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Chromatographic Examination of Dyes Extracted from Coptic Textiles from the Collections of the National Museum in Warsaw[1]

Introduction

The National Museum in Warsaw is currently preparing a permanent exhibition of Coptic art, which will provide an opportunity for the presentation of its collection of 80 Coptic textiles dating from the late third/early fourth century A.D. to the twelfth century A.D. held by the National Museum in Warsaw. Small decorative appliqués, medallions and belts, as well as fragments of larger tapestries and a small conical shaped cap belong to this collection [Urbaniak-Walczak 1999: 401-410].

Chromatographic examination was carried out using HPLC with three methods of detection: diode-array spectrophotometric (DAD), fluorescence (FLD) and mass spectroscopy (MS). The main result of this research was the identification of the individual chemical components of anthraquinone, indigoid and flavonoid dyes of plant or insect origin extracted from sample fibres of different colours taken from the Coptic textiles. The results of the research were aimed at finding the optimum conditions for storage and display of the objects, for the optimization of conservation procedures, and perhaps even to help date the textiles being studied. The final results of the project, which was carried out in cooperation with the National Museum in Warsaw, were of use in the preparation of both a complete study of the natural dyes used in the textiles, and also in the catalogue which accompanied the exhibition of Coptic art.

Literature about the chemical, mainly chromatographic, examination of dyes from historical fabrics is quite extensive [Wouters, Verhecken 1991: 266-269; Cardon, Colombini, Oger 1989: 22-31; Walton, Tylor 1991: 5-7; Derksen, van Beek, de Groot, Capelle 1998: 277-281; Fischer, Bischof, Rabe 1990: 319-331; Nowik 1996; Wouters 1985: 119-128, 1991: 17-21, 1994: 38-45; Wouters, Maes, Germer 1990: 89-92]. Very little attention, however, has been paid to Coptic textiles. The investigation of textile dyes in Christian burials in Egypt from the fourth to sixth centuries A.D. by chemical reaction was pioneered by Pfister as early as the 1930s [Pfister 1935: 1-59]. The first HPLC examination of extracts from four Coptic objects from the third to the eighth centuries was reported by Wouters [1985: 119-128]. From his later works [Wouters 1993: 53-64,1994: 38-45] one can conclude that different compositions of natural dyes were used in different periods of time. For example in the Byzantine period the proportion of madder to kermes in Egyptian textiles was 95/5, while in the early Arabic period, proportion of madder to lac dye was 50/50.

The probable components of colours mentioned in the literature as found in Coptic textiles are listed in Table 1. The main red dyes were common madder (*Rubia tinctorum*) and wild madder (*Rubia peregrina*), with alizarin and purpurin as their main components, kermes (*Kermes vermilio*) with kermsic acid, Armenian cochineal (*Porphyrophora hamelii*) with carminic acid and lac dye (*Laccifer lacca*), with laccaic acids as the main colour components. As far as yellow dyes are concerned, weld (*Reseda luteola*) seems to be the most comonly used, with luteolin and apigenin as its main components. Among the range of blue dyes indigotin was identified, which is both a component of woad (*Isatis tinctoria*) and of indigo

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(*Indigofera tinctoria*). Also Tyrian Purple (*Murex trunculus* and *Murex brandaris*) with dibromoindigotin and monobromoindigotin as their characteristic components could hav been used by the Copts, although only in rare cases, because in Antiquity this dye was very expensive and hence seldom used.

Some dyes exhibit natural fluorescence or can acquire fluorescent properties after complexation with certain metallic cations. The fluorescent properities of carminic acid in aqueous solutions [Rasimas, Berglund, Blanchard 1996: 7220-7229] and indigotin on fibres [Shimoyama, Noda 1996: 27-42; Shimoyama, Noda 1996a: 7-84] have been noted. Flavonoids, which are also food constituents and important antioxidants, have been detected by HPLC through fluorescent detection [Gao, Tian, Zhao, Yang, Deng, Kang 2001: 415-423; Stecher, Huck, Popp, 2001: 73-80; Rodrigez-Delagato, Malovana, Perez, Borges, Montelongo 2001: 249-257; Arts, van de Putte, Hollman 1996: 1746-1751], which also entails a post column derivatization with aluminium [Hollman, van Trijp, Buysman 1996: 3511-3515; Saito, Sugisawa, Umegaki 2001: 174-178]. Enhancement of the fluorescent signal after the addition of aluminium has also been noticed for some red dyes such as alizarin, purpurin, brazilein, emodin, as well as extracts from cochineal and kermes [van Bommel 2001].

Flavanoids have also been the focus of several recent mass spectrometric investigations, due to the ability of the HPLC/MS techniques to identify and selectively quantify them in complex matrices of plant and food extracts [Justesen, Knuthsen, Leth 1998: 101-110; Toyoda, Tanaka, Hoshino, Akiyama, Tanimura, Saito 1997: 2561-2564; Nielsen, Freese, Cornett, Dragsted 2000: 1503-1509; Justesen, Knuthsen 2001: 245-250]. Laccaic acids derived from lac sources have been examined by positive ion electrospray mass spectrometry [White, Kirby 1999: 167-1778].

Results and Discussion

The research based on UV/Vis identification of compounds, was carried out in three stages. First, chromatographic measurements were carried out for purified dyes and natural dyeing substances collected from various sources. Then HPLC data was recorded for extracts of dyes from contemporary dyed fibres. Finally, the extracts from fibres taken from ancient Coptic objects were analyzed under different chromatographic conditions. Identification of dyes was based on retention times and their comparison with standards, as well as on UV/Vis spectra recorded for sample extracts and standards. Alcohol/water extracts from threads from Coptic textiles were investigated, as well as samples after pyridine extraction. The peak absorbance values obtained at 255 nm were used for the determination of the ratio of identified dyes for each extract. It was noted that sensitivity of detection with DAD may vary depending on the gradient of eluent used, even if the same extraction method is applied.

In some cases fluorescence detection can have better selectivity and detectability than UV/Vis detection. Methanolic solutions of Al(III), Ga(III), In(III), Zn(II) were examined as post-column reagents enhancing the fluorescence signal of analyzed dyes. Of these Ga(III) proved to be the best one, and a 10 mmol solution of this cation was used for fluorescence detection of some plant extracts and fifty six water/methanol extracts from the Coptic textiles.

For the plant extracts the results obtained were as those described elsewhere in the academic literature, except for weld where quercetin, kaempferol and rhamnetin were found by postcolumn reaction and fluorometric detector. It was known from literature that the main components of weld are luteolin and apigenin, together with kaempferol [Schweppe 1993]. The detection limits for the fluorescence detector with post-column reaction for quercetin, kaempferol and rhamnetin are several times better than those for luteolin and apigenin for DAD, so the method used allowed us to detect weld in several Coptic textiles in cases where DAD was ineffective.

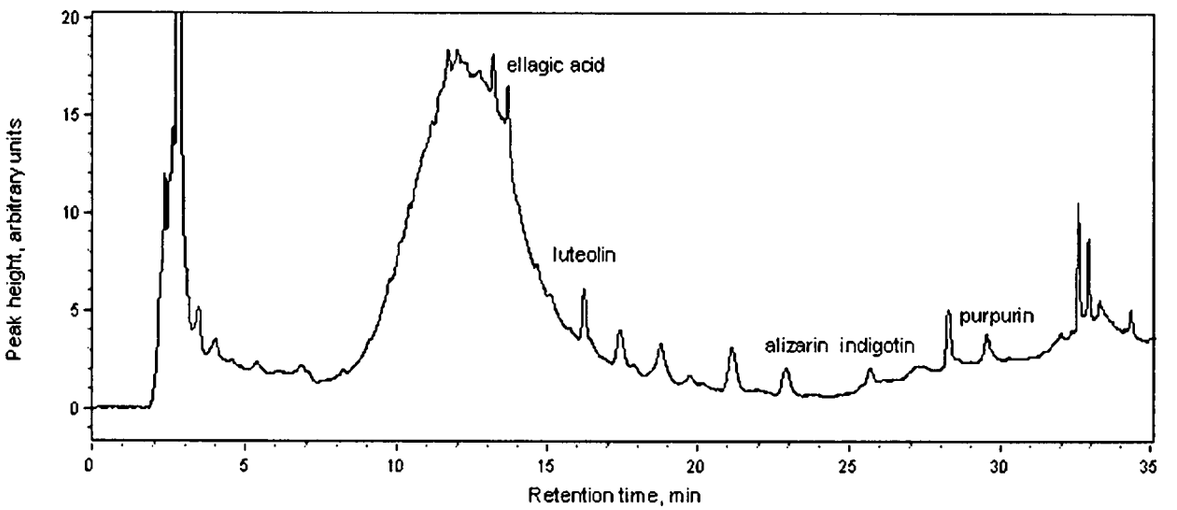
Fluorescence detection with Ga(III) solution as post-column reagent proved to be more sensitive than UV/Vis detection for purpurin, rhamnetin, quercetin, gallic acid, kaempferol and munjistin.

DAD was more sensitive for the detection of carminic acid, ellagic acid, luteolin, alizarin, apigenin, lawsone and indigoid dyes. The sample chromatograms for the extracts from yellow Coptic thread are shown in Fig. 1.

Chromatographic and mass spectrometric behaviour was investigated for selected dye compounds of flavanoid-, anthraquinone- and indigo-types. Most of the examined compounds could be ionized with positive and negative ion electrospray ionization. Difficulties were experienced with ionization by electrospray for indigo and bromated indigos, but these could be ionized by Atmospheric Pressure Chemical Ionization (APCI).

Mass spectrometric detection, utilizing different scanning modes of a triple quadrupole mass spectrometer, combined with the UV detection, was demonstrated to be a powerful approach to the detection and identification of dyes in extracts from archaeological textiles. This approach is extremely useful for cases where a limited amount of the sample material is available and a maximum amount of information needs to be extracted from the samples. MS detection can additionaly provide selectivity that is hard to obtain with UV detection.

DAD 278 nm



FLD

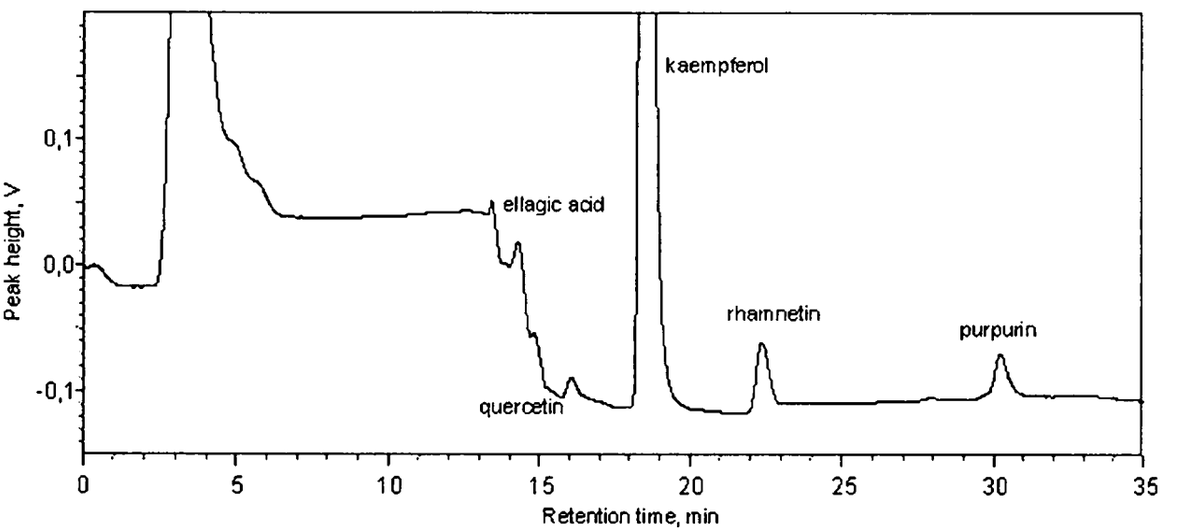


Fig.1. Chromatograms of extracts of yellow Coptic thread (wool, 7th – 9th century) obtained with different detections.

In the samples under investigation the detection capabilities of the LC/MS system were very comparable to those observed for the UV/Vis and fluorescence tests, and even superior for the following analytes: luteolin, apigenin and indirubin. Further conformation of the structure and structure elucidation of unknowns can be obtained by analysis of daughter ion spectra. In this way xanthopurpurin was identified in a few samples as well as monochloroalizarin together with dichloroalizarin in a single sample. The last two are probably products of an extraction procedure, but this hypothesis needs to be confirmed. Comparison of the results for UV/Vis, fluorescence and MS tests for some of the extracts from Coptic threads, together with relative peak area absorbance values obtained at 255 nm are shown in Table 2.

As is shown in Table 1, in some extracts from Coptic textiles new components of significant colours were found. Weld was found in one red sample and its identification was based on the presence of luteolin. Moreover, flavonols: quercetin and kamferol were identified in another four red samples, which could indicate the use of weld as a colorant on these fibres too. Weld was also found in three brown samples and its identification was based on presence of luteolin. Apigenin was also present in one of these samples. In an additional five brown fibres quercetin, kaempferol and rhamnetin were found, quercetin in two and kaempferol by itself on another two, which could suggest the presence of weld in these samples too. Weld was found in one violet sample, where luteolin and apigenin were identified, as well as flavonols in all three samples investigated. Quercetin, rhamnetin and kaempferol were also found in another two violet samples, which might also show the existence of weld in these samples too. Luteolin was found in three black samples, in which the presence of weld was postulated. In these samples which were tested flavonols were also identified (three in two samples, and two: rhamnetin and kaempferol, in one). Tanins were found in four brown samples, one beige and three green. Their identification was based on the presence of ellagic acid. Madder was found on three dark blue fibres. Its identification was based on presence of alizarin and purpurin. It is interesting to note that kaempferol was also found in these dark blue samples.

On one of the silk fibres carminic acid, laccaic acid A, laccaic acid B, purpurin, alizarin, apigenin, luteolin, ellagic acid and gallic acid were present in the diode array detector, as well as carminic acid, quercetin and kaempferol in the fluorescence detector. In the case of this fibre the presence of Armenian cochineal, lac-dye, madder, weld, indigotin and tannins was postulated. So far the simultaneous presence

Table 1. Potential composition of colours used for dyeing of Coptic textiles and new-found components.

Colour	Literature suggested components	New components
Red	Common madder (+ ellagic acid) Wild madder Common madder + indigotin Common madder + tannin Armenian cochineal Kermes Kermes + indigotin Indian lac insect Haematite	Weld
Pink	Common madder	
Beige	Common madder + luteolin	Tannins
Brown	Common madder Common madder + indigotin Wild madder + indigotin Indigotin Madder + kermes or cochineal	Tannins Weld
Orange	Common madder Common madder + wild madder (+ ellagic acid) Common madder + wild madder (+ indigotin) Common madder + weld	
Yellow	Weld Weld + common madder	
Green	Weld + indigotin Weld + indigotin + marzanna	Tannins
Blue	Indigotin (+ ellagic acid)	Madder Weld
Purple	Common madder + indigotin (+ ellagic acid) Common madder + indigo Wild madder + indigotin Wild madder + indigo Common madder Tyrian purple	
Black	Common madder + indigotin (+ ellagic acid) Indigotin	Weld

Table 2. Composition of example Coptic threads.

Sample (date. colour. fibre)	Identified compounds	Method of detection					Identified natural dyes
		DAD (1) hydrolyzate	DAD (2) hydrolyzate	DAD (3) pyridine extract	FLD hydrolyzate	MS hydrolyzate	
A.D. 6th yellow	Luteolin	0.43	0.58			+	Madder
wool	Apigenin	0.04	0.08			+	(Rubia tinctorum), Weld
	Alizarin	0.44	0.29			+	(Reseda luteola)
	Purpurin	0.09	0.05		+	+	
	Kaempferol				+		
	Quercetin				+		
	Rhamnetin					+	
A.D. 4th brown	Alizarin	0.1	0.42			+	Madder
wool	Purpurin	0.9	0.41		+	+	(Rubia tinctorum), Weld
	Munjistin		0.08		+		(Reseda luteola)
	Ellagic acid		0.04				Indigo
	Indigotin	<1%					Tannins
	Kaempferol				+		
	Quercetin				+		
	Rhamnetin				+	+	
	Luteolin		0.05			+	
	Apigenin					+	
	Indirubin					+	
A.D. 7th-9th	Alizarin	0.45	0.14			+	Madder
dark blue	Purpurin	0.21	0.35		+	+	(Rubia tinctorum), Weld
wool	Indigotin	0.22	0.51				(Reseda luteola)
	Indirubin	0.12				+	Indigo
	Kaempferol				+		
	Luteolin					+	
A.D. 7th-9th	Luteolin	0.75	0.27			+	Madder
green	Apigenin					+	(Rubia tinctorum), Weld

Continued on next page.

green	Apigenin					+	(Rubia tinctorum), Weld
wool	Alizarin	0.16				+	(Reseda luteola)
	Kaempferol				+		Indigo
	Quercetin				+		Tannins
	Rhamnetin				+	+	
	Ellagic acid		0.64		+	+	
	Indigotin	0.09	0.09				
	Indirubin					+	
A.D. 7^{th}-9^{th}	Alizarin	0.58	0.48			+	Madder
black	Purpurin	0.42				+	(Rubia tinctorum), Weld
wool	Indigotin			+			(Reseda luteola)
	Indirubin	<1%		+		+	Indigo
	Luteolin		0.1			+	Tannins
	Ellagic acid		0.42				

of carminic acid and laccaic acids has not been reported in extracts from Coptic textiles.

In all these samples luteolin, apigenin, ellagic acid, alizarin and purpurin were identified by the diode array detector on the basis of their retention times and UV-Vis spectra. Rhamnetin, kaempferol and quercetin were detected by the fluorimetric detector on the basis of their retention times only.

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