

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*.

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 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.

The recognition of the dyeing technique (use of dyes and mordants) 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 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 red shades the anthraquinone dyestuffs such as madder, cochineal and kermes were generally used [1] and these dyes of natural origin, used since ancient times, 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.

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 dyeing with natural substances [3]. Accordingly to the ancient recipes the yarns (wool and silk) have been dyed using the three selected natural red dyes.

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.

SEM-EDX analyses were carried out by an 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.

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

III. RESULTS AND DISCUSSION

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. The recipes were taken from a treaty on dyeing with natural substances [3] and differ 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). 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.



Fig. 1. Dyed yarns produced according to ancient recipes

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 thread, acquired by scanning electron microscopy, is reported. The yarn structure is clearly visible.

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). Furthermore, the morphological analysis could make it possible to identify the state of conservation of the yarn on original threads taken from ancient tapestries.

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.

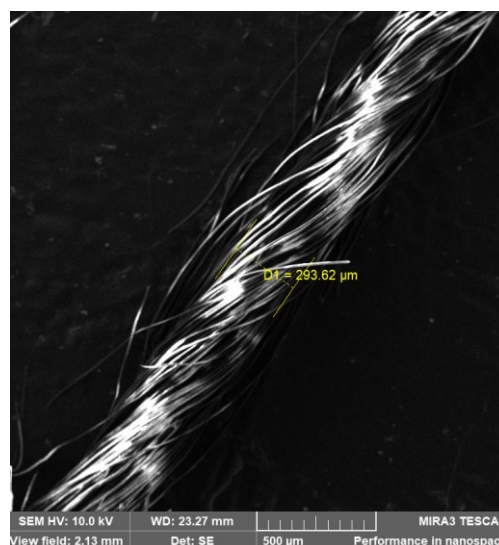


Fig. 2. SEM image of a dyed silk thread

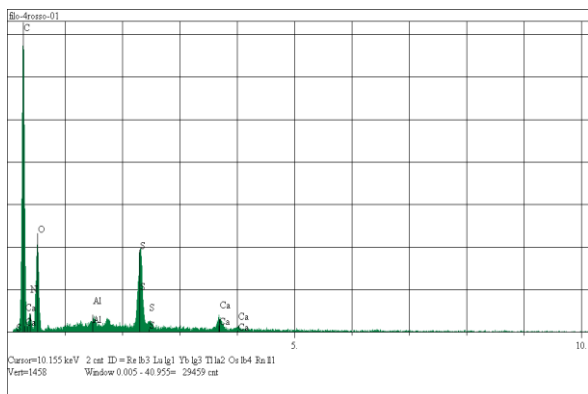


Fig. 3. SEM-EDX analysis acquired on a red dyed thread where the signal of the elements present in the mordant are clearly visible

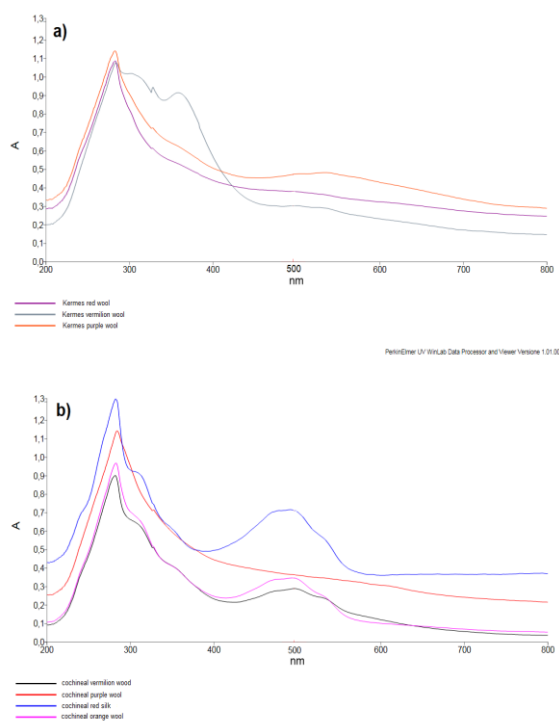


Fig. 4. UV-Vis spectra of natural dyes obtained after extraction from dyed yarns: a) kermes and b) cochineal; the different spectra correspond to different dyeing recipes

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

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 [5, 6, 7]. 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, the dyed yarns will also undergo artificial aging tests and the same measurements performed on the reference standards will be also acquired on the aged samples.

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