


## Article

# Identification of Dyes in Coptic Textiles from the Museum of Faculty of Archaeology, Cairo University

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**Abstract:** High Performance Liquid Chromatography coupled to a Diode-Array-Detector (HPLC-DAD) is used to investigate samples which were extracted from ancient Egyptian textiles (4th–5th c. AD) of the Museum of Faculty of Archaeology, Cairo University. Madder is identified in several samples. According to semi-quantitative results, which are obtained from HPLC peak areas measured at 254 nm, madder that is rich in purpurin and poor in alizarin is identified in samples which were treated (i) only with madder and (ii) with madder and either indigo/woad (*Indigofera* species and other/*Isatis tinctoria* L.) or weld (*Reseda luteola* L.). The madder dye used in these samples could have been originated from *Rubia peregrina* L. However, the possible use of *Rubia tinctorum* L. (or other plants of the *Rubiaceae* family) by the Egyptian dyers cannot be ruled out, particularly if methods were developed by the ancient dyers to affect and control the relative composition of madder dye. The HPLC peak area ratio of alizarin versus purpurin is very high (>2.2) for samples which were treated with madder (probably originated from *R. tinctorum*) and a tannin source. Finally, in some samples, only indigoid dyes (indigo/woad) are identified.

**Keywords:** textile; Egypt; Coptic; dye; madder; indigo; woad; weld; HPLC



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## 1. Introduction

The Coptic textiles of the Museum of Faculty of Archaeology, Cairo University, have been obtained either through excavations that were carried out by the University or as gifts given by the Arab Antiquities House (Museum of Islamic Art), the Committee for the Preservation of Arab Antiquities and several individuals. Examples of these valuable objects are shown in the photographs in Figure 1 [1]. The textiles of the Coptic collection correspond to different periods of the history of Egypt, and they were not subjected to dyestuff analysis in the past.

The origin of materials that were used by the Coptic dyers has been investigated in several previously published studies. Using modern analytical techniques, the following dyes have been identified in ancient Egyptian textiles: Armenian cochineal (*Porphyrophora hamelii* Brandt) [2–6], fustic (*Maclura tinctoria* L.) [7], henna (*Lawsonia inermis* L.) [7], indigoids (*Indigofera* species, *Isatis tinctoria* L. and other) [2–13], kermes (*Kermes vermilio* Planchon) [2,5,6], lac (*Kerria lacca* Kerr) [2–6,12,13], madder (*Rubiaceae* family) [2–13], mollusc purple (*Muricidae* family) [5,6,10,13–17], *Rhamnus* species [4], safflower (*Carthamus tinctorius* L.) [5], soluble redwood (*Caesalpinia* trees) [5,12], tannins [2,4,5,8,10] and weld (*Reseda luteola* L.) [2–13]. Moreover, a dye which should be similar to American annatto (*Bixa orellana* L.) has been included in the results of ancient Egyptian textiles, reported by Verhecken [5].



**Figure 1.** Examples of textiles from the Museum of Faculty of Archaeology, Cairo University.

Identification of dyes in textiles of the cultural heritage is commonly achieved by using High Pressure Liquid Chromatography coupled to a Diode-Array-Detector (HPLC-DAD) [18,19]. The method is employed herein to analyse samples which were extracted from twelve ancient Egyptian textiles of the Museum of Faculty of Archaeology, Cairo University. The HPLC-DAD results are analysed in order to discuss the possible biological origins of the madder dyes that were identified in the investigated samples. Therefore, the goal of the study is to add more data to the existing literature regarding the dyestuff sources used by the famous ancient Egyptian dyers.

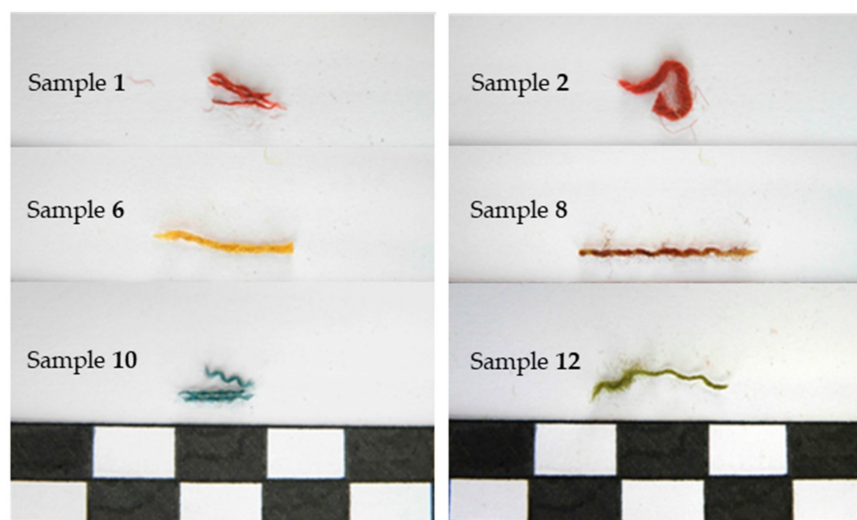
Textile samples, investigated herein, are treated with methanolic solution of hydrochloric acid (HCl) to extract the dyes [20], which are finally dissolved in dimethyl sulfoxide (DMSO) and analysed by HPLC. In the harsh acidic conditions induced by the strong HCl, glycosides are hydrolysed to their parent aglycones. From a chemical point of view, this is clearly a disadvantage of the HCl method. However, when only very small samples from cultural heritage objects (e.g., paintings or even textiles) are available, then the aforementioned hydrolysis might be desirable to increase the chances to detect the important aglycone components. The latter often provide enough information to identify the biological source of a dye fixed on a historical or archaeological textile [21]. Several mild acids that retain glycosides have been suggested for dye extraction such as, for instance, formic [22–28], oxalic [23,25–27,29–32], hydrofluoric [25,33] and trifluoroacetic [23,27,34] acids. Other approaches for dye extraction suggested the use of ammonia-disodium EDTA to preserve glycosyl moieties [35] and an aqueous glucose solution for the extraction of madder [36]. However, regardless of the selected treatment method, the results obtained by

HPLC after the extraction of a dye from a textile do not coincide with the HPLC fingerprint of the biological (animal or plant) source. This is because the composition of a dye attached to a textile fibre is highly affected by the conditions of the dyeing process [37]. Moreover, the composition of a dyestuff source is affected by the geographical locations and growing environments [37].

## 2. Materials and Methods

### 2.1. Samples

Twelve (12) wool samples were extracted from Coptic textiles (4th–5th c. AD), which are preserved in the Museum of Faculty of Archaeology, in Cairo University. Photographs of some of the investigated textile samples are shown in Figure 2. In the Supplementary Materials, photographs of all the studied samples are provided. Samples were first studied using optical microscopy and were then analysed using High Pressure Liquid Chromatography coupled to a Diode-Array-Detector (HPLC-DAD) to identify the dyestuff materials. Identifications were achieved using HPLC-DAD data of standard materials, which are included in Table 1. Suppliers of the standard materials are described in Table 1. Indirubin and rubiadin were generously provided in pure forms by P. Magiatis (University of Athens) and R. Karadag (Istanbul Aydın University), respectively.



**Figure 2.** Examples of samples that were extracted from the Coptic textiles and included in the study. Rectangles of the ruler are 1 cm long.

**Table 1.** UV–Vis absorbance maxima of compounds which were identified in the investigated textile samples. Suppliers which provided the corresponding standard materials are described.

Compound	Supplier	Absorbance Maxima (nm)
Alizarin	Aldrich	248, 278, 429
Apigenin	Fluka	267, 336
Chrysoeriol	Extrasynthese	249, 267, 346
Ellagic acid	Fluka	253, 367
Indigotin	Fluka	243, 285, 606
Indirubin	P. Magiatis (gift)	243, 290, 364, 543
Luteolin	Sigma	253, 265, 345
Purpurin	Aldrich	255, 293, 479
Rubiadin	R. Karadag (gift)	244, 278, 412

## 2.2. Instrumentation

A Zeiss Axioskop 40 polarizing microscope was used to study the textile samples. Chromatography was carried out using an Ultimate 3000 (Dionex) system consisting of an LPG-3000 quaternary HPLC pump with a vacuum degasser, a WPS-3000SL autosampler, a column compartment TCC-3000SD and a UV-Vis Diode Array Detector (DAD-3000). The chromatographic separation was performed on an Alltima HP C18 (250 mm × 3 mm, i.d. 5 µm) Grace (Alltech Associates) column at a stable temperature of 35 °C. The injection volume was 20 µL.

## 2.3. Materials

The following chemicals were used to operate the chromatographic system: HPLC grade water (H<sub>2</sub>O, ChemLab, Zedelgem, Belgium), HPLC grade acetonitrile (CH<sub>3</sub>CN, ChemLab) and trifluoroacetic acid (TFA) (assay >99.0%, Sigma-Aldrich, St. Louis, MO, USA). Textile samples were treated using HPLC grade solvents of water (H<sub>2</sub>O, ChemLab), methanol (MeOH, J.T. Baker, Radnor, PA, USA) and dimethyl sulfoxide (DMSO, Sigma-Aldrich) as well as pro-analysis grade hydrochloric acid (HCl) 37% m/m (Riedel-de Haën, Seelze, Germany).

## 2.4. Sample Treatment and HPLC Analysis

Textile samples were treated according to the HCl extraction method [20]. In particular, sample was immersed in a hot (100 °C) bath of 400 µL of H<sub>2</sub>O:MeOH:37% HCl (1:1:2, *v/v/v*) for 10 min. The extract was then heated at 65 °C, and the liquid phase was evaporated under a gentle nitrogen flow. The precipitated dyes were dissolved in 200 µL of DMSO. This last step differs from the original method devised by Wouters [20], who suggested the use of H<sub>2</sub>O and MeOH instead of DMSO used herein [38]. DMSO is superior compared to H<sub>2</sub>O and MeOH for dissolving indigoid compounds [39–41]. The solution was centrifuged, and the upper liquid phase was immediately subjected to HPLC analysis. HPLC was operated by using a gradient elution program, which was previously developed for the analysis of natural dyes [42].

## 3. Results and Discussion

The UV-Vis absorbance maxima of the compounds which were identified in the extracts of the textile samples are summarized in Table 1. As shown in the table, compounds that are components of madder (alizarin, purpurin and rubiadin), weld (apigenin, luteolin and chrysoeriol) and indigoid dyes (indigotin and indirubin) were detected in the sample extracts. The HPLC results per sample are summarized in Table 2.

The discussion is organized as follows. First, the results achieved for the samples which were dyed with madder (i.e., samples 1–8) are reported and elaborated. Next, samples in which madder was not found (i.e., samples 9–12) are discussed.

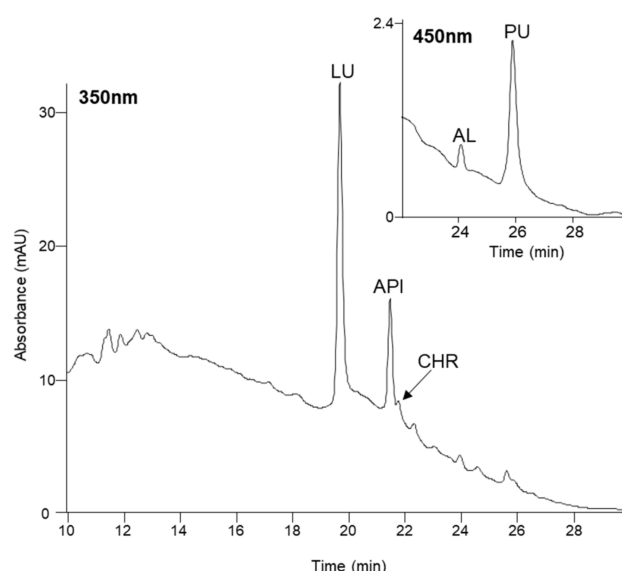
According to the results of Table 2, madder was the most frequently identified dye, and it was found, in total, in eight (1–8) out of 12 samples included in the study. This result is not surprising, as madder has been often found in ancient Egyptian textiles [2–13] and has been used by the dyers since antiquity [21,43]. In four samples (1–4), madder was the only identified dye. These were red samples as shown, for instance, in the photographs of samples 1 and 2 in Figure 2. According to the results of Table 2, rubiadin was detected only in samples 1 and 4, whereas alizarin was found in the extracts of all four (1–4) samples. Apparently, purpurin, the marker compound for the identification of madder, was found in all four (1–4) samples.



**Table 2.** HPLC results for the studied textile samples: detected compounds and identified dyes.

Sample No	Colour	Detected Compounds	Identified Dyes
1	Red	Alizarin, Purpurin, Rubiadin	Madder
2	Red	Alizarin, Purpurin	Madder
3	Red	Alizarin, Purpurin	Madder
4	Red	Alizarin, Purpurin, Rubiadin	Madder
5	Greenish	Alizarin, Purpurin, Indigotin, Indirubin	Madder, Indigo/Woad
6	Yellow	Alizarin, Purpurin, Luteolin, Apigenin, Chrysoeriol	Madder, Weld
7	Red-brown	Alizarin, Purpurin, Ellagic acid	Madder, Tannin
8	Red-brown	Alizarin, Purpurin, Ellagic acid	Madder, Tannin
9	Blue-greenish	Indigotin, Indirubin	Indigo/Woad
10	Blue	Indigotin, Indirubin	Indigo/Woad
11	Blue	Indigotin, Indirubin	Indigo/Woad
12	Green	Indigotin, Indirubin, Luteolin, Apigenin, Chrysoeriol	Indigo/Woad, Weld

In four other samples (5–8), madder was identified along with other dyes. In particular, in sample 5, madder was found in mixture with an indigoid dye, which can either be indigo or woad. Mixing madder and indigo/woad to imitate true, mollusc purple was a common practice in ancient Egypt [6]. However, purple threads in sample 5 were not visible by naked eye or under the microscope. Instead, the sample appeared to be rather greenish, as shown in Figure S1 of the Supplementary Materials. The chromatographic analysis of sample 6 is shown in Figure 3. The latter is provided as an example of the HPLC studies that were performed on the investigated samples. Apigenin, luteolin and chrysoeriol (weld components) were detected when the monitoring wavelength was set to 350 nm, whereas HPLC peaks corresponding to alizarin and purpurin (madder components) were revealed at a higher wavelength (450 nm). A direct comparison of the two HPLC profiles of Figure 3 should be carefully considered, as the two chromatograms were collected at different wavelengths. However, it can be observed that the peak areas of madder components are substantially lower than the corresponding areas of the weld components. The HPLC peak area ratio of luteolin versus purpurin, measured at 254 nm, was around two. Consequently, weld was the dominant dye in sample 6, and this is in agreement with the yellow colour of the sample, which is revealed in the photograph of Figure 2.



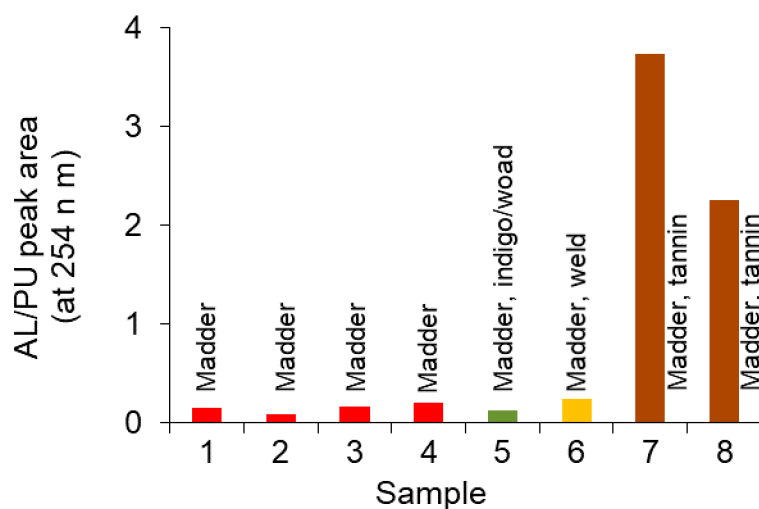
**Figure 3.** HPLC chromatogram of sample 6 collected at 350 nm showing the detections of luteolin (LU), apigenin (API) and chrysoeriol (CHR). The detections of alizarin (AL) and purpurin (PU) are revealed using a monitoring wavelength of 450 nm.

According to the results of Table 2, in the chromatograms of samples 7 and 8, madder components and ellagic acid (tannin) were detected. Tannins are very common in the flora; they possess interesting antimicrobial properties [44] and have been used both as dyes to produce black dyed fibres and as adhesives to promote the stabilization of colourants on textile substrates. The presence of tannin in samples 7 and 8 results in a dark hue compared to the usual red colour of madder. Hence, the colour of samples 7 and 8 appeared to be red-brown, as revealed, for instance, in the photograph of sample 8 (Figure 2) and in the Supplementary Materials (sample 7).

The term *madder* is used to describe different plants that belong to the *Rubiaceae* family. Important species which are often described in studies of objects of the Mediterranean cultural heritage are *Rubia tinctorum* L., *Rubia peregrina* L. and *Galium* species. *R. tinctorum* is found in Central and Southern Europe, Northern Africa and Central Asia, whereas *R. peregrina* (wild madder) has a range mostly restricted to Central and Southern Europe and Northern Africa [43,45,46]. *Galium* species can be found in any continent, whereas *Asperula tinctoria* L., which was probably also important in antiquity, is included in the native flora of Europe [43,45,46].

The HPLC results, collected from the analysis of samples extracted from cultural heritage objects, are often used to identify the exact plant species of madder dyes, lakes and paints [10,12,47–51]. In particular, the ratio of the HPLC peak areas of alizarin and purpurin was suggested as a criterion to identify *R. tinctorum* and *R. peregrina* [52]. It has been reported that *R. tinctorum* is rich in alizarin, whereas purpurin is the dominant anthraquinone in extracts of *R. peregrina* [52]. It should be noted, however, that purpurin is the main colouring compound in *Galium* and *Asperula* species [43]. Moreover, the large amount of rubiadin might be another marker for identifying *R. peregrina* [10,52], but more recent studies have raised concerns about the reliability of this criterion [49].

In the following, an attempt is carried out to discuss the possible biological sources of the madder dyes used in the studied textiles. The discussion focuses mainly on *R. tinctorum* and *R. peregrina*, which could have been used by the Egyptian dyers. It is stressed that the potential use of *Galium* and *Asperula* species cannot be ruled out. However, there are no chemical criteria (e.g., marker compounds or compositional data) that could be used to identify with confidence the use of these plant species in historical textiles. Figure 4 shows the ratios of the HPLC peak areas of alizarin versus purpurin (AL/PU) for samples 1–8. Peak areas were measured using HPLC chromatograms which were collected at 254 nm. This wavelength was used in the past to investigate *R. tinctorum* and *R. peregrina* samples [52], and it was, therefore, selected in the present study for comparative purposes. According to the results of Figure 4, madder dyes used for the treatment of the four samples (1–4) in which no other dye was found were poor in alizarin compared to purpurin. Likewise, small peak areas of alizarin compared to purpurin were measured for samples 5 and 6 in which madder was found in mixture with an indigoid dye and weld, respectively. It is reported that, for samples 1–6, the HPLC peak area ratio AL/PU measured at 254 nm ranged from 0.08 to 0.25. The low values of the AL/PU ratio indicate that alizarin was contained in samples 1–6 in small, but not negligible, amounts compared to purpurin. The results can offer support to the scenario that suggests that *R. peregrina* was used to treat samples 1–6; other possible sources, which are rich in purpurin, are of course the *Galium* and *Asperula* species. Moreover, as alizarin was detected in amounts that cannot be considered as negligible, the potential use of *R. tinctorum* cannot be excluded. Furthermore, it is possible that the Egyptian dyers had developed methods to affect the relative composition of madder plants before or during the dyeing process. For example, the relative composition of madder lakes which were prepared using *R. tinctorum* was tuned using materials and methods that were available in the past [53]. Control of the relative composition of the madder source provides control to the resulting colour of the final object. Madder rich in purpurin tends to induce a red-crimson hue [43] to the textile, which could be have been desirable by the ancient Egyptian dyers.



**Figure 4.** Ratios of HPLC peak areas of alizarin versus purpurin (AL/PU) for textile samples that were dyed with madder. Other dyes were identified in some samples as indicated. Dye identifications were reproduced from Table 2. Peak areas were measured using HPLC chromatograms which were collected at 254 nm.

As shown in Figure 4, a different result was obtained for samples 7 and 8, in which madder was identified along with tannin (ellagic acid). For these samples, the HPLC peak area of alizarin was higher than the corresponding area of purpurin, and the ratio AL/PU was  $>2.2$ . Consequently, *R. peregrina* cannot be the biological source of the madder dye used in samples 7 and 8. These samples were most likely dyed with *R. tinctorum*; *Galium* and *Asperula* species cannot be ruled out.

According to the results of Table 2, indigoid dyes were identified in samples 5 (in mixture with madder), 9–11 and 12 (in mixture with weld). Despite some noteworthy attempts [54], the development of a widely accepted method for distinguishing between indigo (*Indigofera tinctoria* L. and others) and woad (*Isatis tinctoria* L.) by HPLC is not available. Consequently, in Table 2, it is reported that the aforementioned samples could have been dyed either with indigo or woad. Both biological sources contain indigotin and indirubin in lower amounts.

As described in Table 2, in samples 9, 10 and 11, no other dye, apart from indigo/woad, was detected. Samples 10 and 11 were blue in colour whereas sample 9 had a greenish hue (Figure 2 and Supplementary Materials). As described above, in sample 5, indigo/woad and madder were identified. Another mixture often used in antiquity was that of blue indigo/woad with yellow weld to produce green dyed textile fibres [55]. This mixture was used to treat sample 12. The resulting green colour of sample 12 is revealed in the corresponding photograph of Figure 2.

#### 4. Conclusions

The following dyes were identified by HPLC in samples extracted from twelve ancient Egyptian textiles (4th–5th c. AD) of the Museum of Faculty of Archaeology, Cairo University: madder, weld (*Reseda luteola* L.) and indigoid dyes which can be either indigo (*Indigofera* species and other) or woad (*Isatis tinctoria* L.). These identifications were achieved as alizarin, purpurin, rubiadin (madder components), apigenin, luteolin, chrysoeriol (weld components), indigotin and indirubin (indigo/woad components) were detected in the chromatograms of the investigated samples. Moreover, ellagic acid was detected, indicating the presence of tannin sources. In some of the studied samples, madder was the only detected dye. It is reported that these samples were treated with a madder source which was rich in purpurin and poor in alizarin. This result is based on semi-quantitative results obtained from HPLC peak areas, which were measured at 254 nm. In other samples, madder was found in mixture with indigo/woad and weld. The HPLC chromatograms for

these samples revealed (again) the presence of a madder source with low alizarin versus purpurin HPLC peak area ratio. These results can offer support to the scenario, which suggests that wild madder (*R. peregrina*) was used to treat the aforementioned samples. However, as alizarin was detected in amounts that are not negligible, the potential use of common madder (*R. tinctorum*) cannot be excluded, particularly if methods were developed by the Egyptian dyers of the past to affect and control the relative composition of madder dye. Madder dyes rich in alizarin (probably originated from *R. tinctorum*) were detected only in samples treated with madder-tannin mixtures. Finally, it is noted that the potential use of other madder species (*Galium* and *Asperula* species) by the Egyptian dyers cannot be ruled out by the chemical results.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/heritage4040176/s1>, Figure S1. Photographs of samples which were included in the study.

**Author Contributions:** Conceptualization I.K. and O.A.-K.; methodology, I.K.; investigation, P.K.; data curation, I.K. and D.M.; writing—original draft preparation and review and editing, I.K. and O.A.-K. All authors have read and agreed to the published version of the manuscript.

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