

A multi-analytical approach for the characterization of red dyestuffs used in ancient tapestries: construction of a reference database

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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. 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 highlighted. The samples thus obtained 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. Attention has been also paid to develop a non-destructive approach to be applied *in-situ* for the analysis of the ancient tapestries.

I. INTRODUCTION

The study and conservation of textiles and tapestries are of primary importance for the preservation of cultural heritage. Alteration of morphological, physical-mechanical and chemical properties, 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 artefacts, degradation phenomena such as tensions and alterations can be also triggered due to the different reaction of the original materials to external environmental factors.

The recognition of the dyeing technique (use of dyes and mordants, i.e generally inorganic salts which allow to fix the dye on the yarns) is of primary importance both from the historical-artistic point of view and for conservative purposes.

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 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 database.

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

The identification of natural dyes is quite challenging and represents one of the most complex tasks since they are often mixed with other substances, i.e. other dyes to obtain different shades or mordants, with which they interact to form a complex system.

The recognition of the materials employed in a work of art represents a factor of fundamental importance:

obtaining information on natural dyes means tracing back to the resources available in a certain period and in a specific geographical area. Furthermore, from a conservative point of view, it is possible to define, through the knowledge of the solidity of the dyes and the alteration phenomena, the cleaning, restoration and conservation parameters to be applied to the product. The study of the dyeing techniques adopted in the past is somewhat arduous, because this sector developed within the shops and was often handed down orally, in order to keep the procedures used for the creation of the precious colors secret.

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, has been 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.

II. MATERIALS AND METHODS

The three natural colorants considered were madder, cochineal and kermes. The recipes followed for the standards preparation were taken from a treaty on dying with natural substances [3]. Accordingly to the ancient recipes the yarns (wool and silk) have been dyed using the three selected natural red dyes. Before performing the dyeing operations of the yarns, the coloring substances were extracted from the plant material (for the madder) and animals (insects, for kermes and cochineal) according to the indications of the recipes. These were shredded with a mortar, immersed in a beaker with demineralized water and left to decant from one night to a whole day, at room temperature or heating, depending on the dye. At the end of the process the solution was filtered and was ready to be used in the dye bath.

At first our researches focused on defining the method of extraction of the natural substances from the yarns. Although several studies and analytical methods are already present in the literature, in our case, after some tests, mainly based on some preliminary results obtained by HPLC, different extraction methods were applied.

Extraction of dyes from wool and silk samples for HPLC analyses has been performed following this procedure: samples were suspended in 3 mL of MeOH

with 100 μ L of HCl 37% and placed in a water bath at 70 $^{\circ}$ C for 1 h. Then, the extracts were filtered through a 0.45 μ m membrane filter, evaporated under a N₂ gentle stream and re-dissolved in 3 mL of MeOH [2]. On the same solution UV-Vis spectra were acquired.

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.

SEM-EDX analyses were carried out by a Hitachi instrument, model TM 1000 equipped with an EDX detector Quantum X.

Raman spectra were acquired by a Thermo Fisher Raman iXR instrument (785 nm as excitation line) equipped with a microscope. The measurements were performed directly on the dyed yarns.

III. RESULTS AND DISCUSSION

During this research, the historical dyes most used in the dyeing of textiles in the 1600s were taken into consideration [4].

Considering that each tapestry manufacture was supplied at specific workshops that used different raw materials, mordants, solvents and procedures, for the creation of the diagnostic standards, as a reference for the historically used methods for dyeing, the recipe book of Maria Elda Salice [3], one of the most experts in Italy in this field, was considered. 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. Starting from the 3 selected dyes (kermes, madder and cochineal) and from 2 fibers (wool and silk), more than 20 standards 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 recipe used, are shown.,



Fig. 1. Dyed yarns produced according to ancient recipes

The recipes [3] used differed mainly for the type of mordants (such as potassium aluminium sulphate, potassium hydrogen tartrate potassium bicromate) and additives (for example iron sulphate, sodium chloride, nitric acid or tin chloride).

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.

In figure 2 an image of a standard thread, acquired by scanning electron microscopy, is reported. The yarn, having a dimension of about 300 μm , presents a structure is clearly visible. This technique, applied to the original yarns taken from ancient tapestries, allows a morphological analysis that could make it possible the identification of the state of conservation of the tapestry.

A preliminary screening has been carried out on all the reference standards by SEM-EDS in order to highlight the presence of the mordants (figure 3).

Carbon, oxygen, calcium and sulfur are certainly attributable to the composition of the yarn. However, it is worth to notice the presence of aluminium that in this case has been used as mordant. Red colorants were often fixed to the fiber using for example potassium aluminium sulphate.

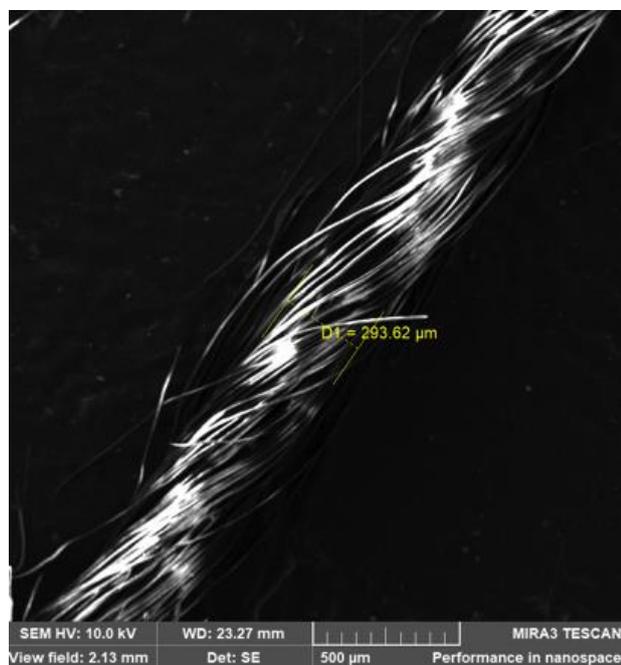


Fig. 2. SEM image of a dyed silk thread

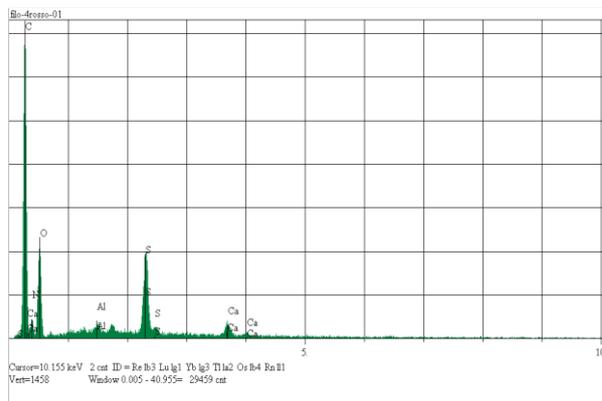


Fig. 3. SEM-EDX analysis acquired on a red dyed thread where the signal of the elements present in the mordant are clearly visible

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.

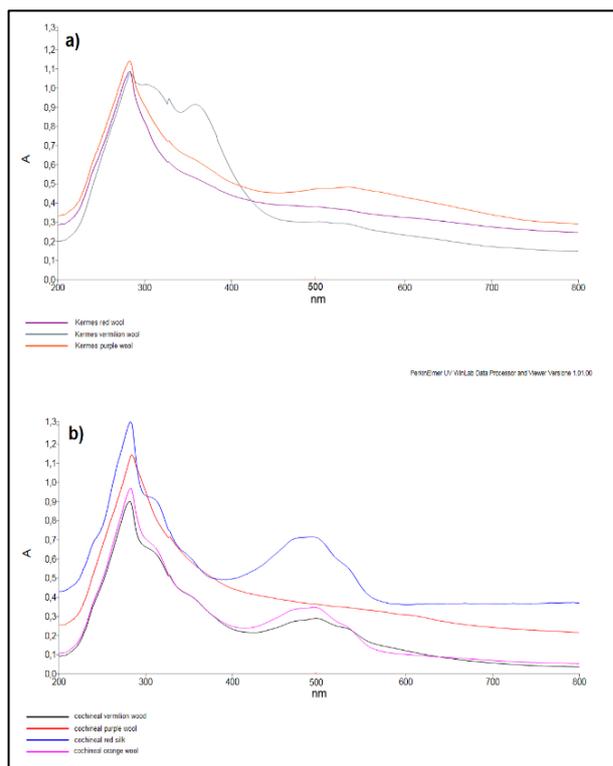


Fig. 4. UV-Vis spectra of natural dyes obtained after extraction from dyed yarns: a) kermes and b) cochineal; the different spectra correspond to different dyeing recipes

The spectra reported in figure 4 refer to threads dyed with kermes (fig. 4a) characterized by three different shades (red, vermillion and purple) and to threads dyed with

cochineal (fig. 4b) 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 absorption peaks highlighted in the UV-Vis spectra were then selected for HPLC dyes identification [5]. Some years ago the use of HPLC with UV/Vis diode array detection) was proposed to identify insoluble red dyes species of historical importance in textile dyeing [6]. Some reviews deals with advances in the use of different chromatographic methodologies applied to the identification and characterization of organic dyes in artworks and historic textiles [6, 7].

By HPLC analysis characteristic peaks for each specific anthraquinone have been identified on the base of the retention time. In particular, we have identified carminic acid for cochineal, kermesic and carminic acids for kermes and the two peaks of alizarin and purpurin characteristic of madder. As an example in figure 5 the chromatograms obtained analysing a yarn dyed with madder are reported. The broad signal which is present in both the chromatograms obtained for wool and silk, is due to the yarn itself and in fact this has been verified injecting solutions obtained subjecting to the same extraction procedure used for the dyed yarns the fibre alone (silk or wool). This confirms that the sample preparation is quite crucial and it is necessary to reach a good compromise between the efficiency of extraction of the dye from the fibre and the quality of the background signal: by making the extraction of the dye more efficient, however, we can lose in selectivity since background signal increases when more drastic conditions are employed.

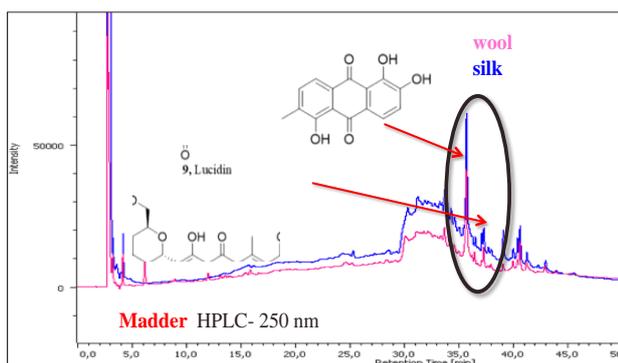


Fig. 5. HPLC chromatograms obtained analyzing two yarns of silk and wool dyed with madder; the signals due to purpurin and alizarin are highlighted.

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 employing a portable micro-Raman spectrometer provided with a 785 nm excitation line. This allowed us to build a useful and extensive personal database of Raman spectra of these materials, even expanding what already present in the literature [8, 9, 10]. The technique was then successfully applied on several threads of wool and silk from ancient tapestries, enabling in some cases the recognition of the dye without subjecting the samples to long and laborious pre-treatments or to the extraction of the dye itself from the fibres. Given the excellent results obtained with the laboratory measurements both on our specimens and on some ancient threads, we finally wanted to test the Raman technique directly on the tapestries and it was possible in some cases the recognition of the dye *in-situ*, taking advantage of a completely non-destructive approach.

Furthermore as a future development of this research, to better reproduce the real conditions, taking into account that inside museums tapestries are subjected to the action of environmental factors [10,11] such as temperature, humidity and light which act together with pollutants (both gases and particles), the dyed yarns will also undergo artificial aging and soiling tests and the same measurements performed on the reference standards will be also acquired on the aged samples.

IV. CONCLUSIONS

This study reports preliminary results obtained characterizing, by a multi-analytical approach, some reference standards of dyed yarns produced in laboratory following ancient recipes. This step is mandatory since the proper identification of natural dyestuffs (and in particular red dyes) in archaeological textiles or other pieces of art requires a comparison with reference samples.

Together with the construction of a reference data set, some protocols have been developed for dyes identification by the different analytical techniques. The same protocols will be applied to the analysis of real samples taken from ancient tapestries.

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