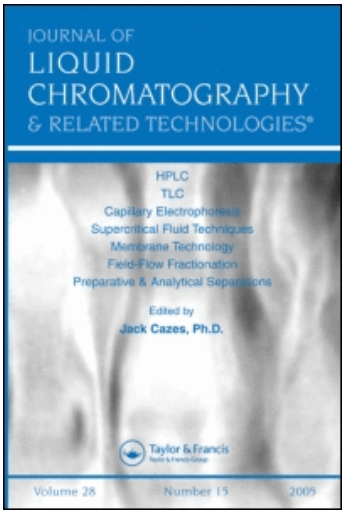

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Identification and Quantitative Determination of Madder by High Performance Liquid Chromatography: Application to Historical Textiles

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Abstract: A reversed phase HPLC method has been developed for the identification and quantification of madder applied to an old textile. An isocratic method was used for the identification of alizarin and purpurin, the main pigments in the madder plant, which were identified and quantified in cotton and wool reference samples and in the unknown textile.

FTIR-spectroscopy was also used for the identification of pigment and fiber of the unknown sample.

Keywords: Alizarin, FT-IR spectroscopy, Isocratic HPLC, Madder, Purpurin, Textile

INTRODUCTION

In the study of historical textiles, the knowledge of the natural colorants used assists in their dating and locating their origin.

Many non-destructive methods have been used to investigate the historical textile materials: Use of scanning electron microscope

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(SEM) has been reported for understanding the deterioration of the textile materials,[1,2] optical microscopy mainly for identifying the fibres,[2] IR and FTIR spectroscopy,[2–4] ultra violet/visible (UV-Vis) spectroscopy,[5–7] three dimensional fluorescence spectrum,[8] thin layer chromatography TLC,[4,9–11] and high performance liquid chromatography HPLC[12–19] have all been used to investigate the dyes on the textiles, both qualitatively and quantitatively; with all the limitations of the reliability concerning results characteristic of each one of them. HPLC proved to be a useful tool to detect the components of such organic natural compounds even when only present as traces.[20–23]

The aim of this work was the identification and quantitative determination of a sample extracted from a sample of an old textile of the early 20th century from the area of Western Macedonia, Greece by using reversed phase HPLC. Little information was available regarding the organic pigments present in textiles from this area, however, since madder was the pigment used mainly for achieving red hues, cotton and wool samples dyed with madder were used as references.

Micro FTIR spectroscopy measurements were also made as a confirmation of the results obtained by the HPLC analysis.

EXPERIMENTAL

Materials

Alizarin (Sigma-Aldrich Co, Germany) and purpurin (Fluka, USA) were used for standard solution preparations and for the development of a preliminary chromatographic method. The latter was further developed to achieve sufficient separation of the coloring components of madder (Kremer Pigmente, Germany). HPLC grade acetonitrile, ACN (J.T. Baker, Holland), trifluoroacetic acid, TFA (Merck, Germany), hydrochloric acid, HCl 37% (Riedel de Haen, Germany), HPLC grade methanol (J.T. Baker), and HPLC grade water (Merck, Germany) were used for the liquid chromatography.

Commercially available cotton and wool fabric was used for the dyeing with madder (reference samples, known textiles).

Instrumentation

The HPLC measurements were carried out using an Ultimate 3000 HPLC system (Dionex, USA) consisting of an ISO-3100A pump, a

DQ-1210 vacuum degasser, a TCC-3000 column oven, an ASI-100 injector with 20 μL sample loop, and a UV-Vis VWD-3400 detector.

The separation was carried out in an Alphabond C_{18} 125A 10 U 300 mm × 3.9 mm HPLC column (Alltech Associates Inc, USA) thermostated at 25°C. Isocratic elution took place with the mixture ACN/H_2O (0.1% TFA) = 55/45 within a time period of 15 min and flow rate 1.5 mL/min.

Chromeleon data system 6.8 Build 2212 was employed for data acquisition and processing.

FTIR spectra were recorded with a Perkin Elmer Spectrum GXII spectrometer. This was equipped with an AutoIMAGE microscope equipped with a 100 × objective lens through which focusing on a selected point on the sample was possible, and a MCT detector cooled with liquid nitrogen. The spectra were collected in reflectance made in the range of 4000–700 cm^{-1} with a resolution of 4 cm^{-1}, an aperture of 100 × 100 μm and 150 scans per measurement. Three IR spectra from different areas of each sample were recorded and the average spectrum was calculated.

A Zeltex Vistacolor dyeing apparatus was used for dyeing the cotton and wool samples with madder.

Methods

Madder extraction was made by heating an aqueous dispersion of the plant material at boiling temperature for 10 min and allowing to stand for 24 hr.[24]

The extract was used as dyeing liquor for the dyeing of cotton and wool samples at 100°C for 1 hr.[24,25]

Sample Preparation for the HPLC Analysis

All the standard solutions and the extracts from the reference samples (known textiles) and the unknown old one (5 mg) were treated with a solution mixture of H_2O:MeOH:HCl 37% (400 μL, 1:1:2 v/v) for 15 min at 100°C in small open ended tubes. This treatment was mainly necessary for the extracts to isolate the organic colorant from its mordant metal. Subsequently, the solutions were evaporated by heating at 50–60°C under nitrogen flow. The dry residues were dissolved in a mixture of H_2O/MeOH = 2/1 (500 μL), the solutions were centrifuged (5 min, 5000 rpm) and filtered through a PTFE filter 0.45 μm (Gelman, Germany).

RESULTS AND DISCUSSION

In Table 1 the chromatographic and spectral characteristics of the main coloring components of madder alizarin and purpurin (mixture of standard compounds 1:1 w/w) detected in Figure 1 are given.

These can be identified by their UV-Vis spectra. The wavelength employed for detection, selected against 430 and 480 nm for optimum separation, was 255 nm (Detection at 430 nm and 480 nm was also made).[18]

Concentration calibration curves for alizarin and purpurin at 255 nm were also made. These are linear ($r^2 = 0.99$) in the concentration rate studied and were used for the quantitative analysis of the madder extract (Table 2). The chromatogram of the madder extract treated as described in the experimental is given in Figure 2.

Peak 4 ($R_t = 3.02$) corresponds to alizarin and peak 5 ($R_t = 3.50$) to purpurin. Peaks 1, 2, 3 were not identified.

Madder extract was used for the dyeing of wool and cotton fabrics (reference samples). The isocratic elution chromatograms of the dyed fiber extracts are shown in Figures 3a and b. Figures 4a and b present the chromatograms of the undyed fiber extracts. By comparison of the chromatograms 3a, 4a, and 3b, 4b, the following conclusions were drawn:

Peaks 3 and 4 correspond to alizarin and purpurin in Figure 3a, while peaks 6 and 7 correspond to alizarin and purpurin in Figure 3b. Peak 2 ($R_t = 2.1$) in the chromatogram 3a (wool reference sample) corresponds to the unidentified peaks of the madder extract chromatogram (Figure 2), probably attributed to other coloring constituents of the plant material. These peaks are apparently overlapped in Figure 4b with the main peak of the undyed cotton sample extract, probably due to quercetin, the natural pigment present on the surface of the cotton.

Peak 1 ($R_t = 1.6$) in Figure 3a with the same R_t as the main peak in Figure 4a (undyed wool fiber extract) appears attributable to the wool substrate itself (for instance, a natural pigment of wool).

Table 1. Chromatographic and spectral characteristics of alizarin and purpurin (UV-detection at 255 nm)

Coloring component	R_t (min)	Absorbance maximum (nm)	Corresponding peak
Alizarin	2.975	247,277,430	2
Purpurin	3.450	255,293,381,480	3

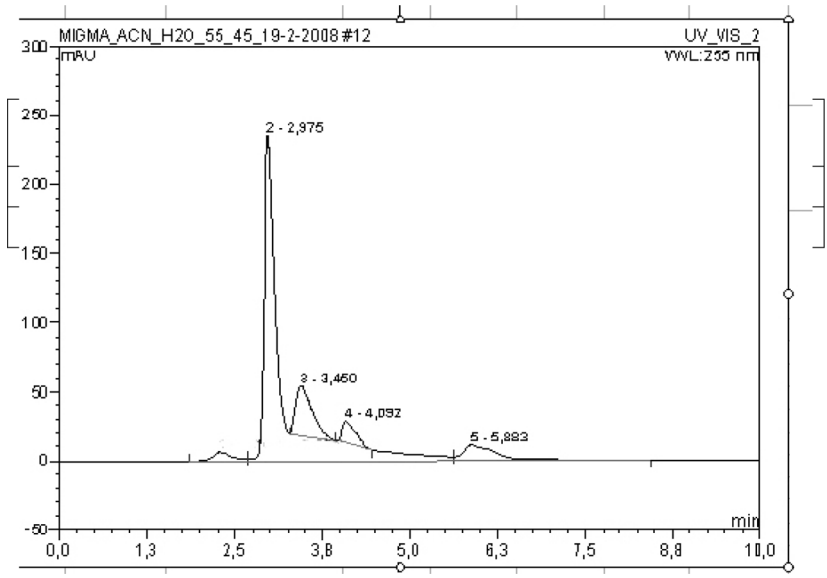


Figure 1. Chromatogram of standard sample mixture (UV-detection at 255 nm).

Application to the Old Textile

Using the extraction procedure described above, the separation procedure was applied to the identification of the dyes used for the dyeing of a textile of the early 20th century in the area of Western Macedonia, Greece.

Figure 5 shows the chromatogram of the unknown sample extract. Peak 1 ($R_t = 1.6$) was attributed to the wool substrate, while peaks 4

Table 2. Quantitation of the coloring components in the plant (madder) extract and the fiber extracts

No.	Amount of alizarin μg/mg (%, o.w.f)	Amount of purpurin μg/mg (%, o.w.f)
1	10.50 (1.05 of plant mat.)	69.24 (6.92 of plant mat.)
2	0.34 (0.03 o.m.f.)	2.12 (0.21 o.m.f.)
3	0.081 (0.008 o.m.f.)	1.19 (0.119 o.m.f.)
4	0.33 (0.03 o.m.f.)	0.78 (0.078 o.m.f.)

1: plant.
2: reference wool sample dyed with madder (known sample).
3: reference cotton sample dyed with madder.
4: old textile (unknown sample).
o.m.f. = on the mass of the fiber.

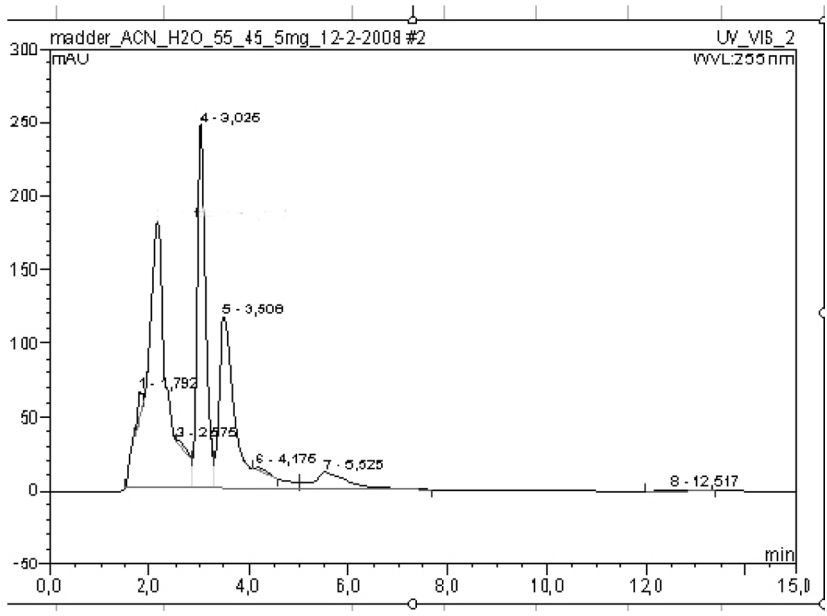


Figure 2. Chromatogram of the plant extract (UV-detection at 255 nm).

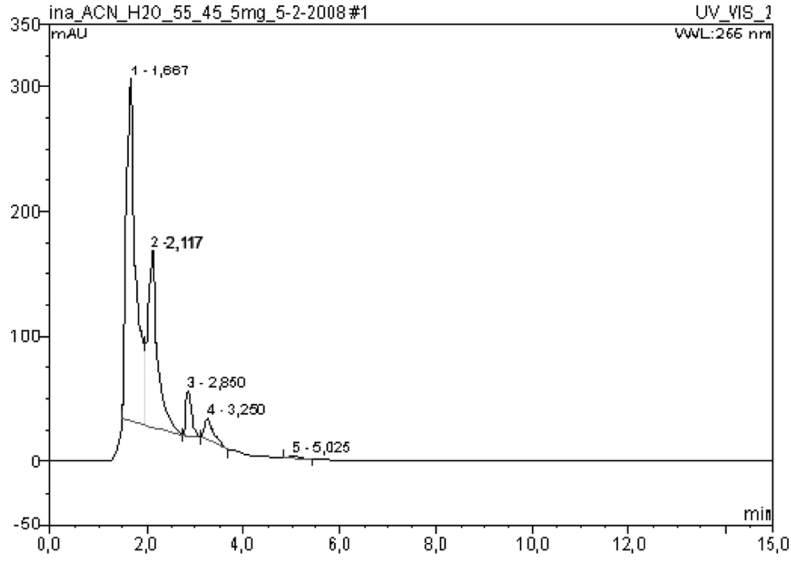
($R_t = 2.92$) and 5 ($R_t = 3.33$) were identified as alizarin and purpurin, and peak 2 was the unidentified peak of madder. A very good agreement between chromatograms 3a and 5 is deduced, indicating that the unknown sample is a wool sample dyed with madder.

A quantitative analysis of the two coloring components detected, alizarin and purpurin, is given in Table 2.

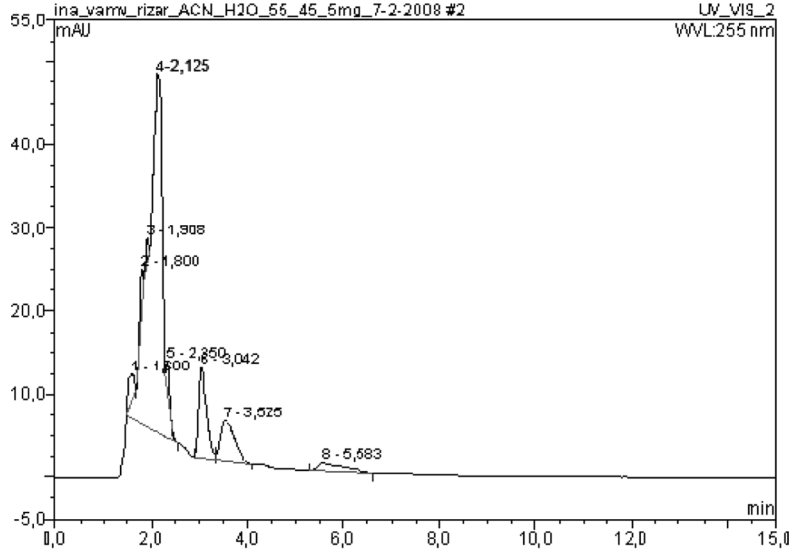
Micro-FTIR Spectroscopy

After the HPLC separation, the old sample was subjected to Fourier transform IR (FTIR) spectroscopic measurement as an additional confirmation of the results obtained by the HPLC analysis. This is a very important non-destructive method for detecting functional groups.

Figures 6 and 7(a, b) present the FTIR spectra of: a standard madder dyed cotton textile, a standard madder dyed wool textile, the old textile, respectively. The absorption bands at 3450 cm^{-1} and 2750 cm^{-1} in the cotton sample spectrum (Figure 6) indicate the presence of hydroxyl groups, broadened due to the inter- and intra-hydrogen bonding observed in cellulose fibers.[2] Those bonds are not found in the unknown textile spectrum, which is identical with the dyed wool standard spectrum.



(a)



(b)

Figure 3. (a) Chromatogram of the wool reference sample extract (UV-detection at 255 nm). (b) Chromatogram of the cotton reference sample extract (UV-detection at 255 nm).

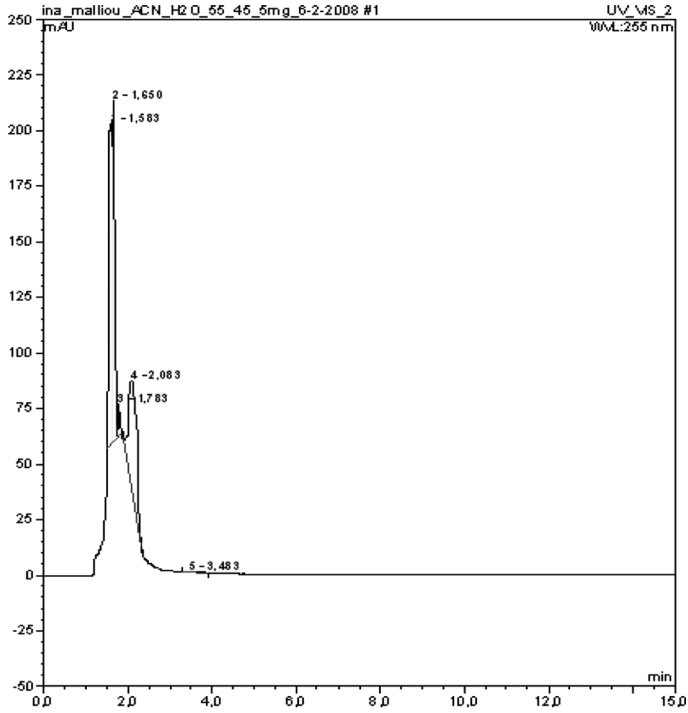


Figure 4. (a) Chromatogram of the undyed wool sample extract (UV-detection at 255 nm). (b) Chromatogram of the undyed cotton sample extract (UV-detection at 255 nm).

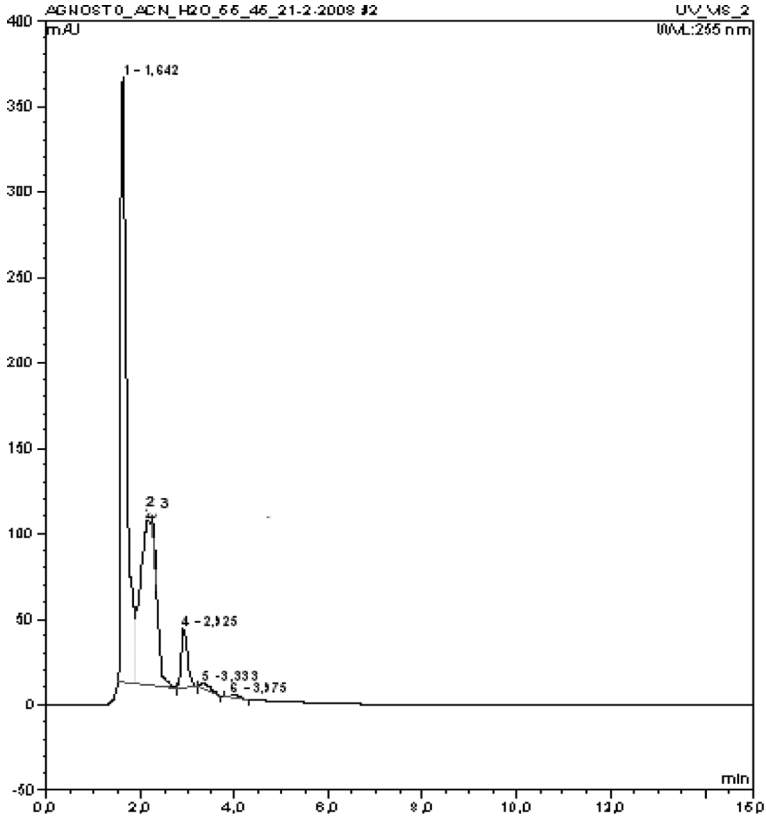


Figure 5. Chromatogram of the unknown sample extract (UV-detection at 255 nm).

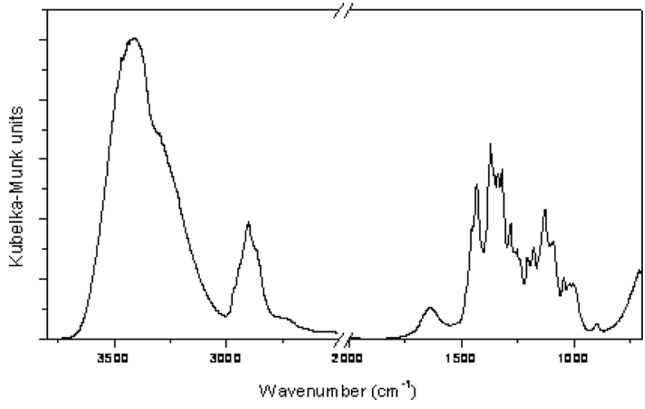


Figure 6. FTIR spectrum of madder dyed cotton textile.

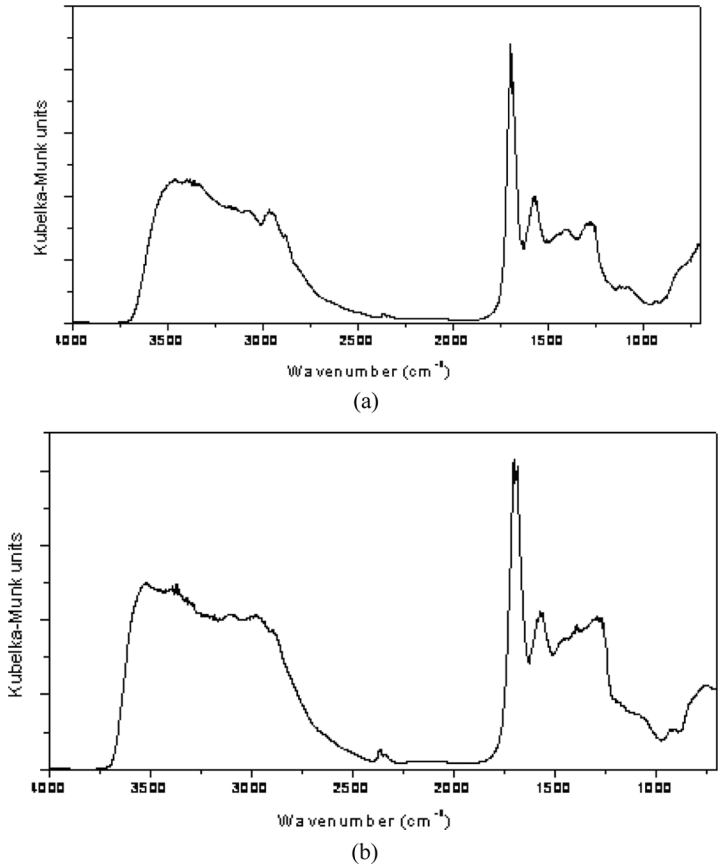


Figure 7. (a) FTIR spectrum of madder dyed wool textile. (b) FTIR spectrum of the old textile.

CONCLUSION

The HPLC method proposed provides a reliable means of both qualitative and quantitative analysis of madder in textiles. For unambiguous identification of an old textile, the appropriate standard compounds were used. FTIR spectroscopy confirmed the conclusions derived from HPLC, with respect to the fiber and the coloring components.

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