separation technique i.e. separated compounds eluted from the chromatographic column are directed to the detector(s). This is extremely useful as most dyes contain several compounds with very similar chemical structures. Consequently, the direct, distinct identification of the dyestuff components, without separation, is usually problematic. Furthermore, mixtures of several dyes have been often used by the dyeing textile industry since antiquity. Second, HPLC provides easily (semi-)quantitative data for the compounds detected in a historical/archaeological sample. This can be extremely important to identify the exact biological source of a dye, as it was shown, for instance, for madder (Wouters 2001), dragon's blood (Sousa et al. 2008) and Tyrian purple (Karapanagiotis et al. 2013; Koren 2008a) species.

HPLC is a micro-sampling technique. Although tiny samples are needed for HPLC analyses, the removal of micro-

samples from some objects, including for instance manuscripts, is practically prohibited. In the case of a textile, however, fibres removed from the object almost effortlessly, because of its physical breakdown can usually provide reliable HPLC results. Furthermore, sampling of a few millimeters of yarn can be performed at the periphery of the textile fragment where the weft and warp yarns are physically crumbling, and thus the physical integrity of the main textile object is maintained (Koren 2008b).

The identification of the colourants contained in historical and archaeological textiles can be important for several reasons, as discussed briefly below.

(i) Dyes correspond to a vast array of chemical compounds with different chemical structures. Natural deterioration and degradation processes developed spontaneously with time, depend highly on the chemical structures of the dyestuff colouring components. For example, in a study where different dyestuff classes were investigated, it was shown that indigo, dragon's blood and curcumin show greater stability in anoxic conditions in comparison with oxygen-rich ones while madder and carminic acid undergo greater degradation (Koperska, et al. 2011). Consequently, the knowledge of the colourants contained in a textile is important to apply effective preventive conservation strategies and maintain appropriate storage conditions.

(ii) The stability of dyes against cleaning procedures, which are applied during textile conservation, is highly affected by the chemical identity of the contained colouring components. Consequently, identification of the materials, including the colourants, that constitute the textile object can prevent damages (e.g. discoloration of the object) which may occur by the use of inappropriate detergents and cleaning methods (Aslanidou et al. 2013).

(iii) Identification of dyes can be important to assess the authenticity of a textile. For example, the identification of Tyrian purple in a religious, ecclesiastical textile of Byzantine origin can be used to date

the object to the Byzantine period, because after the conquest of Constantinople by the Ottomans (start of the post-Byzantine period), the production and use of Tyrian purple stopped abruptly (Karapanagiotis et al. 2013).

(iv) Finally, identification of dyes in a large number of textiles that constitute a particular collection, of the same historical and/or geographical origin, provides useful information with respect to the history of dyes and cultures.

For these reasons, a cooperative project between the research groups of the two authors was implemented to identify the organic colourants contained in textiles which were selected from two important Mediterranean collections: textiles from the Mount Athos in Greece and the Topkapi Palace Museum in Turkey. In particular, HPLC analyses were carried out on samples extracted from forty-six and fifty textiles from monasteries of Mount Athos and the Topkapi Palace Museum, respectively. The investigated textiles correspond roughly to the same historical period, though of different traditions: the objects from the Mount Athos collection are dated between the sixteenth and the early twentieth century. The textiles from the Topkapi Palace Museum fall within a narrower period, from sixteenth to eighteenth century. Mount Athos has been a monastic centre for the Eastern Orthodox Church for centuries, since the early Byzantine times. Consequently, the objects from the Mount Athos collection are ecclesiastical textiles of Byzantine tradition. Objects included in our study from the Topkapi Palace collection are Ottoman textiles. However, it is stressed that for the historical period of interest, Mount Athos was part of the Ottoman Empire. Consequently, the comparison of the analytical HPLC results reported for the two different collections is of great interest, as it can support or reject cross-influence processes between the two cultures, in a period where there were no border restrictions.

In the following, the analysis of a particular textile is presented in detail (section 2).

This case study provides an example, describing the chemical methodology that was followed in the overall investigation, which is described in section 3.

2. CASE STUDY: IDENTIFICATION OF DYES IN A TEXTILE FROM THE TOPKAPI PALACE

2.1 Object

The textile included in the study is a silk velvet (Figure 1, inventory no: 13/1679, Topkapi Palace Museum, Istanbul, Turkey) dated to the sixteenth century.



Figure 1 Silk velvet, 34 x 54 cm (Topkapi Palace Museum, Istanbul, Turkey).

2.2 Experimental

Six samples were removed from the object. Samples were made of silk and corresponded to a variety of colours and hues such as dark red, light red, grey-black, green, bright-yellow and yellow-orange.

Prior to HPLC, samples were treated with methanolic (MeOH) solution of hydrochloric acid (HCl) to extract and solubilize the contained dyes according to the following method (Wouters 1985): (i) sample is immersed in H₂O : MeOH : 37 % HCl (1:1:2, v/v/v) at 100 °C for 15 min. (ii) Then

the liquid phase is evaporated under moderate temperature (65 °C) and gentle nitrogen flow. (iii) The dry residue is dissolved in N,N-dimethylformamide (DMF). (iv) Finally, sample is centrifuged and the upper clear liquid phase is submitted to HPLC analysis.

Samples were analysed using a HPLC system (ThermoQuest) consisted of a P4000 quaternary pump, a SCM 3000 vacuum degasser, an AS3000 autosampler with column oven, a Rheodyne 7725i Injector with 20 µL sample loop and a Diode Array Detector UV 6000LP with a resolution of 1.2 nm. The latter collected spectra from 191 to 799 nm. A reversed phase Alltima HP C18 5 µm column with dimensions 250 mm × 3.0 mm (Alltech Associates) was utilized for separation. The temperature of the column was set to 33 °C. Gradient elution was performed using two solvents consisting of A: 0.1% (v/v) trifluoroacetic acid (TFA) in water and B: 0.1% (v/v) TFA in acetonitrile. The flow rate was 0.5 mL min⁻¹ and the following elution program was applied: 0–1 min: 5% B isocratic; 1–15 min: linear gradient to 30% B; 15–20 min: linear gradient to 60% B; 20–23 min: 60% B isocratic; 23–33 min: linear gradient to 95% B; 33–35 min: 95% B isocratic. Data were received and analyzed using Xcalibur™ (ThermoQuest) software.

2.3 Results and discussion

Figure 2 is provided as an example of a chromatogram collected for a historical sample, extracted from the textile of Figure 1. The colouring compounds detected with HPLC in the samples extracted from the silk velvet are summarized in Table 1. Absorbance maxima of the detected compounds, used for identification purposes, are described in Table 2. Using the data of Table 1, the dyes that were used in the historical object were identified and the results are summarized in Table 3. Identifications summarized in the aforementioned tables are discussed in the following.

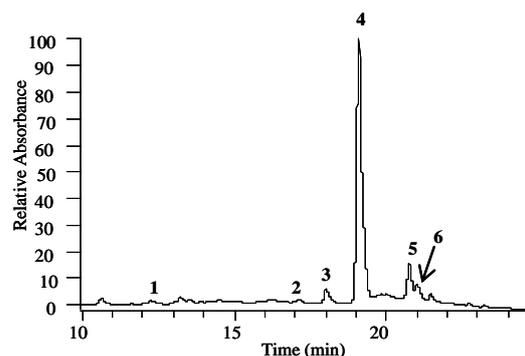


Figure 2 HPLC chromatogram of sample 6, extracted from the textile of Figure 1. The following compounds are identified: (1) carminic acid in trace, (2) fisetin in trace, (3) sulfuretin, (4) luteolin, (5) apigenin and (6) chrysoeriol.

Table 1 HPLC results from samples extracted from the silk velvet, shown in Figure 1.

Sample	Colour	Identified compounds
1	dark red	Carminic acid, Ellagic acid, dcIV, dcVII, Kermesic acid, Flavokermesic acid, Indigotin (trace)
2	light red	Carminic acid, Indigotin (trace)
3	grey-black	Carminic acid, Luteolin (trace), Indigotin, Indirubin
4	green	Luteolin, Apigenin, Chrysoeriol, Indigotin, Indirubin
5	bright-yellow	Fisetin (trace), Sulfuretin, Luteolin, Apigenin, Chrysoeriol
6	yellow-orange	Carminic acid (trace), Fisetin (trace), Sulfuretin, Luteolin, Apigenin, Chrysoeriol

2.3.1 Red samples 1 and 2

The major dye contained in both red samples (1 and 2) is cochineal. This result is based on the detection of carminic acid which is the marker compound for the identification of cochineal. The coccid dye was found in high amounts in the dark red sample (1) allowing thus the detection of other, minor components of cochineal such as dcIV, dcVII, kermesic acid and flavokermesic acid (Table 1). It is noteworthy that the dcII compound, which is the 2-C-glucoside of flavokermesic acid (Statho-

poulou et al 2013), was not detected in the historical sample and therefore the potential use of Mexican cochineal in the silk velvet is unlikely (Wouters and Verhecken 1989). Furthermore, kermesic and flavokermesic acid were detected in very small amounts. These results suggest that Armenian cochineal (*Porphyrophora hameli* Brandt) should have been used for the treatment of sample 1 (Wouters and Verhecken 1989).

Less amount of cochineal was contained in the light red sample (2) and therefore minor components of the coccid dye were not detected in the chromatogram of this sample (Table 1).

Table 2 UV-Vis absorbance maxima of compounds which were identified in the samples of Table 1.

Identified compound	Absorbance maxima (nm)
Apigenin	221, 267, 337
Carminic acid	223, 275, 309, 493
Chrysoeriol	223, 249, 267, 345
dcIV	225, 275, 311, 487
dcVII	223, 277, 309, 487
Ellagic acid	213, 253, 367
Fisetin	219, 247, 321, 359
Flavokermesic acid	223, 283, 343, 431
Indigotin	215, 241, 285, 330, 605
Indirubin	217, 239, 289, 363, 539
Kermesic acid	223, 273, 307, 489
Luteolin	223, 253, 265, 345
Sulfuretin	257, 377, 397

Table 3 Dyes found in the historical samples, according to the identifications of Table 1.

Sample	Dye
1	cochineal, woad/indigo
2	cochineal, woad/indigo
3	woad/indigo, cochineal, weld(?)
4	woad/indigo, weld
5	weld, young fustic
6	weld, young fustic, cochineal

It is interesting to note that the structures of the dcIV and dcVII compounds, detected in sample 1, had remained unknown for a long time. A recent study (Stathopoulou et al 2013), where Nuclear Magnetic Resonance (NMR) and Mass Spectrometry (MS) were employed, showed that the two compounds are α/β C-glucofuranosides of kermesic acid, as shown in Figure 3.

Interestingly, in both red samples 1 and 2 a small amount of indigotin (in trace) was detected, thus suggesting the presence of

an indigoid dyestuff source in both samples. Indigotin is contained in woad (*Isatis tinctoria* L.) and indigo (*Indigofera* species e.g. *Indigofera tinctoria* L.). Woad has been known since antiquity worldwide, while indigo has been imported to the Mediterranean area from India since antiquity (Hofenk de Graaff 2004). Therefore, considering the date of the tested object, its geographical provenance and the fact that indigo and woad cannot be distinguished by HPLC, we cannot reach any specific conclusion with respect to the actual blue dyestuff source used in the silk velvet. It can be either indigo or woad.

Finally, the detection of ellagic acid in sample 1 suggests the use of a tannin product during dyeing. Tannins have been used both as dyes to induce dark-black hues in textiles and as dyestuff adhesives (Hofenk de Graaff 2004).

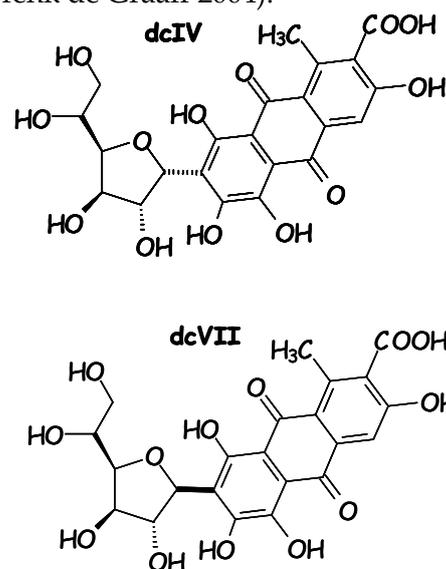


Figure 3 Structures of the dcIV and dcVII components of cochineal which were recently identified (Stathopoulou et al 2013).

2.3.2 Yellow samples 5 and 6

Weld (*Reseda luteola* L.) in mixture with small amounts of young fustic (*Cotinus coggygria* Scop.) were the main dyeing materials used in the yellow samples 5 and 6, according to Table 3. Detected compounds, reported in Table 1, such as luteolin, apigenin and chrysoeriol are contained in weld while fisetin and sulfuretin are components of young fustic (Valianou et al. 2009). Fur-

thermore, a small amount of carminic acid was detected in sample 6, suggesting the presence of traces of cochineal. This might be the reason for the slight colour difference of samples 5 and 6; the former was bright-yellow, while the yellow colour of sample 6 was more reddish (orange).

2.3.3 Green sample 4

The green colour of sample 4 was produced by mixing a blue indigoid dyestuff (either woad or indigo) with the yellow weld (Table 3). Mixing of the two plant dyestuff sources to dye textiles used to be a common procedure. Figure 4 shows, for instance, wool dyed green using indigo and weld, following traditional recipes.



Figure 4 Wool treated with indigo and weld obtaining thus the green colour.

2.3.4 Grey sample 3

An indigoid dyestuff was the main colouring material in sample 3. Both indigotin, the marker compound for the identification of either woad or indigo, and indirubin which is contained in the blue dyestuffs in smaller amounts, compared to indigotin, were detected with HPLC, according to the results of Table 1.

Apart from the indigoid compounds which were recorded in the HPLC chromatogram in high amounts, carminic acid (marker component of cochineal) and luteolin were also detected (Table 1). The detection of luteolin leads to the conclusion that a yellow, luteolin-based dye was used to treat sample 3. No other yellow colouring compound, apart from luteolin, was detected and therefore it is not possible to reach a clear conclusion regarding the natural source of luteolin identified in sample 3. It is important to note, however, that luteolin is contained in weld in higher

amounts than apigenin and chrysoeriol. This is illustrated in Figure 2, where the three weld components labelled 4, 5 and 6 are detected in the chromatogram of sample 6. Consequently, the absence of apigenin and chrysoeriol in the results of sample 3, in which luteolin was detected in small amount, can be attributed to the possible small quantity of weld used in this historical sample. Because weld is the only luteolin-based colourant detected in the other samples (4, 5 and 6) of the silk velvet, it is quite possible that the same plant was used for the treatment of sample 3.

3. DYES IN TEXTILES FROM MONASTERIES OF MOUNT ATHOS AND THE TOPKAPI PALACE MUSEUM

HPLC investigations were also carried out on forty-six (46) ecclesiastical textiles from Mount Athos. The textiles studied are dated between sixteenth to early twentieth century and belong to various monasteries of Mount Athos. Of these, thirty textiles belong to the monastery of Simonos Petra, and nine to the Xeropotamou monastery. Natural dyes identified in the post-Byzantine textiles are summarized in Figure 5a. The HPLC results are presented in a plot: the y-axis corresponds to the number of objects and x-axis describes the identified natural dyes. Consequently, Figure 5a provides an indication about the frequency of use of each natural product by the dyer's of the ecclesiastical objects.

The following natural colouring materials were identified in the textiles of Byzantine origin (Figure 5a): cochineal, soluble redwood, madder, lac (red dyes); young fustic, weld, dyer's broom, old fustic, buckthorn berries (yellow dyes); woad/indigo, logwood (blue dyes); moreover, tannins were detected in several objects. It must be noted that only natural colourants are included in the plot of Figure 5a. In addition to the natural materials, semi-synthetic dyes, such as indigo carmine, fuchsine and rhodamine B were identified in some textiles dated from late nineteenth to early twentieth century.

The HPLC results collected for fifty Ottoman textiles (sixteenth to eighteenth century), which are preserved in the Topkapi Palace Museum, are summarized in Figure 5b. The following natural materials are included in Figure 5b: cochineal, *Rumex* species, madder, lac (red dyes); young fustic, weld, dyer's broom, chamomile, buckthorn berries (yellow dyes); woad/indigo (blue dyes); moreover, tannins were detected in several objects.

Comparison of the results reported in the two plots of Figure 5 is discussed later. In the following, we first focus on the materials included in Figure 5.

3.1 Red dyes

Cochineal is clearly the most commonly used red dye in the objects of the two Mediterranean collections. This coccid dye was discussed previously in section 2.3.1.

Soluble redwood (*Caesalpinia* trees) was found in several post-Byzantine textiles (Figure 5a). The identification of this red dye was achieved by the detection of the type B and type C compounds, which are used as markers for the identification of soluble redwood in historical samples (Nowik 2001). The exact structures of these two compounds are unknown. It was shown, however, that the type B compound is a dehydro-brazilein product, produced probably during the acid hydrolysis step of the dyestuff extraction process (Karapanagiotis et al. 2009). This conclusion was based on detailed LC-MS studies which showed that the deprotonated molecular ion of the type B compound corresponds to $m/z = 265$. Comparison of this result with the deprotonated ion of brazilein ($m/z = 283$), suggests that the type B compound should be a dehydro-brazilein product. For the type C compound, it was recently suggested that it may be a photodegradation product of redwood (Manhita et al. 2013). According to a LC-MS study, the deprotonated molecular ion of the type C compound corresponds to $m/z = 243$ (Karapanagiotis et al. 2009).

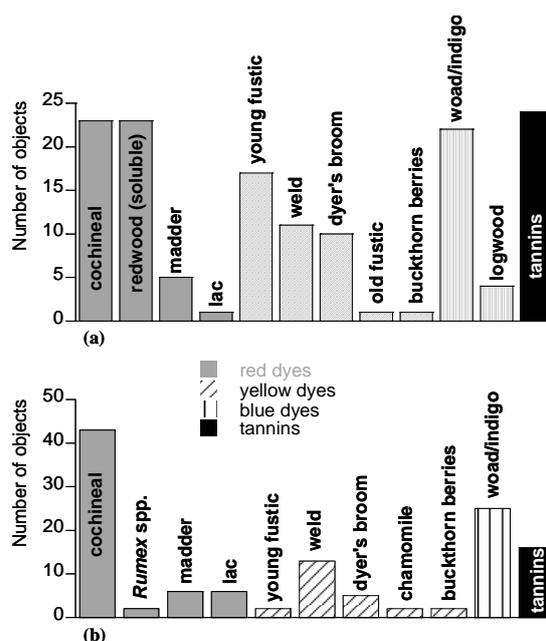


Figure 5 Dyes identified in (a) forty-six and (b) fifty textiles from monasteries of Mount Athos and the Topkapi Palace Museum, respectively.

According to the results of Figure 5, madder was found in textiles of both, post-Byzantine and Ottoman, collections. Identification of madder was based on the detection of purpurin and alizarin, as shown for instance in Figure 6, where the chromatogram of a sample removed from an ecclesiastical object is shown. Other compounds, such as carminic acid, dcIV, dcVII (cochineal components) and ellagic acid (tannin component) are reported in the chromatogram.

In the Mediterranean area there are two species of the *Rubiaceae* family which are dominant and have been used for dyeing since antiquity: *Rubia tinctorum* L., known as common madder and *Rubia peregrina* L., known as wild madder. The chromatogram of Figure 6 shows that alizarin and purpurin are present in comparable amounts. Furthermore, rubiadin, which is usually present in *Rubia peregrina* L. (Wouters 2001) in high amounts, is not detected in Figure 6, thus suggesting that the madder source used to dye the Epitachelion was probably *Rubia tinctorum* L.

It is stressed that the HPLC profiles of the other historical samples where alizarin and purpurin were detected, were similar

with the graph shown in Figure 6: alizarin was always found in comparable amounts with purpurin and rubiadin was not detected. Consequently, the above discussion related to the identification of the madder species used in the sample of Figure 6, can be extended to the other historical samples where madder was identified. Therefore it is concluded that the madder dye reported in Figure 5 was originated from *Rubia tinctorum* L.

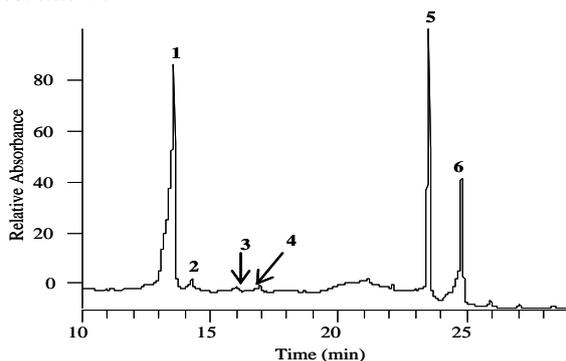


Figure 6 HPLC chromatogram of a red sample extracted from a post-Byzantine Epitrichilion (seventeenth century). The following compounds are identified: (1) carminic acid, (2) ellagic acid, (3) dcIV, (4) dcVII, (5) alizarin and (6) purpurin.

Apart from cochineal, soluble redwood and madder discussed so far, other red dyes included in the results of Figure 5 are lac (*Kerria lacca*, Kerr) and *Rumex* species, detected in few post-Byzantine (lac) and Ottoman (lac and *Rumex* species) textiles. Lac is a coccid dye that contains laccaic acids A, B, C and D (Hofenk de Graaff 2004). It was a common dye and has been reported in several HPLC studies on historical textiles (Hofenk de Graaff 2004). On the contrary, the use of *Rumex* species to dye textiles is not reported very often (Petrović et al. 2012b).

3.2 Yellow dyes

The three most important yellow dyes found in the post-Byzantine textiles (Figure 5a) are young fustic, weld (discussed previously in section 2.3.2) and dyer's broom. These three materials were identified also in Ottoman textiles (Figure 5b) with weld being clearly the most commonly used. Dyer's broom is a material of plant origin

(*Genista tinctoria* L.) which has been used to dye textiles since antiquity. Dyer's broom contains genistein, luteolin, apigenin and other flavonoids (Mantzouris et al. 2011).

Another yellow dye found in objects from both collections is buckthorn berries (*Rhamnus* trees). The material was identified in only one post-Byzantine (Figure 5a) and two Ottoman (Figure 5b) textiles. A detailed LC-MS investigation showed that the dye contains several colouring compounds including rhamnnetin, rhamnazin and emodin, which are usually present in high amounts (Mantzouris and Karapanagiotis 2013).

Finally, other yellow dyes included in Figure 5 are old fustic (*Chlorophora tinctoria* L.) and dyer's chamomile (*Anthemis* species) which were found in few post-Byzantine and Ottoman textiles, respectively, according to the results of Figure 5.

3.3 Blue dyes

As expected, indigoid dyes (woad/indigo) were commonly used in the textiles of both collections. Woad and indigo were discussed above, in section 2. Another blue dye included in the results of Figure 5 is logwood (*Haematoxylum campechianum* L.) which was identified in four post-Byzantine textiles (Figure 5a). Logwood is an interesting dye both for historians and chemists. Historically, it is important to note that logwood is native to America (Hofenk de Graaff 2004) and therefore it was imported to the European continent after the discovery of the New World (1492), which occurred in the same historical period as the fall of the Byzantine Empire (1453). Consequently, the identification of logwood in ecclesiastical textiles provides chemical evidence that the objects belong to the post-Byzantine (and not to the Byzantine) period. From a chemical point of view, it is interesting to note that the identification of logwood in a historical sample treated with the HCl method (Wouters 1985) is based on the detection of a haematein derivative, which is produced after acid hydrolysis (Hulme et al. 2005).

3.4 Tannins

According to the results of Figure 5, tannins were extensively used in the objects of both collections. The identification of tannin products in many post-Byzantine and Ottoman textiles is not surprising, because these materials have been used as adhesives to promote the stabilization of colourants on textile substrates (Hofenk de Graaff 2004). Consequently, the use of a tannin product can be included in the dyeing recipe of any dyestuff. Furthermore, tannins were also used as colourants, to induce dark-black hues in textile fibres.

3.5 Comparison of dyes found in the two collections

Comparison of the natural colouring materials found in the post-Byzantine (Figure 5a) and Ottoman (Figure 5b) textiles leads to interesting comments, as follows.

Most colourants included in Figure 5 were found in both collections: cochineal, madder, lac, young fustic, weld, dyer's broom, buckthorn berries, woad/indigo and tannins are reported in both Figures 5a and 5b.

On the other hand, soluble redwood, old fustic and logwood were found only in post-Byzantine objects (Figure 5a) while *Rumex* species and chamomile are included only in Figure 5b (Ottoman textiles). However, among these five dyes only soluble redwood was found in a large number of objects; old fustic was found in only one textile, *Rumex* species and chamomile in two, and logwood was identified in four objects. Soluble redwoods have been used in Eurasia from ancient times (Hofenk de Graaff 2004). Consequently, the identification of this red dye in twenty two post-Byzantine textiles is not surprising. Its absence from the results of Figure 5b should not be taken into account to underestimate the important role of soluble redwoods in the dyeing industry of the East. The results of Figure 5 should be evaluated alongside with other reports, which indicate that soluble redwoods have been often used in the Orient from ancient times (Hofenk de

Graaff 2004; Karapanagiotis et al. 2011; Verhecken 2005).

Another dye which has been extensively used in the Mediterranean since antiquity is kermes (*Kermes vermilio* Planchon). It is noteworthy that this coccid dye was not found in any of the studied post-Byzantine and Ottoman textiles and therefore is not included in the results of Figure 5.

Another interesting observation that is worth mentioned is the identification of young fustic in a relatively large number of ecclesiastical textiles. According to the results of Figure 5a, young fustic was found in seventeen post-Byzantine objects. On the contrary, it was found only in two Ottoman textiles. This result may suggest that *Cotinus coggygria* had probably an important role in the ecclesiastical textiles. Although this speculation should be taken into account cautiously, it must be noted that it is supported by previously published reports, which describe the identification of young fustic in Italian ecclesiastical garments (Hofenk de Graaff 2004).

Overall, more similarities than differences are observed between the results reported in Figures 5a (post-Byzantine textiles) and 5b (Ottoman textiles). As described previously, most of the identified dyes are reported in both figures. Furthermore, cochineal is the most commonly used coccid red dye in both post-Byzantine and Ottoman textiles of Figure 5. Lac, the other dye of insect origin included in Figure 5, was scarcely identified. Kermes was not found in any post-Byzantine or Ottoman textile. Among the yellow dyes, weld was widely used as it was found in eleven and twelve post-Byzantine and Ottoman textiles, respectively. Natural indigoid dyes (woad/indigo) are included in the results of blue dyes reported in both Figures 5a and 5b.

4. CONCLUSIONS

The following organic colourants were identified in both post-Byzantine (sixteenth to early twentieth century) and Ottoman (sixteenth to eighteenth century) textiles, which are preserved in monasteries of

Mount Athos (Greece) and the Topkapi Palace Museum (Turkey), respectively: cochineal, madder (*Rubia tinctorum* L.), lac (*Kerria lacca*, Kerr), young fustic (*Cotinus coggygria* Scop.), weld (*Reseda luteola* L.), dyer's broom (*Genista tinctoria* L.), buckthorn berries (*Rhamnus* trees), indigoid dyes, either indigo (*Indigofera* species and others) or woad (*Isatis tinctoria* L.) and tannins.

Furthermore, soluble redwood (*Caesalpinia* trees), old fustic (*Chlorophora tinctoria* L.) and logwood (*Haematoxylum campechianum* L.) were found only in textiles of Byzantine origin while dyer's chamomile (*Anthemis* species) and *Rumex* species were detected only in few objects from the Topkapi Palace Museum.

The aforementioned identifications were achieved using HPLC-DAD which was employed to investigate forty-six and fifty post-Byzantine and Ottoman textiles, respectively. As described above, the same colouring materials were mostly identified in the two textile collections of different

cultural identities. This result suggests that the pronounced differences in the styles and motives of the textiles representing the two different, Byzantine and Ottoman, cultures were not accompanied by the use of different dyes. On the contrary, a common dyeing industry might have been developed after the fall of Constantinople, which provided the same coloured textile fibres to the Ottoman and Christian fabric producers. The cultural identity of a textile was given during the production of the fabric, by inducing the appropriate style, design and motive.

However, young fustic can be excluded from the above described conclusion, because this material was found in many and few post-Byzantine and Ottoman textiles, respectively. Consequently, the yellow flavonoid dye may have had a distinguished role in the ecclesiastical textiles of the Eastern and Western Churches, according to the results of Figure 5a and previously published studies (Hofenk de Graaff 2004).

REFERENCES

- Aslanidou, D., Tsiopstias, C. and Panayiotou, C. (2013) A novel approach for textile cleaning based on supercritical CO₂ and Pickering emulsions, *The Journal of Supercritical Fluids*, vol. 76, 83-93.
- Brosseau, C.L., Gambardella, A., Casadio, F., Grzywacz, C.M., Wouters, J., Van Duyne, R.P. (2009) Ad-hoc Surface-Enhanced Raman Spectroscopy methodologies for the detection of artist dyestuffs: Thin Layer Chromatography-Surface Enhanced Raman Spectroscopy and in situ on the fiber analysis, *Analytical Chemistry*, vol. 81, 3056-3062.
- Casadio, F., Leona, M., Lombardi, J.R. and van Duyne, R. (2010) Identification of organic colorants in fibers, paints, and glazes by surface enhanced Raman spectroscopy, *Accounts for Chemical Research*, vol. 43, 782-791.
- Deveoglu, O., Erkan, G., Torgan, E. and Karadag, R. (2013) The evaluation of procedures for dyeing silk with buckthorn and walloon oak on the basis of colour changes and fastness characteristics, *Coloration Technology*, vol. 129, 223-231.
- Deveoglu, O., Torgan, E. and Karadag, R. (2012) High-performance liquid chromatography of some natural dyes: analysis of plant extracts and dyed textiles, *Coloration Technology*, vol. 128, 133-138.
- Ferreira, E.S.B., Quye, A., McNab, H., Hulme, A.N., Wouters, J. and Boon, J.J. (2001) Development of analytical techniques for the study of natural yellow dyes in historic textiles, *Dyes in History and Archaeology*, vol. 16/17, 179-186.

- Gulmini, M., Idone, A., Diana, E., Gastaldi, D., Vaudan, D. and Aceto M. (2013) Identification of dyestuffs in historical textiles: strong and weak points of a non-invasive approach, *Dyes and Pigments*, vol. 98, pp. 136-145.
- Hofenk-de Graaff, J.H. (2004) *The Colourful past: origins, chemistry and identification of natural dyestuffs*, Abegg-Stiftung & Archetype Publications Ltd., Riggisberg, Switzerland & U.K.
- Hulme, A.N., McNab, H., Peggie, D.A., Quye, A., Vanden Berghe, I. and Wouters, J. (2005) Analytical characterization of the main component found in logwood-dyed textile samples after extraction with hydrochloric acid, *ICOM 14th Triennial Meeting*, Earthscan Publications Ltd., London, U.K., 783-788.
- Karadag, R. and Yurdan, T. (2010) Dyestuff and colour analyses of the Seljuk carpets in Konya ethnographic museum, *Studies in Conservation*, vol. 55, supplement 2, 178-183.
- Karapanagiotis, I., Mantzouris, D., Cooksey, C., Mubarak, M.S. and Tsiamyrtzis P. (2013) An improved HPLC method coupled to PCA for the identification of Tyrian purple in archaeological and historical samples, *Microchemical Journal*, vol. 110, pp. 70-80, 2013.
- Karapanagiotis, I., Minopoulou, E., Valianou, L., sister Daniilia and Chryssoulakis, Y. (2009) Investigation of the colourants used in icons of the Cretan school of iconography, *Analytica Chimica Acta*, vol. 647, 231-242.
- Karapanagiotis, I., Theologou, J., Lakka, A., Ozoline A. and Panayiotou, C. (2011) Investigation of the Colouring Materials of Fustat Carpet Fragments, *Archaeometry*, vol. 53, 587-599.
- Koperska, M., Łojewski, T. and Łojewska, J. (2011) Vibrational spectroscopy to study degradation of natural dyes. Assessment of oxygen-free cassette for safe exposition of artefacts, *Analytical and Bioanalytical Chemistry*, vol. 399, 3271-3283.
- Koren, Z.C. (1999) Microscopic and chromatographic analyses of decorative band colors on Nabatean 'En Rahel textiles - Kermes and shaded bands, *Atiqot*, vol. 38, 129-136.
- Koren, Z.C. (2008a) Archaeo-chemical analysis of Royal Purple on a Darius I stone jar, *Microchimica Acta*, vol. 162, 381-392.
- Koren, Z.C. (2008b) Non-destructive vs. Microchemical analyses: The case of dyes and pigments, *9th international conference on non destructive investigations and microanalysis for the diagnostics and conservation of cultural and environmental heritage (ART2008)*, 37.1-37.10.
- Leona, M. and Lombardi, J.R. (2007) Identification of berberine in ancient and historical textiles by surface-enhanced Raman scattering, *Journal of Raman Spectroscopy*, vol. 38, 853-858.
- Manhita, A., Santos, V., Vargas, H., Candeias, A., Ferreira, T. and Dias, C.B. (2013) Ageing of brazilwood dye in wool - a chromatographic and spectrometric study, *Journal of Cultural Heritage*, vol. 14, 471-479.
- Mantzouris, D. and Karapanagiotis, I. (2013) Identification of kaempferol in historical textiles: a case study on textiles of byzantine origin, In, *Kaempferol: Chemistry, Natural Occurrences and Health Benefits*, Villers G. and Fougere Y. (eds), Nova Science Publishers, Inc., New York.
- Mantzouris, D., Karapanagiotis, I., Valianou, L. and Panayiotou, C. (2011) HPLC-DAD-MS analysis of dyes identified in textiles from Mount Athos, *Analytical and Bioanalytical Chemistry*, vol. 399, 3065-3079.
- Nowik, W. (2001) The possibility of differentiation and identification of red and blue soluble dyewoods, *Dyes in History and Archaeology*, vol. 16/17, 129-144.

- Nowik, W., Desrosiers, S., Surowiec, I. and Trojanowicz, M. (2005) The analysis of dyestuffs from first- to second-century textile artefacts found in the Martres-de-Veyre (France) excavations, *Archaeometry*, vol. 47, 835-848.
- Petroviciu, I., Albu, F. and Medvedovici A. (2010) LC/MS and LC/MS/MS based protocol for identification of dyes in historic textiles, *Microchemical Journal*, vol. 95, 247-254.
- Petroviciu, I., Vanden Berghe, I., Cretu, I., Albu, F. and Medvedovici A. (2012a) Identification of natural dyes in historical textiles from Romanian collections by LC-DAD and LC-MS (single stage and tandem MS), *Journal of Cultural Heritage*, vol. 13, pp. 89-97.
- Petroviciu, I., Cretu, I., Vanden Berghe, I., Wouters, J., Medvedovici, A., Albu, F., Creanga, D. (2012b) A discussion on the red anthraquinone dyes detected in historic textiles from Romanian collections, *e-Preservation Science*, vol. 9, 90-96.
- Pozzi, F., Poldi, G., Bruni, S., De Luca, E. and Guglielmi V. (2012) Multi-technique characterization of dyes in ancient Kaitag textiles from Caucasus, *Archaeological and Anthropological Sciences*, vol. 4, 185-197.
- Rosenberg, E. (2008) Characterisation of historical organic dyestuffs by liquid chromatography-mass spectrometry, *Analytical and Bioanalytical Chemistry*, vol. 391, 33-57.
- Serrano, A., Sousa, M.M., Hallett, J., Lopes, J.A. and Oliveira, M.C. (2011) Analysis of natural red dyes (cochineal) in textiles of historical importance using HPLC and multivariate data analysis, *Analytical and Bioanalytical Chemistry*, vol. 401, 735-743.
- Sousa, M.M., Melo, M.J., Parola, A.J., de Melo, J.S.S., Catarino, F., Pina, F., Cook, F.E.M., Simmonds M.S.J. and Lopes J.A. (2008) Flavylum chromophores as species markers for dragon's blood resins from *Dracaena* and *Daemonorops* trees, *Journal of Chromatography A*, vol. 1209, 153-161.
- Stathopoulou, K., Valianou, L., Skaltsounis, A.-L., Karapanagiotis, I. and Magiatis, P. (2013) Structure elucidation and chromatographic identification of anthraquinone components of cochineal (*Dactylopius coccus*) detected in historical objects, *Analytica Chimica Acta*, vol. 804, 264-272.
- Stuart, B. (2007) *Analytical techniques in materials conservation*, John Wiley & Sons, Ltd, U.K.
- Surowiec, I., Orska-Gawryś, J., Biesaga, M., Trojanowicz, M., Hutta, M., Halko R. and Urbaniak-Walczak K. (2003) Identification of natural dyestuff in archeological Coptic textiles by HPLC with fluorescence detection, *Analytical Letters*, vol. 36, 1211-1229.
- Szostek, B., Orska-Gawryś, J., Surowiec, I. and Trojanowicz, M. (2003) Investigation of natural dyes occurring in historical Coptic textiles by high-performance liquid chromatography with UV-Vis and mass spectrometric detection, *Journal of Chromatography A*, vol. 1012, 179-192.
- Valianou, L., Stathopoulou, K., Karapanagiotis, I., Magiatis, P., Pavlidou, E., Skaltsounis, A.-L. and Chryssoulakis, Y. (2009) Phytochemical analysis of young fustic (*Cotinus coggygia* heartwood) and identification of isolated colourants in historical textiles, *Analytical and Bioanalytical Chemistry*, vol. 394, 871-882.
- Verhecken, A. (2005) Relation between age and dyes of 1st millennium AD textiles found in Egypt, In *Methods of dating ancient textiles of the 1st millennium AD from Egypt and neighbouring countries*, de Moor A., and Fluck C. (eds), Tielt, Belgium.
- Wouters, J. (1985) High performance liquid chromatography of anthraquinones: analysis of plant and insect extracts and dyed textiles, *Studies in Conservation*, vol. 30, 119-128.

- Wouters, J. (2001) The dye of *Rubia peregrina* - Preliminary investigations, *Dyes in History and Archaeology*, vol. 16/17, 145-157.
- Wouters, J. and Verhecken A. (1989) The coccid insect dyes: HPLC and computerized diode-array analysis of dyed yarns, *Studies in Conservation*, vol. 34, 189-200.
- Yurdun, T., Karsli-Ceppioglu, S. and Gurcan Oraltay, R. (2012) Investigation of metal wired coloured historical textile using Scanning Electron Microscopy and HPLC-DAD, *Journal of Chemistry and Chemical Engineering*, vol. 6, 591-598.
- Zhang, X., Boytner, R., Cabrera, J.L. and Laursen R. (2007) Identification of yellow dye types in pre-Columbian Andean textiles, *Analytical Chemistry*, vol. 79, 1575-1582.