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Identification of Dyestuffs in a Rare Coptic Garment Using High Performance Liquid Chromatography with Photodiode Array Detection (HPLC-PDA)

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ABSTRACT

The present study was employed A High Performance Liquid Chromatographic method coupled to a Diode-Array-Detector (HPLC-DAD) to identify the dyestuff in dyed wool samples collected from a rare tunic from the Coptic Museum in Cairo. Results indicated that mixtures of organic dyes were used in dying these samples to produce different colours and the most dominant dyes in the samples were madder and indigo. Based on this investigation, it was concluded that the tested dyed samples belong to the 6-7th century which is in agreement with initial dating of samples according to the style of the decoration.

Keywords: Coptic dyed textile samples; HPLC-PDA; Madder; Indigo

1. Introduction

Identification of the dyestuff components that constitute the dyes in a textile object is an important step for providing the appropriate effective conservation treatment. Identification of dyes in archaeological objects not only assists in establishing appropriate strategies for their conservation but it sometimes assists in their dating and locating their origins in addition to providing invaluable insights to the application of appropriate treatments during conservation and restoration work (Szostek, et al, 2003). Dyes identification can be very helpful in dating textiles depending upon the kind of dye and its manufacturing discovery date. Identification of natural dyes can often be done by comparing unknown archaeological dyes with new known ones (Goffer, 1980, Abdel-Kareem and El-Nagar, 2005, Zhang and Laursen, 2005).

Several analytical methods are widely used in the identification of dyes used in historical and archaeological textiles which can provide information as to where, when and how the textiles were dyed (Koren, 1993). Of all of the dye identification methods, HPLC is the most universally useful technique for the detection of a wide variety of dyes (Surowiec, 2003, Ferreira, et al, 2004, Wouters, 2004, Nowik, et al, 2005, Villemereuil and Karapanagiotis, 2006). The most widely used method involves extraction of dyes from textiles, followed by analysis using HPLC coupled to a diode array detector (DAD); this technique has

proven to be useful for identifying single and multiple colored component of many dyes (Schweppe, 1980, Wouters, 1985, Wouters and Rasoria, 1992, Halpine, 1996, Enez and Bohman, 1999, Orske, et al, 2003, Surowiec, et al, 2006). There is no method of dye analysis is effective in identifying historical dyes without using dye standards. Identification of dyes in a mixture is essential because dyes were frequently mixed when used on yarns or several different yarns mixed in a textile. The more dyes and their standards you can compare the unknown sample with- the more potential discovery from unknown samples is possible (Abdel-Kareem and El-Nagar, 2005).

This study is carried to identify the dyes in these samples to help us in their dating. Also dyes identification will be used in establishing a plan for conservation and restoration of these decorations. The main analytical tool employed for dyestuff identification in this study is the High Performance Liquid Chromatography coupled to the Diode-Array-Detector (HPLC-DAD).

2. Material and Methods

2.1 Samples: Historical dyed wool samples in different colours, used in this investigation, were collected from a rare Coptic tunic from the Coptic Museum in Cairo (see figure 1). The date of the tunic was unknown; however the dyed wool samples were dated according to their decoration style that characterized the 6-7 century (Abdel-Kareem, 2002).

Figure 1 A decorated part from the tested dyed tunic from the Coptic Museum in Cairo

2.2 Standard compounds of dyes: Alizarin, employed as reference material, was purchased from Acros Organics (Belgium) and was used as received. Purpurin was obtained as 90% pure from Acros Organics (Belgium) and was purified through multi recrystallization procedures with ethanol before it was used as a reference material. Munjistin (Ayyangar, and Venkataraman, 1956), 6-bromoindigotin (Robin, et al, 1999), indigotin (Tanoue, 2001), and xanthopupurin (Dhananjeyan, 2005) were synthesized and purified according to literature procedures from commercially available starting materials; these compounds were used as standard reference materials in this study.

2.3 Dye extraction techniques: The standard HCl extraction process, which is

widely used for extracting the organic colorants from a textile substrate (Wouters, 1985, Koren, 1993, Wouters, 1994, Hofenk de Graaf, 2004), was adapted and employed in this study for treating the samples. The process is summarized as follows: The dyed wool sample was immersed in H_2O: MeOH: 37 % HCl (1:1:2, v/v/v) at a ratio of 400 µL/1 mg sample at 100°C for 15min. The liquid phase was evaporated (60°C) under gentle nitrogen flow and the dry residue was dissolved in DMF at a ratio of 1ml/1mg sample. The sample was then centrifuged and 20 µL of the solution obtained were injected onto the HPLC column.

2.4 Analysis Method: Analysis was carried out with the aid of an HPLC system (GBC, Australia) which consists of a pump, Rheodyne Injector type 7125 with a 20 µl sample loop, column oven type GBC(TC 300 Controller/Australia) and a Diode Array Detector (DAD) type Knauer 2800 (Germany). The column employed was Hypersil Gold C18 (Phenomenex, USA) 250 x 4.6 mm (5 µm particle size). The temperature of the column was 40 °C. Isocratic elution was performed using a solvent mixture of acetontril / water / methanol (40:38:22%) + 0.1% trifluoroacetic acid as eluent at a flow rate of 1.0 mL/ min. The Diode Array Detector was programmed as follows: 0-6.8 min (290 nm); 6.8-7.5 min (270 nm); 7.5-9.0 min (290 nm); 9.0-10.9 min (289 nm); 10.9 – 14.0 min (280 nm); 14.0 – 19.0 min (300 nm) and 19.0- 60.0 min (289 nm).

3. Results and Discussion

By comparing the obtained data with the standard data in Table 1 and Figure 2, results indicate that the most dominant identified colorants in this textile object are alizarin, purpurin, and indigotin (Table 2). Displayed in Figures 3 and 4 are HPLC chromatograms of some samples; these chromatograms show that the most dominant identified colorants in the extract of the red threads are alizarin and purpurin and the dye used in the red threads is the madder dye. This is in agreement with what other researchers have discovered; Hofenk de Graaf confirmed that the presence of alizarin and purpurin indicates the use of madder, probably from *Rubia tincorum*. Moreover, these results indicates that the examined wool sample may go back in time to a period between the 3rd and the 9th century as it is known from the literatures that madder dye was common in that period on the Coptic textiles (Wouters, 1994). In addition, results show that the identified colorant in the extract of the blue threads is indigotin and the dye used in the blue threads is the indigo source. This information indicates that the examined blue wool sample may go back in time to a period between the 6th and 7th century as it is known from the literatures that indigotin dye was common in that period on the Coptic textiles (Masschelein-Kleiner and Maes, 1978).

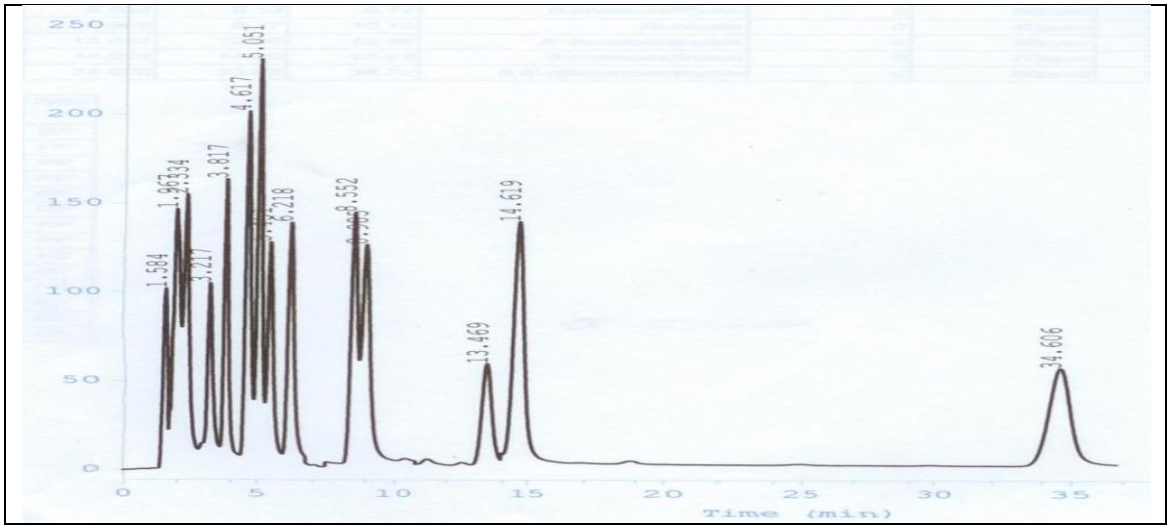

Figure 2: Chromatograms represent the retention times of all standard chromatograms.

Table 1: Represent the retention times of all standard chromatograms

Compound	RT. Time (min)	Concentration (ppm)
Natural red	1.9 + 2.3 + 2.7	50
Alizarin	4.75	50
Indigotin	5.80	30
Xanthopurpurin	6.43	50
Purpurin	6.97	80
Indirubin	7.95	30
6-bromoindigotin	11.13	80
Rubiadin	11.63	40
6'-bromoindirubin	17.92	50
6-bromoindirubin	19.55	70
6,6'-dibromoindirubin	48.37	80

Table 2: The results of dyestuff analysis of investigated old samples

Sample Color	Detected compounds	Identified dyestuff
blue	Indigotin	Indigoid dye source
Dark blue	Indigotin, Alizarin, Purpurin	Indigoid dye source, madder
Red	Alizarin, Purpurin	Madder
Brown	Alizarin, Purpurin	Madder
Green	Indigotin	Indigoid dye source
Purple	Indigotin, Alizarin, Purpurin	Indigoid dye source, Madder
Orange	Alizarin, Purpurin	Madder

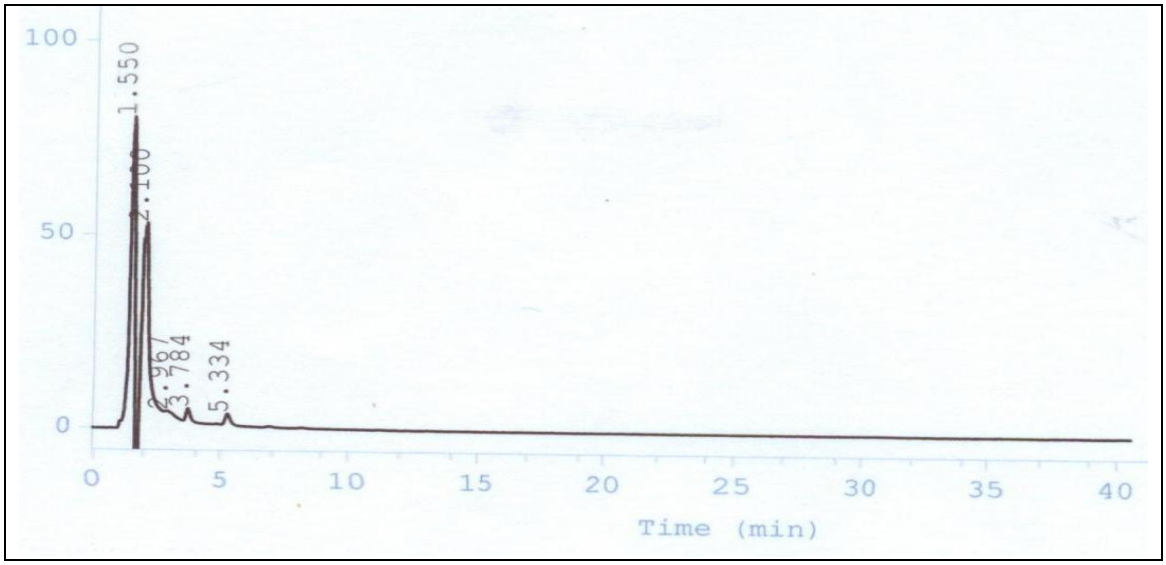

Figure 3: HPLC- PDA Chromatogram of the ancient red sample

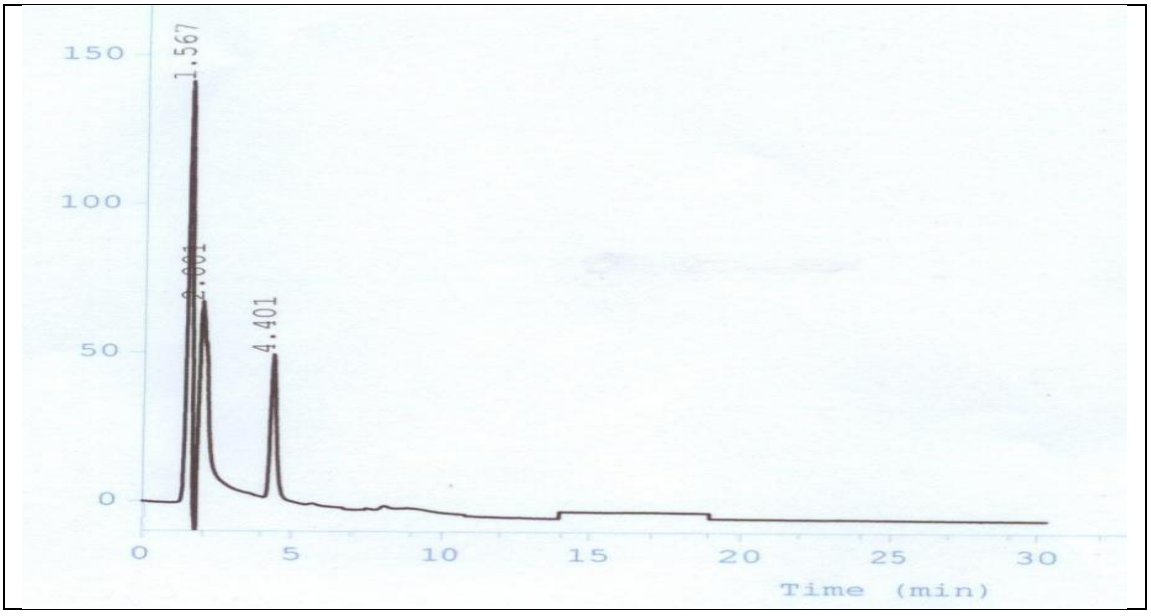

Figure 4: HPLC- PDA Chromatogram of the ancient blue sample

Results also show that the identified colorants in the extract of the brown threads are alizarin and purpurin and that the dye used in the brown threads is the madder dye. Hofenk de Graaf confirmed that the presence of alizarin and purpurin indicates the use of madder, probably from *Rubia tincorum*. To produce the brown colour, the madder may be used with iron mordant. This information indicates that the examined wool sample may belong to the 6th to the 7th century era as it is known from the literatures that madder dye with iron mordant was common used in this period for producing brown color on the Coptic textiles (Masschelein-Kleiner and Maes, 1978). Additionally, the identified colorants in the extract of the purple and dark blue threads are alizarin, purpurin, and indigotin. The difference between these colors is in the percentages of each component in the mixture. This would confirm that the dye used in the purple and dark blue threads is the madder and indogiten dyes. This information indicates that the examined wool sample may belong to the 7th century and later periods as it is known from the literatures that madder dye and indigotin were commonly used as mixture in this period to produce purple and dark blue colors on the Coptic textiles (Wouters, 1994). Finally, results show that the identified colorant in the extract of the green threads is indigotin. These results confirm that the dye used in the green threads is the indigo source and yellow source which may weld. This information indicates that the examined green wool sample may go back in time to the 6th to 7th century era as it is known from the literatures that indigotin dye mixed with weld were common for producing green colors in various shades in this period on the Coptic textiles (Masschelein-Kleiner and Maes, 1978).

4. Conclusions

In this investigation, it was concluded that the most dominant identified colorants in this textile object are alizarin, purpurin, and indigotin and the most dominant identified dyestuffs are madder and indigotin. Moreover, the results obtained from this study revealed that the tunic goes back in time to the 6th century to the 7th century era.

5. Acknowledgements

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