Identification of Natural Dyes on 18th Century Liturgical Textiles from Dubrovnik

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Abstract
In this paper researches were carried out on fragments of textiles from the 18th century from Dubrovnik, for which, based on the design and art-historical analysis, it was determined that it was a part of an object (pluvial, cope) from liturgical vestments (ecclesiastical textiles) of the Dubrovnik diocese. Using modern non-destructive and micro-destructive methods we conducted the identification of green, blue and red as the dominant tones on the artefacts of historical textiles from Dubrovnik. The identification was based on the application of modern complementary techniques: UV/VIS, HPLC, SEM-EDX and FTIR-ATR. We analysed samples of coloured fiber, as well as ones obtained by the extraction of dyes from the dyed fibers. Archival data on natural dyes used in the Dubrovnik region in the period 14-19th century was taken into account in the identification of the historical textile dyes.

Key words: natural dyes, liturgical textile, UV/VIS, SEM-EDX, FTIR-ATR, HPLC, Dubrovnik.

Introduction

The Dubrovnik Republic (lat. Ragusina Republica) was located in the south of the present-day Republic of Croatia. Its peak of economic power was in the XV and XVI century, when it was counted among the most developed countries in the world. It was a country with highly developed maritime economy and independent trading. The richness and splendour of that time is also witnessed in preserved textile objects made of expensive fabric such as brocade, damask and satin, now the property of the Museum of Dubrovnik and Roman Catholic Diocese of Dubrovnik (lat. Dioecesis Ragusinensis) [1].

Many scientific articles deal with research on historic textiles, and their aim is to certify the origin, production techniques, ways of painting and source of dyes, which is also the aim of this paper [2-6]. Analysis of dyes in dyed fibers can be used to confirm the dating of objects and to distinguish the original from a copy, which helps to choose the right conservation and restoration treatments, determine the stability and durability of the original colour on the fabric, and provides an insight into the original appearance of the artwork.

Natural dyes have a very complex chemical structure and composition, which determines the application of modern sophisticated analytical methods of analysis and identification [7-11].

From a review of scientific papers related to this issue, it is evident that the beginning of the 20th century marks the awakening of interest in historical textile and methods of analysis of natural dyes. Separation techniques, such as chromatographic analysis, require an acceptable sample preparation for analysis that usually involves the extraction of dyes from the fibers. In the literature many different methods of the extraction of dyes from fibers are mentioned, and their selection depends on the qualitative and quantitative amount of information that is obtained by extraction. Many papers describe the extraction of dyes with methanol in an acidic medium (HCl/methanol/water 2:1:1) [12-18]. However, with this method glycoside linkages and carboxylic acid are hydrolysed, thus there is an irreversible loss of information about their possible presence on dyed textiles [19, 20]. A mild extraction method given by Zhang and Laursen using 5% formic acid (HCOOH) in MeOH solution proved to be more efficient when extracting anthraquinone and flavonoid dyes from dyed silk, wool and cotton fibres, further preserving glycosidic linkages [18]. Extraction from dyes from coloured textile fibers with hydrochloric acid (3 M) and methanol (1:1, v/v) at a temperature of 100°C, was proven effective for the extraction of anthraquinone and flavonoid dyes from textile fibers [21, 22]. However, in practice this method has proved to be ineffective for the extraction of indigo and indirubin [23].

The methods most commonly used in the identification of dyes are UV/VIS spectrophotometry, then confirmation with chromatographic techniques, such as High-Performance Liquid Chromatography (HPLC) [10, 12, 24-31]. The results of the international Eu-ARTECH project, starting in 2005, showed that the different chromatographic test conditions, in different laboratories, affect the quality of the chromatic separation of components, but they have very little effect on the analytical results, which significantly depend on the optimal method of extraction of dyes. In the literature references for the analysis of historical textile dyes with the HPLC method, crucial is the choice of wavelength detection [29, 32].

Many studies on the determination of the presence of dyes on fiber used infrared spectroscopy [33-38]. With this method Hofken de Graaff in 1969 analysed some natural dyes, and Schwerppe in 1975 focused on indigo. The application of the attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (ATR-FTIR) has proven extremely useful for a small quantity of samples of historical textile materials.

Characteristic of most of the natural dyes derived from plant or animal sources is that they are able to form complexes with metal salts, whereby the colour tone changes depending on the choice of metal (aluminum, chromium, copper, iron and tin). The presence of metal in the structure of coloured fibers can be detected with a scanning electron microscope with an Energy Dispersive X-ray Detector (Scanning Electron Microscopy /Energy Dispersive Spectroscopy, SEM – EDX) [12, 37-43].

For successful analysis of dyes, the best choice has proved to be a combination of different research techniques, which, as mutually complementary, provide a wide range of useful data.
On the historical textiles from Dubrovnik, using modern non-destructive and micro-destructive methods, an analysis of green, blue and red colour tones was done. To get the blue colour tones in Dubrovnik, the most commonly used was Vrbovnik (woad; Isatis tinctoria L.) and some type of lichen, as well as indigo (Indigofera tinctoria L.), which was imported, while in the whole area of Europe the dominant raw material for getting tons of yellow was Katanac (weld; Reseda luteola L.) [44,45]. The yellow colour tone was obtained from the bark of wild apple trees (Malus sylvestris), or from that of maritime rose hip (Punica granatum L.) [44]. Due to the fact that green colour was usually obtained from a mixture of natural dyes, its analysis is much more complex. Thus according to the data from literature, green tones in the Dubrovnik area were obtained by boiling young mulberry leaves (Morus sp.) or by mixing yellow with blue or black ink. Since the entire area of Dalmatia was abundant with mulberry trees, this raw material was also used in the production of high quality silk; thus it was recorded that silk cocoons were sold to Milanese silk factories, at a high price from 1.60 to 2.30 florins per pound. Various shades of red, according to written sources, were obtained from the bark of the Brazilwood (Caesalpinia echinata), dried female scale insects (Kermes vermilio), sea snails (Murex trunculus) or dried roots of the Madder plant (Rubia tinctorum L.) [44-50].

The identification of dyes on the textile artifact from the 18th century was based on the application of modern complementary techniques: UV/VIS, HPLC, SEM-EDX and FTIR-ATR.

**Experimental**

**Material**

Analyses were performed on a fragment of textiles originating from a cope (known in Latin as pluviale) (Figure 1, inv. No. PT) that was once part of a set of liturgical vestments which consisted of 16 objects made from the same fabrics and techniques. Data about this were written by hand in the inventory of the cathedral in Dubrovnik from 1951. Today preserved are only 3 objects: the chasuble, dalmatic and pluvial, which are stored in Dubrovnik Cathedral of the Assumption of Mary, built in 1713 after the previous cathedral was destroyed in an earthquake. The set is dated to the Rococo style period, the time around 1750. Although the documents from the archives of the cathedral nowhere specify its origin and date of acquisition, this liturgical set can yet be linked to the purchase of textile for the cathedral in the 18th century [51-53].

**Analysis methodology**

In the case of samples from Cultural Heritage, due to the small quantity of material, the analysis methodology is given as follows (Figure 2).

**Instrumentation and software**

Analysis the current situation of artefacts was investigated using a scanning electron microscope. By applying SEM – EDX (Quantax, Bruker AXS Microanalysis), metals in the dyed fibers were detected.

The dyed samples of fibers from the 18th century and undyed samples of silk fibers were recorded by FTIR-ATR (Perkin Elmer Spectrum 100, USA) in four scans at a resolution of 4 cm⁻¹ in a wavelength range from 4000 to 400 cm⁻¹. Analysis of the spectra obtained was carried out using software for data processing – OMNIC Spectra Software 9.1.24. For analysis of the extract solution of dyes, the following methods were used: UV/VIS (spectrophotometer Varian Cary® 50, USA) and HPLC (Agilent 1220, Hewlett-Packard, Germany) – the chromatographic system was controlled by ChemStation software.

HPLC conditions:– C18 column 4.6 x 150 mm, 5 μm (4.6 x 150 mm and 5 μm particle size, ZORBAX Eclipse XDB (Agilent Technologies 1220), mobile phase A = 10% of methanol/water, v/v, B = 100% of methanol, gradient at start 16% B, at 15 min 90% B, at 23 min 100% B and 30 min 60% B, flow rate 0.5 ml/min, temp. 25°C, injection vol. 10 ml, identification wavelength 254 nm.

**Reagents**

All reagents were analytical grade: methanol (HPLC-hipergradient grade), dimethylformamide DMF (HPLC – gradient grade), formic acid (HPLC – gradient grade) from Merck, Germany.

As a database of natural dyes for HPLC analysis, various sources in literature were used: [2, 15, 29, 30, 57, 58], data Eu-ARTECH Project (Eu-ARTECH Project – Analytical strategies for natural dyestuffs and cultural heritage objects, http://www.organic-colourants.org; 10.05.2013.)

Extraction of dyes from textile and analysis

Fibers (0.002 g) were treated in a solution of 5% Formic acid /MeOH at 100°C for 10 minutes. After treatments, solutions were filtered with a filter (Chromafil PET – 45/25, Macherey-Nagel). The solvent then evaporates. A volume of 250 μl of the mixture MeOH; DMF (1:1, v/v) was added to the dry residue, and the mixture was heated for 5 min. at 100°C. Measured – HPLC, UV/VIS.

Results and discussions

Heritage preservation of historical textiles demands an interdisciplinary approach. Fundamental to preservation is to begin planned research and analysis using non-destructive methods, with the key element being the choice of proper methods to be carried out on very small samples.

Ingredients set based on the morphological characteristics of the samples seen under a visible electron microscope SEM and analysis by FTIR-ATR, using the software program OMNIC Spectra Software 09.01.24., allowed to obtain a very high percentage of matching the test sample with a reference sample of fibers from the database. It was found that the raw material composition of the fibers of silk, which is seen in the SEM photographs, is in a considerable degree of degradation (Figure 3).

By using SEM-EDX analysis, it was possible to determine various mordants in the coloured samples. SEM-EDX analysis (Table 1) demonstrated the presence of a metal Fe in a sample of green tones (PT_green) and Al metal in a sample of red tones (PT_red).

In the printout the SEM-EDX of PT for the blue tone has not proven the presence of Fe and Al metal.

ATR-FTIR analysis

The attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (ATR-FTIR) technique did enable the comparison of different samples and some individual dye components of coloured samples to be distinguished. However, this technique is used only to complement others. Infrared spectroscopy is a simple, fast and effective way to characterize the molecular structure of substances. However, based on the absorption maximum (peak) characteristic for the energy vibration of individual bonds in the molecule, we would gain complete knowledge of the corresponding chemical structure (Schwepe, H. Handbuch der Naturfarbstoffe, 1992.).

In order to obtain quality IR spectra of dyes from the fiber, subtraction was conducted. Reference spectra of undyed silk fibre was subtracted from the spectrum of colored sample, the result is a spectrum that can be interpreted as an IR spectrum of unknown dyes. Figure 4 (see page 116) shows the ATR/ FTIR spectra of historical silk textiles as a subtraction result (coloured silk/uncoloured silk; Thermo Scientific* OMNIC Spectra Software). It obtains spectra that correspond to those of dyes on the fiber.

In the absorption band (Figure 4) of sample PT_red colour tone, there is an evident peak at a wavelength of 1714, 1685 and 1587 cm^-1, which are from the Spectral database: Schweppe Collection peaks typical for Broc – madder and cochineal.

![Figure 3. SEM images of fibres: a) sample PT_ weft, b) sample PT_ warp.](image)

Table 1. Printout of the SEM-EDX of PT: a) green sample b) red sample

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<td>a</td>
<td>E1 AN Series</td>
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<td></td>
<td>O 8 K-series</td>
<td>27.61</td>
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<tr>
<td></td>
<td>Cl 17 K-series</td>
<td>1.09</td>
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<td></td>
<td>Ca 20 K-series</td>
<td>1.09</td>
<td>1.09</td>
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<tr>
<td></td>
<td>Fe 26 K-series</td>
<td>0.21</td>
<td>0.21</td>
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<td></td>
<td>Total: 100.00</td>
<td>100.00</td>
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carmine-(Dactylopius coccus Costa). The FTIR-ATR absorption band at 1685 cm\(^{-1}\) is a characteristic peak of the C = O group. The maximum absorption obtained is in the UV/VIS range of \(\lambda_{\text{max}} \) 335 nm and 539 nm, which, according to the scientific literature, can be attributed to the presence of alizarin (330 nm) (Figure 6.a).

The functional groups observed in the FTIR-ATR spectrum of the sample of blue colour tone PT_blue (Figure 5, the spectrum line 2) on the basis of a comparison with the database show characteristic IR absorption bands in the region of 1430-1290 cm\(^{-1}\) (CH in-plane with the band), with a pronounced absorption band at 1605 cm\(^{-1}\) (C=O band stretching), characteristic of indigoid dyes (indigoid dyes). It can be assumed that as a natural source of colouring in a blue tone, woad or indigo was used.

This is supported by the fact that in the UV / VIS absorption spectrum (Figure 6.b) a maximum absorption is obtained in the field of \(\lambda_{\text{max}} 605 \) nm, which is characteristic for the blue tone of natural dyes such as indigo or woad.

For sample PT_green colour, from researching in databases, some characteristic FTIR-ATR absorption bands on the basis of which it would be possible to reach a conclusion about the origin of the natural dyes (Figure 5, the spectrum line 1) are not observed. With UV / VIS analysis it was observed that the spectrum of the PT_green tone sample has a pronounced maximum absorption in the blue area, \(\lambda_{\text{max}} 609-619 \) nm, and less pronounced maximum absorption in the yellow area, which is typical for a mixture of dyes (Figure 6.c).

To confirm the green tone of the test sample recorded on a FTIR-ATR using Omnic software program, subtraction was performed in order to selectively obtain information for each colour that is a mixture of green tone (Figure 5). From the FTIR – ATR spectrum of the green tone sample PT_green (line 1), a blue tone sample PT_blue was subtracted (subtract the FTIR – ATR spectrum) (line 2) to give a new range of unknown dyes (line 3).

After the subtraction of a range of unknown dyes (line 3, Figure 5) on the basis of a database for individual compounds in the band from 1700 to 1100 cm\(^{-1}\), significant similarities between absorption bands and characteristic values for the dye Katanac (weld) (Reseda luteola L.) can be seen.

**HPLC analysis**

In the SEM photomicrographs (Figure 3), it was observed that the fibers are already, to some degree, degraded by the method selected for extracting with a mixture of methanol/conc. formic acid (9.5/0.5, v/v), which will not cause further damage, in order to obtain reliable results that relate exclusively to the dye. This is a method for the mild extraction of dyes from textile samples without hydrolysing the glycosidic linkages, and constituents of the dye can be identified.

For analysis of HPLC results, a database which is based on the wavelength of detection at 254 nm was used [29].

Based on HPLC chromatograms (Figure 7, see page 118), the pattern of the red colour tone, PT_red, has a highlighted peak at a retention time of 30 min., confirming the presence of Purpurin, while retention times at 31 min. confirmed the presence of Pseudopurpurin. The retention time at 20 min. confirmed the presence of Alizarin.

The clear signals detected are those of Purpurin and Pseudopurpurin, which clearly indicate that the roots of the madder plant (Broc) were used to produce the reddish colour. The two leading dye compositions...
ponents detected show that Purpurin and Pseudopurpurin are in major abundance over Alizarin. The dye that was used for producing this red-purple colour was probably wild madder, which is a Purpurin-rich source. SEM-EDX analysis (Table 1) of the sample PT_red proved the presence of Al metal, which indicates that madder (broc) is a mordant dye.

Based on the HPLC chromatogram (Figure 8, see page 118) of the sample PT_blue, retention times are obtained as 27, 28 and 29 min. (characteristic for indigotin and indorubin) and a number of smaller peaks at 16-26 min., characteristic of flavonoid components (a flavonoid component). According to the literature, this chromatogram is characteristic of natural dyes derived from Vrbovnik (woad, Isatis tinctoria L.), from which a blue colour tone is obtained. According to historical sources, indigo was purchased as pure dye that obtains retention times of the indigoid basic components of 2-29 min. Since Vrbovnik (woad) was widely used in Europe, it can be assumed that a blue dye was obtained from this plant.

On the HPLC chromatogram of the sample PT_green (Figure 9, see page 118), a retention time of 26-27 min., characteristic of indigoid dyes or woad (woad), and an especially pronounced peak at ~ 28 min., characteristic of indigotin, are observed. The retention times are characteristic for the dye obtained from Vrbovnik (woad).

The retention time in the range of 4-26 min., and especially accentuated peaks at ~ 5 min. (gallic acid) and ~ 13 min. (ellagic acid) are attributed to the yellow component of flavonoid dyes. Based on this, it can be assumed that the green tone obtained from Vrbovnik (woad) and Katanac (weld; Reseda luteola L.) was complexed with iron, as the most frequently used sources of yellow. This is supported by the SEM-EDX analysis, in which the sample showed the presence of metal Fe, which can otherwise be used as yellow flavonoid dyes.

On the basis of stylistic analysis design and archival data on the procurement of mass vestments for the Dubrovnik Diocese, it can be assumed that the pluvial that belonged to a complete set of Mass vestments from Dubrovnik Cathedral was probably imported from some of the most important European centers of the time. This is supported by the fact that Venetian red was obtained from madder.

**Figure 6.** UV/VIS absorption spectrum of samples a) PT_red, b) PT_blue & c) PT_green.
mAU
10
15
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25
30
35
40
0
5
10
15
20
26
24
32
34
30
34
27.5
15

that the roots of the madder plant (Ruprechtia tinctoria) were used to produce the reddish colour. The two dye components detected show that Purpurin and Pseudopurpurin are in major abundance over Alizarin. The dye that was used for producing this red-purple colour was probably obtained as 27, 28 and 29 min. (characteristic for indigotin and indorubin) and a number of smaller peaks at 16-26 min., characteristic of flavonoid components (a flavonoid component).

Based on the HPLC chromatogram (Fig. 7) of red (PT_red) coloured silk, 18th century, wavelength 254 nm was used [29]. For analysis of HPLC results, a database which is based on the wavelength of detection at 254 nm was used [29].

Figure 7. HPLC chromatogram of red (PT_red) coloured silk, 18th century, wavelength 254 nm.

Figure 8. HPLC chromatogram of blue coloured silk (PT_blue), 18th century, wavelength 254 nm.

Figure 9. HPLC chromatogram of green coloured silk (PT_green), 18th century, wavelength 254 nm.

Also weaving techniques (point rentre or effetto Berc) and cloth located on a fragment of textile suits fabrics that were produced in Lyon, France, at that time [60-62]. In support of the above-mentioned statement is the fact that in the archives of the cathedral a regulated purchase of textiles was mentioned. Although everything indicates that the fabric was procured externally, based on all available data, it cannot be ruled out that the raw materials for its production may still come from Dubrovnik, and then as a valuable commodity distributed further by commercial routes.

pokeweed or by combining them [59]. Also weaving techniques (point rentre or effetto Berc) and cloth located on a fragment of textile suits fabrics that were produced in Lyon, France, at that time [60-62]. In support of the above-mentioned statement is the fact that in the archives of the cathedral a regulated purchase of textiles was mentioned. Although everything indicates that the fabric was procured externally, based on all available data, it cannot be ruled out that the raw materials for its production may still come from Dubrovnik, and then as a valuable commodity distributed further by commercial routes.
**Table 2. Results of analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dye</th>
</tr>
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<tbody>
<tr>
<td>PT_red</td>
<td>Broc.madder (Rubia Tinctorum L.)</td>
</tr>
<tr>
<td>PT_blue</td>
<td>Vrbovnik (woad) (Isatis Tinctoria L.)</td>
</tr>
<tr>
<td>PT_green</td>
<td>Vrbovnik (woad) (Isatis Tinctoria L.) and Katanač (weld) (Reseda luteola L.)</td>
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</table>

■ Conclusion

By studying morphological characteristics of the samples with a visible electron microscope, SEM, considerable damage and degradation of fibres were observed. In this case FTIR spectra of natural dyes confirm that they do not provide a complete answer about their structure. In the absorption band of sample PT_red, evident peaks at a wavelength of 1714, 1685 and 1587 cm⁻¹ are typical for *Broc* – madder or cochineal carmine-(Dactylolpius coccus Costa). Based on the absorption band (PT_blue) at 1605 cm⁻¹, it can be assumed that as a natural source of colouring in blue tone *Vrbovnik* – woad or indigo are used. After subtraction of the spectrum of blue colour from that of green colour, on the basis of a database for individual components in the band from 1700 to 1100 cm⁻¹, significant similarities between absorption bands and characteristic values for dye *Katanač* (weld) (Reseda luteola L.) can be seen.

Comparison of chromatograms (HPLC) of dye extracted from the 18th century textile (chasuble, dalmatic and pluvial, which are stored in Dubrovnik Cathedral of the Assumption of Mary) for red coloured fibre (PT_red), this red-purple colour was probably *wild madder*, which is a Purpurin-rich source. SEM-EDX analysis proved the presence of Al metal, evidence that madder (Broc) is a mordant dye.

For the sample PT_blue the retention times of 27 and 29 min. were obtained (characteristic for indigotin and indorubin) and a number of smaller peaks at 16-26 min. are characteristic for flavonoid components. Since *Vrbovnik* (woad) was widely used in Europe, it can be assumed that this blue dye was obtained from this plant.

On the HPLC chromatogram of the sample PT_green, the retention times are characteristic for dye obtained from *Vrbovnik* (woad, blue dye), and the particularly accentuated peaks at ~ 5 min. (gallic acid) and ~ 13 min. (ellagic acid) can be attributed to the yellow component of flavonoid dyes. The green tone sample PT_green obtained from a mixture of *Vrbovnik* (woad) and *Katanač* (weld) (Reseda luteola L.) was complicated with iron (SEM-EDX analysis showed the presence of Fe metal in the sample).

Although the fiber composition and dye-stuffs identified in the liturgical textile under study in this paper (Table 2) are in agreement with data commonly reported about the material used in the Dubrovnik area, it is not possible with absolute certainty to determine the exact origin of the textile analysed.

This study contributes to the creation of a universal database of samples of original natural dyes from many parts of the world, enriching our common global heritage.

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