Chemical analysis of Murex-dyed textiles from wadi Murabba'at, Israel

Article *in* Journal of Archaeological Science: Reports · September 2015
DOI: 10.1016/j.jasrep.2015.08.003

CITATIONS
5

READS
374

4 authors:


Naama Sukenik
Israel Antiquities Authority
10 PUBLICATIONS **19** CITATIONS
SEE PROFILE


Alexander Varvak
Bar Ilan University
30 PUBLICATIONS **448** CITATIONS
SEE PROFILE


Zohar Amar
Bar Ilan University
53 PUBLICATIONS **701** CITATIONS
SEE PROFILE


David Iluz
Beit Berl College
82 PUBLICATIONS **662** CITATIONS
SEE PROFILE

Journal of Archaeological Science: Reports 3 (2015) 565–570

Contents lists available at ScienceDirect

Journal of Archaeological Science: Reports

journal homepage: http://ees.elsevier.com/jasrep

Chemical analysis of Murex-dyed textiles from wadi Murabba'at, Israel

Naama Sukenik [a,*], Alexander Varvak [b], Zohar Amar [c], David Iluz [d,e]

[a] National Treasures Department, Israel Antiquities Authority, Israel
[b] HPLC Unit, Faculty of Life Sciences, Bar-Ilan University, Ramat-Gan 5290002, Israel
[c] The Martin (Szusz) Department of Land of Israel Studies and Archaeology, Bar Ilan University, Israel
[d] The Mina and Everard Goodman Faculty of Life Sciences, Bar-Ilan University, Ramat-Gan 5290002, Israel
[e] Dept. of Environmental Science and Agriculture, Beit Berl College, Kfar Saba 44905, Israel

ARTICLE INFO

Article history:
Received 12 April 2015
Received in revised form 29 July 2015
Accepted 4 August 2015
Available online xxxx

Keywords:
Royal purple
Hexaplex trunculus
Armenian cochineal
HPLC
Dye
Murabba'at caves

ABSTRACT

In this article we shall focus on the chemical and chromatographic analyses that were used in the study of three textiles that were found in a cave in wadi Murabba'at, the Judean desert. The textiles date to the Roman period, and were dyed with a prestigious purple dye. High Performance Liquid Chromatography (HPLC) identified the Murex sea snail *Hexaplex trunculus* as a source of dye for the three textiles. Nevertheless, the dyeing process was not uniform. The color of one textile was modified to greenish-blue, apparently by exposure to the sun during the dyeing process. The two other textiles were subject to a double-dyeing process, and underwent a second dipping in a dye solution extracted from the Armenian cochineal insect. This process resulted in a reddish-purple color, which was indicative of high status. This is the first time that this dyeing technique was identified in ancient textiles from Israel. The multi-disciplinary research also identified different origins for the textiles.

1. Introduction

Textile-dyeing has been practiced since prehistoric times, using dyes that are extracted from both plant and animal sources. Modern analytical techniques make it possible to identify individual dye components from textiles that are thousands of years old. Besides understanding past technological capability in general and the dyeing industry in particular, the study of dyes extends our knowledge regarding trade networks, the economic and social status of the owners, and changing fashions.

A comprehensive study of dyed textiles that were found in caves in the Judean Desert and date to the Roman period was undertaken in 2013 (Sukenik, 2013). In the course of the study three outstanding textiles, which had been found at wadi Murabba'at, were identified. One of the textiles (no. 22, IAA. 490073; Fig. 1) was decorated with greenish-blue stripes. Each of the other two (no. 12, IAA no. 490063, Fig. 2; no. 20, IAA no. 490070; Fig. 3) was decorated with a band (*clavi*) of reddish-purple color (for details, see Sukenik et al., 2013). The sources for the dye that was used to color the textile were identified as Murex and scale insects. The use of Murex-derived dyes identifies these textiles as high-prestige items.

The Murex sea snail was the most expensive dye source in the Hellenistic and Roman periods. It was used to produce the Royal Purple mentioned by Aristotle (*Historia Animalium*, V, 15), Vitruvius (*De Arcitectura*, VII, 13.1), Pliny (*Naturalis Historia*, VI, 201; IX, 125–142; XXXV, 44–45) and other contemporary sources. Today, most researchers agree that the blue color (*Tekhelet*), as well as the purple hue (*Argaman*) — that were mentioned in the Bible (for example, in Exodus 26:1; Esther 8:15) — were produced from the Murex sea snail (Elsner and Spanier, 1987, 125–126; Ziderman, 2008). The final color depends on exposure to light, and ranges from shades of bluish-purple when the dye solution is exposed to sunlight, to reddish-purple when it is not (Elsner and Spanier, 1985, 126). Vitruvius, who observed this phenomenon, wrote that the color purple "*does not yield the same colour everywhere, but is modified naturally by the course of the sun*" (*De Arcitectura*, VII, 13.1). Experiments indicate that blue color results also from heating the dyed wool (see also Elsner and Spanier, 1985 126).

Three species of sea mollusks of the Muricidae family that were common in the Mediterranean were the primary source for purple dye: *Hexaplex trunculus* (Banded Dye-Murex, also known as *Murex trunculus*), *Bolinus brandaris* (Spiny Dye-Murex, also known as *Murex brandaris*) and *Stramonita haemastoma* (Red-mouthed Rock-shell, also known as *Thais haemastoma*) (Cardon, 2007, 566–871). The dye, which is extracted from the hypobranchial gland under the mollusk's mantle (Spanier and Karmon, 1987), belongs to the class of vat dyes, dyestuffs which must be reduced to soluble leuco form, before they

* Corresponding author.
E-mail addresses: naamasuk@gmail.com, naamas@israntique.org.il (N. Sukenik), Alexander.Varvak@mail.biu.ac.il (A. Varvak), amarzoh@gmail.com, zohar.amar@biu.ac.il (Z. Amar), iluzda@gmail.com (D. Iluz).

http://dx.doi.org/10.1016/j.jasrep.2015.08.003
2352-409X/

Fig. 1. Textile no. 22 (Clara Amit, courtesy of the Israel Antiquities Authority).

can be used for dyeing (Koren, 1996; Koren and Verhecken-Lammens, 2013). Vat dyeing involves biochemical and photochemical reactions, and complex reduction and oxidation processes that required the use of various additives, and would have required a number of days in ancient times (Cooksey, 2001, 737–738; Karmon, 1993, 36). This complex process was successfully reconstructed only after a considerable number of repeated experiments (Edmonds, 2002; Kanold, 2005; Koren, 2005). The high quality of this dye is reflected in its color fastness. It withstands repeated washing and exposure to the sun, preserving its hue for many years. The beauty of the color and the difficulty of obtaining and using it were among the reasons that made it the most expensive dye in the Roman period.

Although the composition of the Murex dye is not completely clear (Michel and McGovern, 1990), it is obvious that the final shade is affected by certain colorants, e.g. indigotin (IND) and indirubin (INR) which are found in plant sources such as woad (*Isatis tinctoria* L.) and the indigo plant (*Indigofera tinctoria* L.), as well as in several species of shellfish (Clark et al., 1993; Koren, 2006; Wouters and Verhecken, 1991). Other compounds: 6-monobromoindigotin (MBI), monobromoindirubin (MBIR), and 6,6-dibromoindigotin (DBI), which are the ones that confer the purple color, are present only in mollusk dyes (Koren, 2008a, 386; Wouters and Verhecken, 1991, 269). Other minor components, such as isatinoids and indirubinoids, were also recognized (Tables 1 and 2; Koren, 2006), but since they are often absent from archeological textiles, will not be discussed here.

The proportions of these components in the dye are affected by many factors, such as the sex and age of the mollusks, the geographic location, the dyeing process, and the method of analysis (Cardon, 2007,

Fig. 2. Textile no. 12 (Clara Amit, courtesy of the Israel Antiquities Authority).

Fig. 3. Textile no. 20 (Clara Amit, courtesy of the Israel Antiquities Authority).

556–557; Cooksey, 2001; Koren, 2008a, 388–389; Michel et al., 1992b). Nevertheless, a clear trend with respect to the ratios of the dye substances in each of the species was found (Table 2; see also Koren, 2008a; Michel and McGovern, 1990; Michel et al., 1992a), a trend which helps to identify the species of the Murex used in the dyeing of archaeological textiles with a high level of certainty. In this paper we shall describe the chemical and chromatographic analyses that were used in the study of the three textiles from wadi Murabba'at.

2. Materials and methods

Extracts of dyed fabrics were analyzed using HPLC-DAD (Hitachi LaChrom Elite Chromatography) system, a method that has been widely used since 1985 for the identification of dyes found in archaeological artifacts (Wouters, 1985). It is considered the most appropriate method for archaeological textiles since it requires only a small sample, ensuring minimal destruction. At the same time this method is reliable, with a high degree of accuracy and separation capability, qualities which are crucial for the identification of minor compounds in archeological textiles (Hofenk de Graaff, 2004; Koren, 1995, 2008b; Taylor, 1986).

A unique aspect of HPLC-DAD analysis lies in its ability to identify compounds based not only on the retention time, but also based on their UV–visible absorbance spectra, which are acquired continuously and in real time during a chromatography run. This technique confers several distinct advantages in comparison with analysis using a HPLC detector which only acquires preset wavelengths. First, it allows the optimal wavelength to be selected for analysis of a given dye, increasing detection sensitivity and enabling accurate quantification. Second, HPLC-DAD may reveal presence of a chromatographically overlapping impurity which has a very close retention time, but a distinct UV–visible spectrum. Even for these composite peaks, identification of target compound and/or impurity may still be achieved.

Table 1
Retention time and spectral wavelengths identification of the compounds found in dyed wool with *Hexaplex trunculus*.

	Retention time (min) Protocol B	λ_{max} (nm)
IS	4.24	241, 300
IND	8.87	241, 286, 613
INR	10.14	289, 363, 542
MBI	12.10	242, 289, 348, 608
MBIR	14.81	243, 298, 366, 536
DBI	16. 90	292, 303, 351, 601
DBIR	24.94	254, 301, 368, 544

Table 2
Amounts % of the compounds are found in the Mollusk species.

Mollusk species	IND	INR	MBI	MBIR	DBI	DBIR
Hexaplex trunculus	**39.69**	13.85	**32.41**	7.84	6.26	1.81
	24.08	15.33	**34.36**	14.96	5.89	4.61
Gland material from *Hexaplex trunculus*	**40.92**	14.10	**32.99**	7.99	7.05	<1
	49.68	<1	**44.66**	2.59	2.24	<1
Bolinus brandaris	4.47	<1	13.41	<1	**82.09**	<1
	3.94	<1	**22.59**	<1	**71.95**	1.52
	1.58	<1	10.12	<1	**85.11**	1
Stramonita haemastoma	<1	<1	4.30	<1	**68.84**	**26.68**
	<1	<1	1.21	<1	**71.98**	**26.73**
	1.41	<1	4.26	<1	**89**	5.23
	<1	<1	1.761	<1	**91.13**	7.10
	<1	<1	5.85	<1	**68.60**	**25.48**
	1.16	<1	4.31	<1	**62.99**	**31.51**

The bold numbers indicate the high percentage of the compounds that were found in each sample.

Table 3
Linear gradient elution of protocols A and B.

Protocol A:		Protocol B:		
Buffer A:	Acetonitrile	Buffer A:	0.5% (w/v) phosphoric acid	
Buffer B:	100 mM ammonium acetate pH 4: acetonitrile (9:1)	Buffer B:	Methanol	
Flow rate:	1 ml/min temp 30 °C	Buffer C:	H_2O	
Time (min)	% A	Time (min)	% A	% B
0	0	0	10	50
5	0	3	10	80
15	22	20	10	80
30	35	25	10	90
35	35	30	10	90
38	100	33	10	50
40	100	40	10	50
42	0			
50	0			

2.1. Modern standards

In the first stage of the study, unspun wool, dyed with known dyestuffs, was analyzed. The dyes that were analyzed included purple that was obtained from the Murex species *H. trunculus*, *B. brandaris* and *S. haemastoma*, and bordeaux-red that was extracted from the scale insects Kermes (*Kermes vermilio*), Armenian cochineal (*Porphyrophora hamelii*) and American cochineal (*Dactylopius coccus*). The dyeing procedure is described in detail in Section 2.1.1 below. In each test, the characteristic chromatogram was obtained, and the color compounds were identified by particulars of their retention time (R_t) and their characteristic absorbance spectra, including the wavelengths of the absorbance peak in the UV–visible spectrum (λ_{max}). The dye substances were isolated and compared to findings from similar studies.

2.1.1. Dyeing with Murex extract

Samples of wool weighing 2 g each were dyed with dyes that were produced from three species of Murex under laboratory conditions. One gram of Murex gland-tissue was used for each samples of fleece. The solution was prepared by adding water at a temperature of 85 °C to 1 g of Murex gland tissue in a standard beaker. Three grams of sodium hydroxide was added, and the solution stirred. Twelve grams of sodium hydrosulfite ($Na_2S_2O_4$) was then mixed in, stirred slowly to avoid oxygenation, followed by 4.5 g of either citric acid (household grade) or ammonium sulfate. The two-gram wool samples were then placed in the solution and incubated for at least 15 min, before they were removed from the beaker and exposed to air.

2.1.2. Dyeing with scale-insect extract

Extracts from the three species of scale insects were used to dye samples of wool as above. Identical dyeing protocol was used for all three species. Dried insects were heated to 70 °C in tap water for half an hour. After obtaining a red solution, alum-treated wool samples were incubated in it for one hour.

2.2. Extraction and sample preparation

Minute samples, weighing 1–3 mg, were taken from the modern dyed strands of wool and from the archaeological textiles, and dissolved in 150 μL dimethyl sulfoxide (DMSO), and heated for 10 min at 95 °C. The liquid was then separated from the sample and transferred to a sterile Eppendorf tube via centrifugation.

2.3. HPLC analysis protocol

Extracts of both the modern and archaeological samples were analyzed using a Hitachi LaChrom Elite Chromatography system running EZ Chrom Elite v. 3.2.1 software. The system consisted of an L-2130 binary pump, L-2200 autosampler, L-2300 column oven (column temperature of 30 °C was used for all analyses), and an L-2455 Diode Array Detector, set to acquire chromatogram spectra in the range of 200–700 nm, with extracted chromatograms at 254 nm, 454 nm, and 554 nm. The chromatographic column was a GraceSmart RP18, 5 μm, 250 mm × 4.6 mm ID. Two analytical protocols were used: protocol A for analysis of red and yellow dyes (Table 3), and protocol B for analysis of indigoid dyes. All the samples were analyzed using protocol A. If indigotin was identified, they were submitted to protocol B analysis, which gives accurate and quantifiable analysis of the various indigoids and detects the Murex-derived dyestuff.

3. Results of analysis, modern samples

The results of the analysis of the modern samples which were dyed with *H. trunculus* and analyzed according to protocol B, are presented in Table 1. Several components were identified according to their retention time and the absorbance spectra (Figs. 4-5): indigotin (IND) and its derivatives, monobromoindigotin (MBI) and dibromoindigotin (DBI), with absorbance maxima between 601 nm and 613 nm; indirubin (INR), monobromoindirubin (MBIR), and dibromoindirubin (DBIR) with absorbance maxima between 536 nm and 544 nm. In addition we identified isatin (IS), which is found in plant sources but also in several species of shellfish, with absorbance maximum at 300 nm (and see Koren, 2006, 51).

Repeated HPLC analyses of the wool samples that were dyed with extract of *H. trunculus* revealed that the relative quantities of IND, MBI,

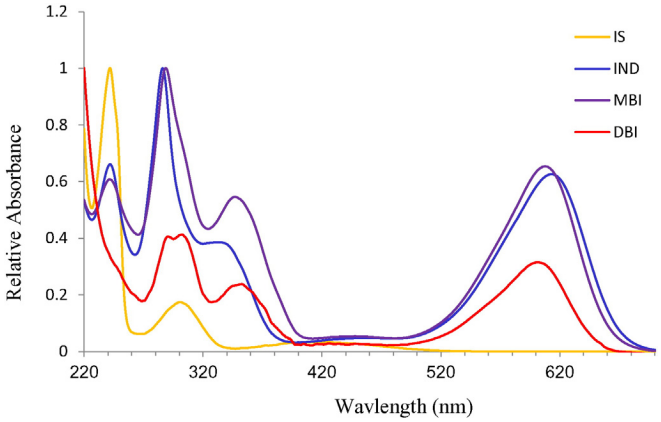

Fig. 4. UV–visible spectra of the compounds found in Murex species (IND, IS, MBI, DBI).

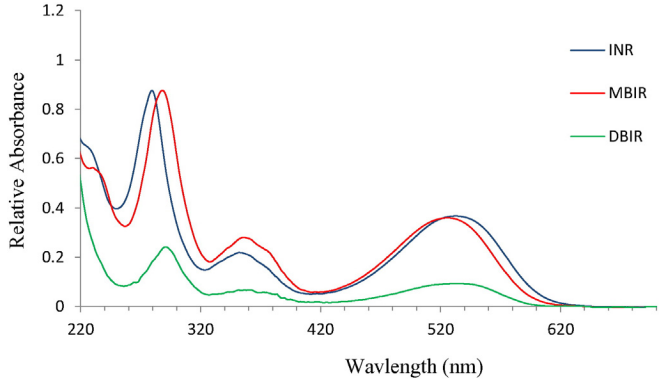

Fig. 5. UV–visible spectra of the compounds found in Murex species (INR, MBIR, DBIR).

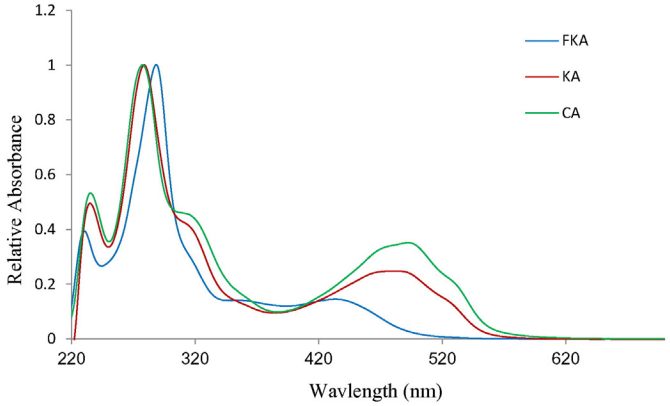

Fig. 6. UV–visible spectra of the compounds found in coccid scale insect (FCA, KA, CA).

and DBI are different for each test run (Table 2). It is possible, however, to see a clear trend: IND and MBI are the most abundant compounds (more than 24% and 32% of the total dye content respectively), while DBI is always present in relatively small quantities (less than 7% of total dye). Similar results were obtained when treated gland material (dye preparation that was not used to stain wool, but underwent heating and exposure to light) was tested (Table 2). In wool samples that were dyed with extracts from *B. brandaris* and *S. haemastoma*, DBI was determined to be the primary component (over 62%) responsible for the characteristic red hue. In contrast, the proportion of IND in dyes derived from these two mollusks was low (less than 5%) and was not always detected in the chromatography (Table 2). These results are in agreement with previous observations (Koren, 2008a, 338; Michel et al., 1992a; Michel and McGovern, 1990), and enable us to identify with confidence the species that best matched the samples analyzed.

The results obtained from the modern samples that were dyed with dyes extracted from scale insects and analyzed according to protocol A are presented in Table 4. Three main components that are known in the American cochineal insect (*D. coccus*) were identified in the modern samples: carminic acid (CA), with maximum absorbance of 492 nm, kermesic acid (KA), with maximum absorbance of 487 nm, and the component of flavokermesic acid (FKA), with a peak at 434 nm (Table 4; Fig. 6). These components were also found in other insects (*Coccidae* spp.) known to the dyeing industry in antiquity: Oak Kermes (*K. vermilio* and *Kermes echinatus*), which was used in the Middle East (Amar et al., 2005), Armenian cochineal (*P. hamelii*), which is found on roots of grass plants (Gramineae) in the Ararat Mountains in Turkey and Armenia (Cardon, 2007, 646–652; Donkin, 1977, 849–853), and the Polish cochineal (*Porphyrophora polonica*), which lives on roots of plants from the carnation family. Only two components — KA and FKA — were identified in the wool dyed using extract from the European Oak Kermes (*K. vermilio*) and from the Israeli species (*K. echinatus*). These components give the fabric its red-orange hue. CA, which gives the wool a red-purple hue, is completely absent in Oak Kermes (Amar et al., 2005, 782; Wouters and Verhecken, 1989, 192), but is the main dye-component in the Armenian cochineal and the American cochineal. According to the literature, KA and FKA have been detected in Armenian cochineal insects, but only in minute quantities (Wouters and Verhecken, 1989, 194). These distinctions help discriminate between the species and determine the source of the insect-dye at the species level.

Table 4
Retention time and spectral wavelength identification of the compounds found in species of Coccid scale insect, according to protocol A.

	Retention time (min) Protocol A	λ_{max} (nm)
Carminic acid	11.93	234, 278, 492
Kermesic acid	16.2	240, 280, 487
Flavokermesic acid	18.9	246, 288, 434

4. Results and discussion: analysis of the archaeological textiles

The components of the dyes were identified according to their particular retention time (R_t) and their characteristic absorption spectra, which included wavelengths of absorbance peaks in the UV–visible spectrum (λ_{max}). All three textiles from wadi Murabba'at were submitted to protocol B, and the results of the analysis at 554 nm are shown in Table 5 and Fig. 7; the results at 454 nm and according to protocol A are shown in Table 6 and Fig. 8.

The results for textiles nos. 12 and 20 were similar, and they are therefore discussed together.

4.1. Textile no. 22

The components detected in the extract from a blue-green thread in textile no. 22 according to protocol B were IND at 8.93 R_t (238 nm, 286 nm, 613 nm λ_{max}; Table 5; compare with Fig. 4), MBI at 11.65 R_t

Table 5
Results of the archaeological textiles obtained with protocol B, detection at 554 nm.

	Retention time (min)	λ_{max} (nm)	
Mur. 12	8.93	238 nm, 286 nm, 613 nm	IND
	11.71	287 nm, 337 nm, 608 nm	MBI
Mur 20	8.96	240 nm, 286 nm, 613 nm	IND
	11.75	285 nm, 343 nm, 608 nm	MBI
Mur 22	8.93	238 nm, 286 nm, 613 nm	IND
	11.65	238 nm, 289 nm, 348 nm 607 nm	MBI
	16.65	292 nm, 302 nm, 351 nm, 601 nm	DBI

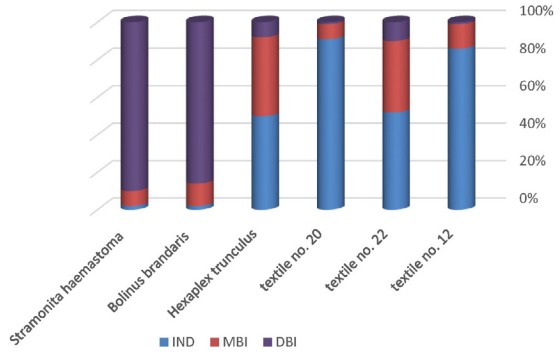

Fig. 7. Relative presence of dye components at 554 nm of archaeological textiles compared with modern fleeces dyeing with three species of sea mollusks.

Table 6
Results of the archaeological textiles obtained with protocol A, detection at 454 nm.

	Retention time (min)	λ_{max} (nm)	
Mur. 12	12.49	231 nm, 277 nm, 492 nm	Carminic acid
Mur 20	12.51	229 nm, 278 nm, 491 nm	Carminic acid
Mur 22	–	–	–

(238 nm, 289 nm, 348 nm 607 nm λ_{max}) and DBI at 16.65 R_t (292 nm, 302 nm, 351 nm, 601 nm λ_{max}). IND is found in plant sources such as woad (*I. tinctoria* L.) and the indigo plant (*I. tinctoria* L.), but it is also found in several species of shellfish (Clark et al., 1993; Koren, 2006). MBI and DBI, on the other hand, occur only in mollusk-derived dyes (Table 5; see also Wouters and Verhecken, 1991). It can therefore be determined with certainty that the textile was dyed with genuine shellfish dye. Moreover, based on the percentages of the substances identified, it can be established that the source of the purple color used to dye this textile was *H. trunculus*. According to the chromatogram (Fig. 7), there was high percentage of IND (52%) and MBI (38%), with only a minor percentage of DBI (10%). This chromatogram is particularly characteristic of *H. trunculus* (Table 2), in contrast to *B. brandaris* and *S. haemastoma*, in which the concentration of IND was low (2%) and the concentration of DBI was high (86–90%) (Table 2; see also Michel et al., 1992a; Koren, 2008a; Koren and Verhecken-Lammens, 2013).

4.2. Textiles nos. 12 and 20

The components that were detected in textiles nos. 12 and 20 according to protocol B were similar to those found in textile no. 22 (Table 5; Fig. 7). IND was detected at 8.93 R_t and 8.96 R_t, with a typical spectrum (238 nm/240 nm, 286 nm, 613 nm λ_{max}), while MBI was detected at 11.71 R_t and 11.75 R_t, with a typical spectrum (287 nm, 337 nm, 608 nm and 285 nm, 343 nm, 608 nm λ_{max}). According to the chromatogram (Fig. 7), the most abundant colorant is IND (>86%), followed by MBI (8–13%). Hence, it can be determined that these two textiles were colored with a dye substance obtained from *H. trunculus* (compare to Table 2). In addition, according to the chromatogram of the analysis by protocol A at 454 nm, there is another peak at 12 min (spectrum 231 nm, 277 nm, 492 nm; see Table 6), which is appropriate for CA (compare with Table 4). CA is found in various species of insects (*Coccidae spp.*) that were known to the dyeing industry in antiquity. Oak Kermes (*K. vermilio* and *K. echinatus*), which was used in the Middle East, can be discarded as a source, because it does not contain any CA (Fig. 8; see also Wouters and Verhecken, 1989; Amar et al., 2005). American cochineal (*D. coccus*), which contains high concentration of CA is a New World insect, originally endemic to Central and South America (Cardon, 2007, 619–632), and can therefore also be discarded as a source. Historical research date the earliest use of the Polish cochineal (*P. polonica*), which also contains CA, to the 6th or 9th centuries CE (Cardon, 2007, 644; Forbes, 1964, 102), considerably later than the date attributed to the textiles examined in this study. In addition, Polish cochineal contains a significant quantity (over 30%) of KA as well as CA (Wouters and Verhecken, 1989, 193). This combined evidence rules out Polish cochineal as a source of dye substance in this context. On the other hand, CA is a significant (93%) component in the Armenian cochineal (*P. hamelii*) extract (Fig. 8) and we can therefore assume that the textiles were dyed with dyes derived from *Murex* and Armenian cochineal. Nevertheless there is still a possibility that they were used other species of "crimson dyeing scale insect" that is rich in carminic acid (Cardon, 2007: 655–656), but only future research can state so with certainty.

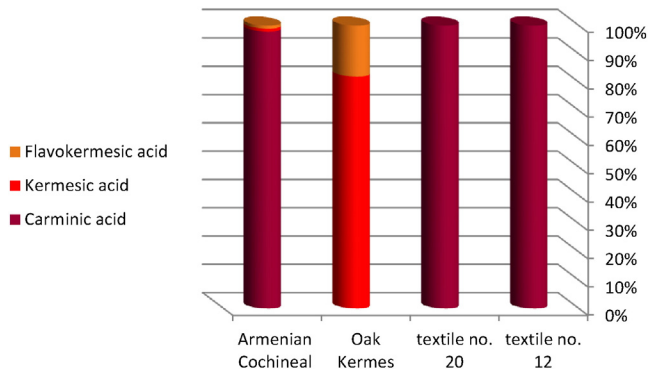

Fig. 8. Relative presence of dye components at 454 nm of archaeological textiles compared with modern fleeces dyeing with Armenian cochineal and Oak Kermes species insects.

5. Discussion and conclusion

The chemical analysis of the textiles from wadi Murabba'at identified a dye that was extracted from the *H. trunculus* sea mollusk in all three. The hue of textile no. 22 is derived exclusively from this source. Its greenish-blue tint indicates that the dye solution was exposed to sunlight during the dyeing process, causing photodebromination of the reduced leuco-dye that produced the blue color (Elsner and Spanier, 1985). Alternatively, the dyed textile may have been heated to produce this color (Ziderman, 2008, 41). Our findings indicate that *H. trunculus* was the source for rare hues of blue, which have been reported in very few textiles anywhere in the world: among them one textile in the Katoen Natie Collection in Belgium which has blue fibers whose color was produced from the *Murex* snail (Koren and Verhecken-Lammens, 2013, 31), and a blue textile that was found at a burial site in Pazyryk, Siberia (Polosmak et al., 2006, 43). It is possible that textile no. 22 was dyed using the same technique as the *Tekhelet* textiles that are mentioned in ancient Jewish sources (for example, Ex. 39:24; Num. 15:38), and our study therefore contributes to the extensive research relating to this subject (Elsner and Spanier, 1987; Ziderman, 2008).

The reddish-purple color of textiles nos. 12 and 20 was identified as the result of a double-dyeing process using Banded Dye-Murex (*H. trunculus*) and Armenian cochineal (*P. hamelii*) or similar of crimson dyeing scala insect that is rich in carminic acid. Ancient textile producers were aware of the various available techniques for manipulating and transforming color during the dyeing process. They took advantage of the properties that cause Murex-derived dyes to change color under exposure to sunlight, and of the changes brought about by combining dye solutions. They used the double-dyeing technique to transform and enhance the color of fleeces that had been dyed purple with colorant obtained from shellfish. A second dipping in a dye that was produced from the madder plant (*Rubia tinctorum* L.), or in a prestigious red dye as the one extracted from the coccid scale insect (*Coccidae* spp.), produced new and unique hues of purple such as the deep wine-red bordeaux color, which was considered prestigious in the Roman period (Born, 1937, 113; Jidejian, 1969, 151).

Ours is the first finding in Israel of a textile that was double-dyed with a combination of Murex/insect derived dyes. The technique of obtaining reddish-purple colors by double-dyeing with sea snails and insects was mentioned by Pliny the Elder and was called *Hysgine* (*Naturalis Historia* IX, 141). A similar technique was identified in a number of other textiles dated to the Roman Period: a textile from Palmyra (Böhmer and Karadag, 2003, 92; Pfister, 1934, nos. T.18, T.19); another from the Roman fortress Maximianon in eastern Egypt, where a Roman-period textile was double-dyed with Kermes and *H. trunculus* (Wouters et al., 2008: 13; textile no. 95.33039.9); and two textiles from Didymoi, another Roman fortress on the road to Berenike (Cardon et al., 2011: 202–203). Presumably, this dyeing technique was widely used for apparel worn by the upper classes, indicating the popularity of the reddish-purple shade. The identification of the dyes allows us to suggest with a considerable degree of confidence that textiles nos. 12 and 20 from wadi Murabba'at are imports, since they were dyed with the

Armenian cochineal, an insect that was not prevalent in the Land of Israel. This assumption is supported by microscopic examination of the two textiles which revealed that they were spun in a manner characteristic of imported textiles. The blue textile no. 20, on the other hand, was spun in a way that suggests local origin (Sukenik et al., 2013, 51).

Our interdisciplinary study, which combined analytical chemistry, archaeological evidence and study of historical records made it possible to identify individual dye-components, and the techniques that were used to dye three Roman-period textiles. However, the results take us beyond the ancient textiles themselves. The study provides an insight to the people behind the finds from the wadi Murabba'at cave, and expands our knowledge of the purple-dyeing industry in Israel during the Roman period in general.

Acknowledgments

The authors thank Dr. Orit Shamir, curator of Organic Materials at the Israel Antiquities Authority for her help, Rafi Yavetz of the School of Marine Sciences, Ruppin Academic Center, for his help in obtaining sea snails, the Society for Protection of Nature in Israel for permission to collect mollusks for our study, and Smadar Gabrieli for the English editing.

References

Amar, Z., Gottlieb, H., Varshavsky, L., Iluz, D., 2005. The scarlet dye of the holy land. Bioscience 55, 1080–1083.
Böhmer, H., Karadag, R., 2003. New dye research on Palmyra textiles. Dyes Hist. Archaeol. 19, 88–92.
Born, W., 1937. Purple in classical antiquity. Ciba Rev. 1 (4), 111–118.
Cardon, D., 2007. Natural Dyes: Sources, Tradition, Technology and Science, Archetype, London.
Cardon, D., Nowik, W., Granger-Taylor, H., Marcinowska, R., Kusyk, K., Trojanowicz, M., 2011. Who Could Wear True Purple in Roman Egypt? Technical and Social Considerations on Some new Identifications of Purple from Marine Molluscs in Archaeological Textiles. In: Alfaro, C., Brun, J.-P., Borgard, P.H., Pierobon Benoit, R. (Eds.), Textiles y Tintes en la Ciudad Antigua, Universitat de València - Centre Jean Bérard (CNRS-EFR), Purpurae Vestes III, Valencia, pp. 197–214.
Clark, R.J.H., Cooksey, C.J., Daniels, M.A.M., Withnall, R., 1993. Indigo, woad, and Tyrian Purple: important vat dyes from antiquity to the present. Endeavour 17, 191–199.
Cooksey, C.J., 2001. Tyrian purple: 6,6′-dibromoindigo and related compounds. Molecules 6, 736–769.
Donkin, R.A., 1977. Insect dyes of western and west-central Asia. Anthropos 72, 847–880.
Edmonds, J., 2002. The mystery of imperial purple dye. Hist. Dyes Ser. 7, 1–38.
Elsner, O., Spanier, E., 1985. The dyeing with Murex extracts. An unusual dyeing method of wool to the Biblical sky blue. Proceedings of the 7th International Wool Textile Research Conference 5, pp. 118–130.
Elsner, O., Spanier, E., 1987. The past, Present and Future of *Tekhelet*. In: Spanier, E. (Ed.), The Royal Purple and the Biblical Blue Argaman and *Tekhelet*. Keter, Jerusalem, pp. 167–177.
Forbes, R.J., 1964. Studies in Ancient Technology, Volume 4, Fibres and Fabrics of Antiquity. E.J. Brill, Leiden.
Hofenk de Graaff, J.H., 2004. The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs. Archetype Publications, London.
Jidejian, N., 1969. Tyre Through the Ages, with a Foreword by Emir Maurice Chehab. Dar El Mashreq Publishers, Beirut.
Kanold, I.B., 2005. The Purple Fermentation vat Dyeing or Painting Parchment with *Murex trunculus*. Dyes in History and Archaeology 20. Archetype Publications, London, pp. 150–154.
Karmon, N., 1993. The Purple dye Industry in Antiquity. In: Sorek, C., Ayalon, E. (Eds.), Colors from Nature: Natural Colors in Ancient Times, Eretz Israel Museum, Tel Aviv, pp. 35–37.
Koren, Z.C., 1995. An efficient HPLC analysis scheme for plant and animal red, blue and purple dyes. Dyes Hist. Archaeol. 13, 27–37.
Koren, Z.C., 1996. Historico-chemical analysis of plant dyestuffs used in textiles from ancient Israel. In: Orna, M.V. (Ed.)Archaeological Chemistry: Organic, Inorganic and Biochemical Analysis, ACS Symposium Series 625. American Chemical Society, Washington, D.C., pp. 269–310 (Ch. 21).
Koren, Z.C., 2005. The First Optimal all-*Murex* all-Natural Purple Dyeing in the Eastern Mediterranean in a Millennium and a Half. Dyes in History and Archaeology 20. Archetype Publications, London, pp. 136–149.
Koren, Z.C., 2006. HPLC-PDA Analysis of Brominated Indirubinoid, Indigoid, and Isatinoid Dyes, Chapter 5. In: Meijer, L., Guyard, N., Skaltsounis, L., Eisenbrand, G. (Eds.), Indirubin, the Red Shade of Indigo. Life in Progress Editions, Roscoff, France, pp. 45–53.
Koren, Z.C., 2008a. Archaeo-chemical analysis of royal purple on a Darius I stone jar. Microchim. Acta 162, 381–392.
Koren, Z.C., 2008b. Non-Destructive vs. Microchemical Analyses: The Case of Dyes and Pigments, Art 2008 — 9th International Conference, Jerusalem, pp. 37.1–37.10.
Koren, Z.C., Verhecken-Lammens, C., 2013. Microscopic and chromatographic analyses of molluskan purple yarns in a late Roman period textile. e-Preserv. Sci. (e-PS) 10, 27–34.
Michel, R.H., McGovern, P.E., 1990. The chemical processing of royal purple dye: ancient description as elucidated by modern science, part II. Archeomaterials 4, 97–104.
Michel, R.H., Lazar, J., McGovern, P.E., 1992a. The chemical composition of the indigoid dyes derived from the hypobranchial glandural secretions of *Murex* molluscs. J. Soc. Dye. Colour. 108, 145–150.
Michel, R.H., Lazar, J., McGovern, P.E., 1992b. Indigotin dyes in Peruvian and Coptic textiles of the university museum of archaeology and anthropology. Archeomaterials 6, 69–83.
Pfister, R., 1934. Textiles de Palmyre. Editions d'art et d'histoire, Paris.
Polosmak, N.V., Kundo, L.P., Balakina, G.G., Mamatyuk, V.I., Vasilyev, V.G., Karpova, E.V., Malakhov, V.V., Vlasov, A.A., Kraevskaya, I.L., Dovlitova, L.S., Korolyuk, E.A., Tsareva, E.G., 2006. Textiles from the "Frozen" Tombs in Gorny Altai 400–300 BC: An Integrate Study. Publishing House of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk (in Russian).
Spanier, E., Karmon, N., 1987. Muricid Snails and the Ancient dye Industries. In: Spanier, E. (Ed.), The Royal Purple and the Biblical Blue Argaman and *Tekhelet*. Keter, Jerusalem, pp. 179–192.
Sukenik, N., 2013. Dyes in Textiles from the Early Roman Period in the Judean Desert Caves: Chemical, Historical, and Archaeoloical Aspect. Bar-Ilan University, Ramat-Gan (in Hebrew).
Sukenik, N., Iluz, D., Shamir, O., Varvak, A., Amar, Z., 2013. Purple dyed textiles from wadi Murabba'at: historical, archaeological and chemical aspects. Archaeol. Text. Rev. 55, 46–54.
Taylor, G.W., 1986. Natural dyes in textile application. Color. Relat. Top. 16, 53–61.
Wouters, J., 1985. High performance liquid chromatography of anthraquinones: analysis of plant and insect extracts and dyed textiles. Stud. Conserv. 30.
Wouters, J., Verhecken, A., 1989. The coccid insect dyes: HPLC and computerized diode-array analysis of dyed yarns. Stud. Conserv. 34, 189–200.
Wouters, J., Verhecken, A., 1991. High-performance liquid-chromatography of blue and purple indigoid natural dyes. J. Soc. Dye. Colour. 107, 266–269.
Wouters, J., Vanden Berghe, I., Ghislaine, R., Breniaux, R., Cardon, D., 2008. Dye analysis of selected textiles from three roman sites in the eastern desert of Egypt. Dyes Hist. Archaeol. 21, 1–16.
Ziderman, I., 2008. The biblical dye *Tekhelet* and its use in Jewish textile. Dyes Hist. Archaeol. 28, 36–44.