

## RED ORGANIC COLORANT USED TO DYE TEXTILE ARTIFACTS: FROM MOCK-UP SAMPLES PREPARATION TO ANALYTICAL CHARACTERIZATION

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### Abstract

*The study here presented concerns the characterization with chromatographic (high-performance liquid chromatography, HPLC) and spectroscopic (Raman spectroscopy and UV-Vis spectroscopy) techniques, of red dyestuffs used to dye the yarns of ancient tapestries. Following the ancient recipes the yarns (wool and silk) have been dyed using natural red dyes such as madder, kermes and cochineal. This allowed the preparation of mock-up samples used to realize a reference database. By SEM-EDX (scanning electron microscopy coupled with energy dispersive X-ray analysis) the yarns morphology has been investigated and the presence of the metals responsible for the specific mordants employed has been confirmed. Attention has been also paid to develop a non-destructive approach to be applied in-situ.*

**Keywords:** Dyestuffs; Tapestries; Raman; HPLC

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### Introduction

Organic colorants extracted from a variety of natural sources have been used since antiquity for textile dyeing purposes [1, 2]. The earliest evidence of coloured fibres date back to 30,000 years ago. A dye is a mixture of several components (for example anthraquinone derivatives are used for red dyes) and depending on the mordant employed (i.e. generally a metal) different shades can be obtained.

Tapestry is one of the oldest forms of woven textiles. Egyptian tomb paintings from circa 3000 BC clearly depict weavers working on a tapestry. In Europe the development of this art dates back to the 14th century. Today the art of tapestry survives in small production and for the restoration purpose. As regard as their usage, tapetries were employed for decorative purpose or were used for thermal insulation.

Detailed characterization of dyes in textile artefacts could reveal important information concerning historical textiles relative to the specific dye species, the area of the world where these come from and the dyeing technique. In particular the recognition of the dyeing technique (use of dyes and mordants) is also of primary importance both from the historical-artistic point of view and for conservative purposes. The study and conservation of textiles and tapestries in fact is of primary importance for the preservation of cultural heritage. Alteration of

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morphological, physical-mechanical and chemical properties [3], including colour change (photodegradation) and oxidative phenomena in yarns and corrosive phenomenon in the specific case of metallic yarns are quite common. In particular colour fading and metal thread tarnishing are the most obvious signs of tapestry deterioration. Furthermore since tapestries are polymateric artifacts, degradation phenomena such as tensions and alterations can be also triggered due to the different reaction of the original materials to external environmental factors.

In this study, in order to reconstruct a database of standards useful for the subsequent identification of dyes used in ancient tapestries, wool and silk yarns have been dyed following the ancient recipes. The subsequent identification of the dyes in real samples taken from ancient tapestries will be possible thanks to the comparison with the reference standards.

Natural anthraquinones represent the most commonly used natural colorants for textile dyeing until the late 19th century. For obtaining the red shades the anthraquinone dyestuffs such as madder, cochineal and kermes were generally used since ancient times [1, 2] and these natural dyes, together with brazilwood, are the target analytes considered in this work.

A full characterization based on both chromatographic (high-performance liquid chromatography, HPLC) and spectroscopic techniques (Raman spectroscopy and UV-Vis spectroscopy) has been carried out on the reconstructed standard samples, i. e. dyed silk and wool yarns. By SEM-EDX (scanning electron microscopy coupled with energy dispersive X-ray analysis) the threads morphology and the conservation state in the case of threads taken from ancient tapestries, can be investigated. It is worth to notice that the development of non-destructive methods for the identification of materials is of primary importance in the field of the study and conservation of works of art. In the present study, a portable Raman instrument has been employed for the analysis of the laboratory-dyed yarns with the aim to apply it directly for the *in-situ* analysis of ancient tapestries. The mock-up samples prepared have been studied in order to build a reference database that can be used later for the identification of the dyes used by the ancient tapestry manufacturers.

## Experimental

### Materials

The four natural colorants considered were madder, cochineal, kermes and brazilwood. The recipes followed for the mock-up samples preparation were taken from a treatise on dying with natural substances [4]. Accordingly, to the ancient recipes the yarns (wool and silk) have been dyed using selected natural red dyes such as kermes, cochineal, madder and brazilwood.



Fig. 1. Dyed yarns produced according to ancient recipes

The extraction of dyes from wool and silk samples for HPLC analyses has been performed by means of the following procedure: samples were suspended in 3 mL of MeOH with 100  $\mu$ L of HCl 37% and placed in a water bath at 70 °C for 1 h. Then, the extracts were

filtered through a 0.45  $\mu\text{m}$  membrane filter, evaporated under a  $\text{N}_2$  gentle stream and re-dissolved in 3 mL of MeOH [5]. On the same solution UV-Vis spectra were acquired.

### Methods

SEM-EDX analyses were carried out by a Hitachi instrument, model TM 1000. UV-Vis spectra were collected by a Perkin Elmer lambda 25 instrument. HPLC measurements were performed by a Hplc Jasco Lc 4000 series (Pump 4185 PU, Detector PDA 4010) instrument following the analytical conditions reported in Table 1.

**Table 1.** Analytical conditions used for HPLC analysis.

Time (min)	% Eluent (A)	% Eluente (B)
0	95	5
25	70	30
30	40	60
38	5	95
65	95	5

Raman spectra were acquired by a BWTek i-Raman EX device, equipped with a fiber optic probe and a 1064 nm Nd-YAG laser source. All the measurements were performed directly on the dyed yarns. A spectral range between 100 and 2500  $\text{cm}^{-1}$  was investigated with a resolution of about 4  $\text{cm}^{-1}$ , while the laser power was tuned between 40 and 120 mW according to the sample characteristics. In order to acquire spectra with a good signal to noise ratio, the latter were obtained as the sum of 10 or 20 accumulations, depending to the sample response.

## Results and discussion

For identification of dyes on textiles the standards, i. e. fibers coloured with the given dyestuff under different dyeing conditions, are needful. Even if in the literature some studies have been reported where reference samples have been prepared [6], nevertheless to our knowledge it is the first time that a so extensive set of reference dyes has been realized. In particular starting from selected dyes (kermes, cochineal, madder and brazilwood) and from two fibers (wool and silk), more than 30 mock-up samples were obtained, characterized by different shades. In figure 1 some skeins of yarns dyed in laboratory with kermes and showing different shades depending on the employed recipe are shown. The recipes were taken from a treatise on dyeing with natural substances [4] and differ mainly for the type of mordant (such as potassium aluminium sulphate, potassium hydrogen tartrate, potassium bicromate) and additives (for example iron sulphate, sodium chloride, nitric acid or tin chloride).

We are aware of the fact that every ancient textile manufacture had its own "secret" recipes, however, in order to standardize the procedures, we decided to consider a single reference text [4].

The identification of the chemical nature of the natural dyestuffs on real samples taken from ancient tapestries is quite challenging and it can only be pursued through a multi-analytical approach.

A preliminary screening has been carried out on all the reference standards by SEM-EDX in order to highlight the presence of the mordants. In figure 2 an image of a thread, acquired by scanning electron microscopy, is reported. The yarn structure is clearly visible.

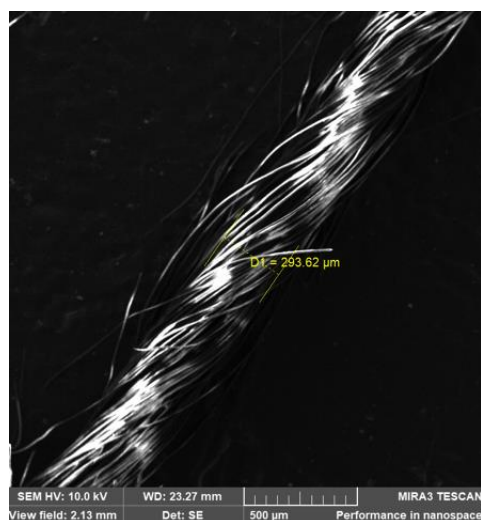


Fig. 2. SEM image of a dyed silk thread

The metals present in the mordents employed in the recipes have been confirmed. As it is well known from the literature, SEM-EDX is widely used for the identification of metals present in very low concentration in artifact of different typology [7-12]. Furthermore, the morphological analysis could make it possible to identify the state of conservation of the yarn on original threads taken from ancient tapestries.

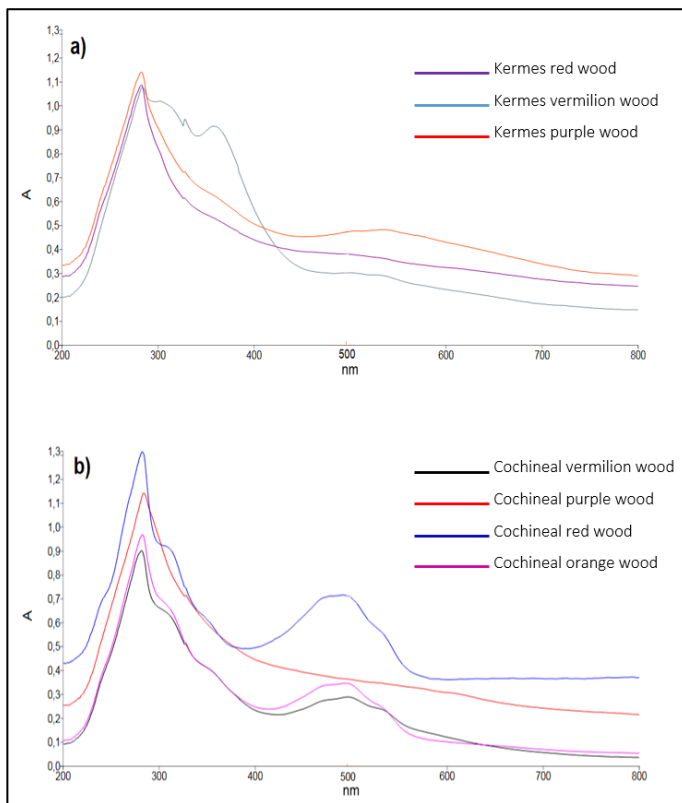
Natural anthraquinones are the most commonly used natural colorants for textile dyeing until the late 19th century. The identification of anthraquinones is challenging due to the small size of historical samples, diversity of potential dye sources, variable extraction procedures and dyeing methods, presence of structurally analogous chromophores, and possible presence of degradation products and contaminants. In particular, rather challenging is the discrimination between kermes and cochineal. Kermes is the dye from the famel of *Kermes vermilio* (Planchon) which lives on a species of oak, *Quercus Coccifera*, growing in the Mediterranean basin. Now it is very rare but it must once have been abundant being the principal insect dye in Europe before the discovery of America and thus of cochineal [2, 13]. Cochineal is obtained from the insect *Dactylopius coccus* (Costa) and other species living on the nopal cactus and is native from Mexico from where it was imported into Europe.

In order to optimize the separation of the dyestuffs by HPLC, UV-Vis spectra were acquired on the solutions obtained by extracting the dyes from the yarns. Selection of sample preparation methods and extraction protocols are of immense importance in HPLC analysis of historical samples to maximise chances of successful analysis [1, 6].

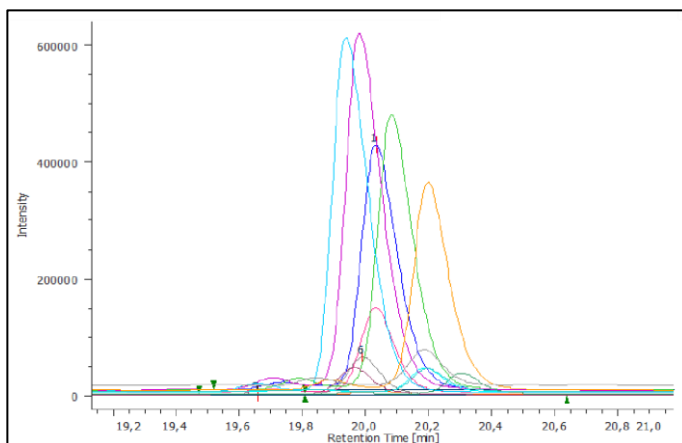
The spectra reported in figure 3 refer to threads dyed with kermes (fig. 3a) characterized by three different shades (red, vermilion and purple) and to threads dyed with cochineal (fig. 3b) showing four different shades (vermilion, purple, red and orange). In both cases the differences observable among the spectra are ascribable to the specific complex formed between the dye and the metal present in the mordant employed in that specific recipe. The more intense absorption peaks in the UV-Vis spectra were then selected for HPLC dyes identification [5].

By HPLC analysis characteristic peaks for each specific anthraquinone have been identified on the base of retention time. In particular, we have identified carminic acid for cochineal, carminic and carminic acid for kermes, pupurine and alizarine for madder and brazilin for brazilwood. As an example, the chromatogram reported in figure 4 refers to

samples prepared extracting the colorant from yarns (silk and wood) dyed with cochineal using different mordents.



**Fig. 3.** Uv-Vis spectra of natural dyes obtained after extraction from dyed yarns: a) kermes and b) cochineal; the different spectra correspond to different dyeing recipes



**Fig. 4.** Chromatograms obtained analyzing natural dyes obtained after extraction from yarns dyed with cochineal following different recipes

The anthraquinone characteristic of cochineal is carminic acid which has been highlighted at about 20 min. The peak shift observable could be due to the fact that the mordant is different (depending on the recipe). Furthermore, it is worth to notice that for each chromatogram a second peak having a much lower intensity is present at lower retention time. Accordingly, to what observed in a previous study [14] this second peak at lower retention is due to component dcII which is clearly present in Mexican cochineal and it is almost absent in Armenian cochineal [14]. This allows us to state that our colorant was Mexican cochineal.

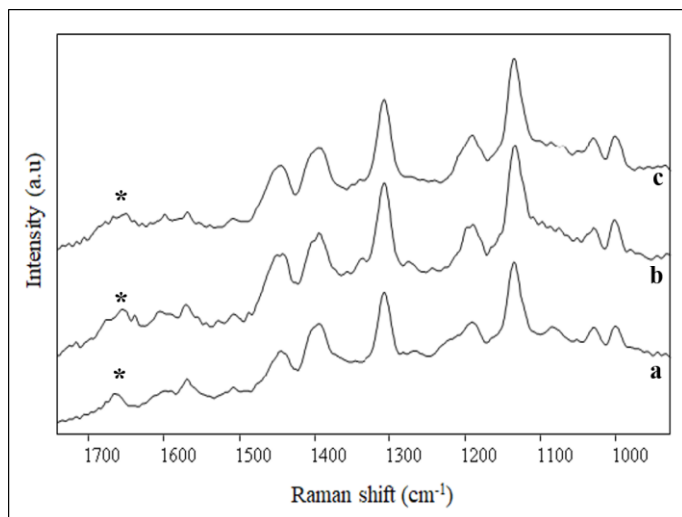
The identification of the dyes by Raman spectroscopy was performed comparing the Raman spectra recorded on the threads with the ones available in the literature [1, 15-21].

Actually, the employment of nearIR excitation compared to the visible one, resulted in a significantly reduced fluorescence of organic colorants.

Finally, since one of the main purposes of this work was to evaluate the applicability of Raman spectroscopy for the identification of dyes directly on tapestries, the same systematic study on wool and silk threads dyed in the laboratory was also carried out by a portable Raman spectrometer provided with 1064 nm excitation line. This allowed us to build a broad database of Raman spectra of these substances, even expanding what already present in the literature.

Figure 5 shows the Raman spectra acquired for some of the amaranth-red threads dyed with brazilwood; spectrum a) and spectrum b) were obtained respectively on silk and wool yarns and in both cases they were mordanted with  $KAl(SO_4)_2$  and  $C_4H_5O_6K$ , i. e. the same recipe was used (those samples were denominated brazilwood 1a and brazilwood 1); spectrum c) was recorded on a woolen thread mordanted instead with  $K_2Cr_2O_7$  and  $C_4H_5O_6K$  (denominated brazilwood 2).

The three spectra are almost superimposable and correspond to what is reported in the literature for brazilwood [15]; they all show characteristic bands at 1447 (m), 1393 (m), 1304 (s), 1189 (m), 1132 (s), 1030 (w) and 1009 (w)  $cm^{-1}$ . Furthermore, very weak signals at 1597 and 1570  $cm^{-1}$  (also attributable to brazilwood) are detectable in particular in spectrum c, while the weak and quite broad band at about 1660  $cm^{-1}$ , indicated in figure 5 by an asterisk, belongs to the fiber.



**Fig. 5.** Raman spectra of: a) brazilwood 1a (silk); b) brazilwood 1 (wool); c) brazilwood 2 (wool)

The next step of the research, actually still in testing phase, was to employ this technique directly on threads of wool and silk from ancient tapestries. The goal in fact would be the identification of the coloring materials without subjecting the samples to long and laborious

pre-treatments or to the extraction of the dye itself from the fibres, as is necessary in the case of HPLC analysis.

Given the promising results obtained with the laboratory measurements on our specimens and on some ancient yarns, we are going to proceed with the experimentation testing the Raman technique directly on the tapestries to develop a method for the recognition of the dye *in-situ*, taking advantage of a completely non-destructive approach.

Furthermore, as a future advancement of this research, to better reproduce the real conditions of the materials present in ancient tapestries, the dyed yarns will also undergo to artificial aging tests; then the same measurements performed on the fresh-prepared mock-up reference materials will be also acquired on the aged samples.

## Conclusions

The proper identification of natural dyestuffs in archaeological textiles or other pieces of art requires a comparison with reference samples. As a consequence, a reference data set of dyed yarns (mock-up samples) has been realized and protocols have been developed for red dyes identification mainly by means of HPLC and Raman analysis. Main red colorant such as kermes, choccineal, madder and brazilwood have been characterized. In future a Raman protocol for in-situ analysis of ancient textiles and tapestries will be developed.

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