

Identification of natural dyes in some archaeological Iranian carpets by non-destructive MALDI TOF MS

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Abstract

The present study introduces a non-destructive method of analysis by MALDI TOF Mass spectrometry to identify the natural dyes in four Iranian archaeological carpets, dated back to the 17-18th century, and attributed to Sarband and Tabriz cities. The study aims to unveil a method of analysis that may not have been used in dye analysis and to identify the samples taken from these carpets, which have reached a high rate of deterioration, and need a rapid intervention to be preserved. The study proved the use of natural indigo in blue, light blue, navy, and pale navy in the four carpets. The use of natural indigo (as a blue dye) has also been proved in oily, light oily, and greenish-blue samples in the four carpets along with weld and Persian berries dyes in the light oily color sample in Tabriz II. The madder and cochineal pigments were proven to be used in dyeing with the coppery red color in the first Sarband carpet. The madder and yellow dye were used for dyeing with coppery red color in the second Tabriz carpet. The madder dye has been proven to be used in dyeing with the coppery red and brick red in the third/fourth carpet. The results showed the use of weld dye in the beige color in the third/fourth carpet, while, no dye was detected in the beige color in the first and second carpet, as well as the pale yellow color in the second carpet. The examined Mass method proved a non-invasive, very fast, and high ability in identifying many dyes' compounds, without any dyes extraction or sample preparation. The method was unable to distinguish between compounds of the same molar mass, e.g. indigotin and indirubin compounds in indigo. So far, and according to the followed methodologies, the method detected relatively few numbers of dyes' compounds, so, the type of dye isn't confirmed due to the presence of the same compound in more than one dye. Due to its many features; the study recommends more research about this method to unveil the reasons for the less detected compounds, and whether it can be overcome.

keywords:

Natural dyes, Iranian carpets, MALDI TOF MS, Investigation and Analysis, Non-destructive.

INTRODUCTION

The liquid chromatography method coupled with mass spectrometry is characterized by its high ability to detect the dyeing compounds in the dye material, but it is required to extract the dye first from the fibers, and this process is not so easy, as it requires a laboratory and many chemicals and accuracy in the implementation, as well as the more amount of required carpet fibers. With the development of the analysis technique by mass spectrometry, the method was able to identify the organic components of many materials by means of their molar mass directly from a very accurate sample that may be difficult to be observed with the naked eye, and the result appears in few seconds.

The time of flight mass spectrometer has been used to identify some types of biological spoilage in books and in archaeological museum collections, and the method has also been successfully

used in identifying cellulose ethers used as an adhesive material in the restoration of heritage collections. The author also used the method in identifying the types of dyes and skin used in Iranian leather tapestry embroidered with threads.

The research problem appears in the great effort, high cost, and long time required to conduct the dye extraction from its fibers. It needs a suitable laboratory equipped with many tools and many types of high-quality chemicals. Therefore, the idea of the research aimed at using and evaluating the MALDI TOF MS in identifying the natural dyes in four Iranian carpets preserved in the Agricultural Museum in Cairo. These carpets are in a poor state of preservation, and suffer from an inappropriate museum display environment, so the current study puts these carpets in the spotlight for preservation and maintenance.

MATERIALS AND METHODS

Case-study carpets

This study includes four Iranian archaeological carpets preserved in the Carpet Hall inside the Museum of Heritage Collections at Agricultural Museum in Cairo, and all of them are dated back to the 17-18th century AD (according to museum records and what was confirmed by the archaeological study).

First carpet (Sarband): A rectangular carpet of natural wool, measures about 840 x 420 cm, with a Museum Record No. 119.

Second carpet (Tabriz): A rectangular wool carpet, measures about 180 x 120 cm, with a Museum Record No. 114.

Third and fourth carpets (Tabriz): Both carpets are also made of natural wool, dyed with dyes of different colors and degrees, and they are attributed to the city of Tabriz. with a Museum Record No. 115 and 116. Each carpet measures 800 x 85 cm. The two carpets are completely similar in size and decoration elements.

These carpets are all deteriorated, and displayed in a wrong way, as they are suspended from the top or in the middle of a cylindrical bar fixed to the wall of the room, which is about six meters high. These carpets also suffer from an inappropriate museum display environment, as there are no devices to control the temperature or humidity, and the hall is completely devoid of any means for ventilation or air renewal, as well as inappropriate lighting. Also, some of these carpets suffer from thinning in the pile in many areas (especially the tree of life carpet), of course, for old uses.

All these factors that affected carpets caused that they became vulnerable to suffer from all types of deterioration. Therefore, this study puts these carpets in the spotlight, in preparation for their treatment, maintenance, and displaying them in a suitable way after treatment.

Sampling:

The different colors found in the four carpets were screened, and some very small six fibers were gently collected from each carpet. These small fibers are sufficient to perform the analysis and to identify the dye through identifying the compounds present in each dye.

First carpet: 1 light blue, 2 pale navy blue, 3 copper red, 4 pale yellow, 5 olive green, 6 beige.

Second carpet: 1 light blue, 2 dark blue, 3 light olive, 4 copper red, 5 pale yellow, 6 beige.

Third carpet: 1 light blue, 2 navy blue, 3 teal, 4 copper red, 5 light brick, 6 beige.

Fourth carpet: 1 light blue, 2 dark blue, 3 teal, 4 copper red, 5 light brick, 6 beige.

Mass spectrometry:

To determine the sources of dyes used in the dyeing of the case study carpets; a mass spectrometer - MALDI - Time of Flight (from Bruker, University of Science and Technology in the Czech Republic) was used to analyze about 3 mm of the color fiber in a negative reflection mode.

RESULTS

The study proved using natural indigo in blue, light blue, navy, and pale navy in the four carpets. The use of natural indigo (as a blue dye) has also been proved in oily, light oily, and greenish-blue samples in the four carpets along with weld and Persian berries dyes in the light oily color sample in Tabriz II. The madder and cochineal pigments were proven to be used in dyeing with the coppery red color in the first Sarband carpet. The madder and yellow dye were used for dyeing with coppery red color in the second Tabriz carpet. The madder dye has been proven to be used in dyeing with the coppery red and brick red in the third/fourth carpet. The results showed the use of weld dye in the beige color in the third/fourth carpet, while, no dye was detected in the beige color in the first and second carpet, as well as the pale yellow color in the second carpet.

CONCLUSIONS:

The use of natural Indigo dye in the light blue, blue, navy, and pale navy samples collected from the four carpets.

The use of natural indigo dye (as a blue dye) in oily, light oily, and greenish-blue samples collected from the first, second and third / fourth rugs respectively, in addition to a yellow dye likely to be the weld dye, in addition to the Persian berries in the light oily sample collected from the second carpet.

The use of madder and cochineal dyes for dyeing copper red in the first carpet, while the dyes of madder and safflower were used to dye with copper red color on the second carpet. As for madder dye alone, it has been proven to be used in dyeing in copper-red and brick-red in the third / fourth carpet.

The use of the weld dye in the beige fiber collected from the third / fourth carpet.

No dyes were identified in the beige fibers of the first and second rugs, as well as the pale yellow on the second carpet.

The MALDI TOF MS has proved a great ability in identifying many compounds in the natural dyes, in a non-destructive way.

The method is characterized by speed in identifying the dyeing compounds in a few seconds, without any preparation or extraction of dyes from the wool fibers.

The method showed that it does not differentiate between compounds with a single molar mass, and that the compounds that have been detected are relatively few so far, and sometimes it is not sufficient to determine the type of dye due to its presence in other dyes.

Additional study is required to determine the reason of the lack of detected compounds, and whether this reason could be overcome.

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