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## 15

# The First Optimal All-Murex All-Natural Purple Dyeing in the Eastern Mediterranean in a Millennium and a Half

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### Introduction

PHOENICIAN PURPLES and BIBLICAL BLUES, the most royal and sacred of all ancient dyeings, were produced from Levantine sea snails of the family Muricidae. These mollusks may have been in use for the production of the Royal purple pigment from as early as perhaps 4,000 years ago. A number of articles have appeared describing the species – commonly called murex – that were used in this ancient biochemical industry.<sup>1</sup> The chemistry of the dye and its production from the glandular fluid precursors has been studied,<sup>2</sup> and also reviewed.<sup>3</sup> Analytical methods have been developed for the study of the pigment,<sup>4</sup> which consists of numerous isomeric brominated and unbrominated indigoids, indirubinoids, and other colorants.<sup>5</sup>

Ancient historical accounts, especially that of Pliny the Elder,<sup>6</sup> which describe dyeing with molluskan species, have been scrutinized in the light of modern science.<sup>7</sup> An experimental reconstruction of the natural dyeing process that could have been practiced in antiquity, however, has eluded decipherment, until recently.<sup>8</sup> Pliny recorded his famous 2,000-year-old description of the various stages of the ancient purple dyeing craft in the Roman empire, as he understood it. But his account suffers from incomplete information and has not been fully comprehended; this has frustrated those researchers who wish to

reconstruct that ancient majestic craft. Pliny's report was sufficient for a general description of the process, but various suppositions and experimental attempts actually to reproduce an all-natural dye vat, based, at least in part, on interpreting Pliny's 'menu', were either unsuccessful or implausible, as discussed later.

This paper reports on the first successful experimental reconstruction of the maximal (that is, best possible) all-murex completely natural dyeing that could conceivably have been practiced by the ancient eastern Mediterranean purple dyer. This reconstructed dyeing process utilizes an all-murex fermentative dye vat for both the dye and reductant sources, and also makes optimal use of the total dye content by dyeing 'in-the-shell'. These two findings were not previously reported upon. This work is based on experiments performed at the author's laboratory between 1993 and 2000<sup>9</sup> and presented at the *Dyes in History and Archaeology* meeting in Amsterdam in November 2001.<sup>10</sup>

The natural fermentative reduced dye vat was exhausted with three sequential dyeings and the colorimetric properties of each of these dyeings were measured according to the CIELab coordinate system using a computerized reflectance spectrophotometer. This is also the first published report on the quantitative color characterizations of modern all-natural real-purple dyeings.

## The murex family of snails

The family of sea snails whose common appellation is simply the murex family belongs to the order Neogastropoda.<sup>11</sup> In the Israeli portion of the Mediterranean sea there are over 700 species of mollusks,<sup>12</sup> of which 16 are Muricidae species.<sup>13</sup> Only three members of this clan, however, have been associated with purple dyeing along the Mediterranean basin, and especially along the coasts of what are now Israel and Lebanon. These Levantine species include *Hexaplex trunculus* (Linnaeus, 1758), also known as *Murex trunculus*, *Phyllonotus trunculus*, *Trunculariopsis trunculus*, or simply as ‘trunculus’; *Bolinus brandaris* (Linnaeus, 1758), also known as *Murex brandaris* or ‘brandaris’ for short; and *Stramonita haemastoma* (Linnaeus, 1766), also known as *Thais haemastoma*, *Purpura haemastoma* or ‘haemastoma’. In his treatise, Pliny offers various colorful descriptions of purple-producing snails and the geographical areas thought to possess the best types.<sup>14</sup>

Several important first-hand observations of the discovery of the murex family of sea snails at various archaeological excavations have been described.<sup>15</sup> From the circumstantial archaeological and historical records, one can safely assume that these mollusks, dating from as early as about 1700 BC, were generally used for purple dyeings, which later became known as Phoenician or Tyrian purples. The chemical evidence, however, decisively confirms that these murex snails were, in fact, in use for this craft at least by the middle of the 2nd millennium BC.<sup>16</sup> This conclusion is based on the ‘chemical fingerprinting’ of modern murex snails and comparing the constitution of their dyestuff with that of residual pigmentation found on various fragmentary potsherds from ancient dyeing vats. In all those chemical analyses, the main component of both the modern and the ancient pigment was 6,6'-dibromoindigo (DBI), which, in this part of the world, is obtainable solely from the murex family of snails.

The colorless brominated and unbrominated indoxyl sulfate precursors to the dye components and the requisite enzyme purpurase are all contained within the

hypobranchial gland of the living animal.<sup>17</sup> Upon puncturing the gland, or when the animal expires, the enzyme comes into contact with these precursors and hydrolyzes them, as a result of which they are then able to undergo a series of photochemical and oxidative reactions to form the final pigment. The relevant portion of Pliny's description of the dye extraction stage contains a colorful description of the ‘vein’ containing the famous ‘flower of purple’:

Purples live seven years at most. They stay in hiding like the murex for 30 days at the time of the rising of the dog-star. They collect into shoals in spring-time, and their rubbing together causes them to discharge a sort of waxy viscous slime. The murex also does this in a similar manner, but it has the famous flower of purple, sought after for dyeing robes, in the middle of its throat: here there is a white vein of very scanty fluid from which that precious dye, suffused with a dark rose color, is drained, but the rest of the body produces nothing. People strive to catch this fish alive, because it discharges this juice with its life; and from the larger purples they get the juice by stripping off the shell, but they crush the smaller ones alive with the shell, as that is the only way to make them disgorge the juice.<sup>18</sup>

The purple pigment produced from *Hexaplex trunculus* snails has been found to contain not only the famous DBI dye component, but also a plethora of isomeric brominated and unbrominated indigoids, indirubinoids and related compounds, found by means of HPLC analyses.<sup>19</sup>

## Purple dyeing – very brief history

This ancient color craft constituted one of the most complex of all industrial biochemical processes practiced in antiquity. Purple dyeing may have originated as early as about 4,000 years ago according to the archaeological record mentioned above, and perhaps the first discoverers of this enterprise were the Minoans of Crete. This supposition is based on the discovery of murex shells from that period

at various Aegean sites, and also on wall paintings from that era.<sup>20</sup> This ‘Aegean theory’ of the discovery of purple dyeing, however, is inconclusive as it is based on indirect archaeological evidence. Although a molluskan purple paint pigment was discovered at Thera, no such purple residue has yet been found from an archaeological Aegean site in a dyeing context, such as on a vat fragment. It is a safe, ‘politically correct’ archaeological course to take in stating that, whereas the Minoans and related peoples may have discovered this dyeing craft, history has nevertheless correctly credited the Phoenicians with, at the very least, perfecting the industry and producing royal purple-dyed textiles prized above all others.

Pliny discusses the processing of the gland, or ‘vein’, and the dyeing stage in the following passage:

Subsequently the vein of which we spoke is removed, to this salt has to be added, about a *sextarius* [Roman pint] for every hundred *libras* [Roman pounds]; three days is the proper time for it to be steeped, as certainly the fresher it [the extract] is the much stronger it is, it should be heated in a leaden pot, and with a single *amphora* [48 *sextarii*] of water to every *quinquagenas* [fifty] *libras* [Roman pounds] of dye and kept at a uniform and moderate temperature by a pipe brought from a furnace some way off. This will cause it gradually to deposit the portions of flesh that are bound to have adhered to the veins, and after about nine days the cauldron is strained and a fleece that has been washed clean is dipped for a trial, and the liquid is heated up until fair confidence is achieved. A ruddy color is inferior to a blackish one. The fleece is allowed to soak for five hours and after it has been carded is dipped again, until it soaks up all the juice.<sup>21</sup>

Pliny then continues his narrative regarding the production of different hues of purple by mixing various snail species, and also discusses the robes bearing purple coloration as well as the extravagant prices of such purple dyeings.<sup>22</sup>

The Bible also mentions two closely related – zoologically and chemically – sacral dyeings, which modern chemical and historical research has also discovered to be produced from either the same or different Muricid sea snail species: the Biblical blue, *tekhelet*, and the Priestly purple, *argaman*. These two sacred molluskan dyes, together with the reddish scale-insect dye – Sacral scarlet, *shani* – are first mentioned in the Bible soon after the narrative that depicts the Exodus of the Israelites from Egypt.<sup>23</sup> Biblical scholars have attributed this event to about 3,300 years ago,<sup>24</sup> a period contemporaneous with an already well-established purple craft along the Mediterranean basin.

Archaeological and historical evidence indicate that murex-dyeing died out in the eastern Mediterranean about a millennium and a half ago, some time towards the end of the Byzantine period in the 7th century AD, when new forces changed the geopolitical landscape of this region. As Bridgeman states:

Under Muslim rule purple dyeing at Tyre and other places along what is now the Lebanese-Israeli coast ceased, hence the only surviving centers of purple manufacture were those of Asia Minor and Greece which remained under Byzantine Imperial control.<sup>25</sup>

The Islamic conquest of the Middle East began in about AD 632, and Muslim control over that area was established in approximately AD 660. Historical accounts note that the coastal residents were strong supporters of the Byzantine empire, and, with the oncoming conquest, emigrated from these areas to other parts of the realm that were still under Byzantine control.<sup>26</sup> This created a population void, and the new Muslim rulers resettled these areas with those who were loyal to that new regime.<sup>27</sup> Those fleeing Byzantine coastal residents undoubtedly included dyers of purple. Jewish sources, as noted by Herzog,<sup>28</sup> also indicate that the dyeing of blue or violet *tekhelet* – purple's relative – ceased to exist at the shores of ancient Israel at about that period. Hence, it is

a safe conjecture to conclude that murex dyeing died out along the shores of present-day Israel and environs about 1,350 years ago.

### Modern investigations into natural purple dyeing

Modern dyeings using the pigment extracted from murex snails can be relatively easily produced by using synthetic auxiliary chemical reagents, specifically the reducing agent sodium dithionite (also called sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ ) in a solution made alkaline by either ammonia or caustic soda (sodium hydroxide,  $\text{NaOH}$ ).<sup>29</sup> Such woolen dyeings from synthetically reduced *Hexaplex trunculus* pigments are performed today<sup>30</sup> for the production of the ritual bluish *tekhelet* threads worn on each of the four corners of a garment, such as a prayer shawl (*talit*), as prescribed by the Bible:

Speak to the Children of Israel and tell them that they make for themselves a tassel (*tzitzit*) on the corners of their garments for generations, and they shall put on a corner tassel a twisted thread of *tekhelet*.<sup>31</sup>

A method for the production of *tekhelet* is by way of the photodebromination of the reduced leuco-dye, as first suggested by Elsner,<sup>32</sup> and later adopted by other writers. The photodebromination process has been quantitatively analyzed, both colorimetrically and chromatographically, as previously described.<sup>33</sup>

In the last two decades, only a handful of researchers have reported on possible schemes for producing a completely natural dyeing with murex snail pigments. A true chemical dyeing requires that the dye be rendered soluble prior to the act of dyeing in order to allow the individual dye molecules to penetrate the interiors of the fibers: simply smearing the pigment on a textile or other substrate is a surface treatment, as in painting, and is not dyeing.

The first modern attempt at the re-enactment of the ancient practice of dyeing with the murex purple pigment is due to the

French-Lebanese Joseph Doumet, who in 1980 published a monograph describing his processing of the pigment.<sup>34</sup> He succeeded in producing purple-dyed woolens and silks in an alkaline solution by means of metallic tin present in the processing vessel as the reducing agent. Pliny stipulated that the purple dyeing should be performed in a 'leaden pot', as mentioned in the citation above, and Doumet inferred that 'lead' may not have referred to the lead metal itself, but to 'white lead', a Roman term for tin. Lead was not successful in reducing the pigment. His use of a metallic reducing agent, such as tin, however, was an unlikely source for the ancient scientific craft of processing the pigment, especially when the use of a metallic reductant is unnecessary for the reduction of the purple pigment, as will be described later. Further, while the Bible, for example, does mention the use of tin, its earliest mention is in the fourth book of the Pentateuch.<sup>35</sup> The citation is always in the context of its utilization as a valuable metal, either by itself or alloyed with copper – never as an ingredient to be employed in any kind of chemical processing, where it is essentially destroyed as a metal. Another strong argument against the conjecture that tin (in the vessel) was used in antiquity to reduce the purple pigment is based on direct archaeological evidence: various potsherds from ancient Phoenician dye vats have been found, and these were of a clay, not metallic, nature.

The second venture to discover a plausible, completely natural process for murex dyeing is due to the late Professor Otto Elsner,<sup>36</sup> the founder of the Department of Textile Chemistry at Shenkar, the author's institution in Israel. He performed much research into the 'purple problem' and offered varying claims as to the nature of the reducing agent responsible for the dissolution of the pigment. His suppositions that reduction was produced by the sulfur in the wool protein keratin and/or in the mercaptans released by the dye precursors, however, have been shown not to be valid, according to further experiments that Professor Elsner himself conducted, as well as by those performed by the author.

Michel and McGovern attempted to reduce the purple pigment with tin or lead at pH's above 10.<sup>37</sup> Such very alkaline conditions would, however, destroy the proteinic wool.

John Edmonds of England successfully employed a fermentation vat for purple dyeing.<sup>38</sup> He used a dried sample sent from Israel, which consisted of purple pigment mixed with some of the snail's flesh; this sample was obtained by excising the glands of *Hexaplex trunculus* snails. Edmonds reduced the pigment by means of vinegar-preserved (and dead) cockles, and subsequently dyed using this solution. But these cockles are not native to the Mediterranean shore, and thus would not have been used by the Phoenicians or the Israelites for their purple enterprises. In addition, the excision method of separating the glandular flesh from the snail would not have produced a maximum dye output, as a significant amount of purple pigment stains the remainder of the snail, which is normally discarded.

This article reports on the first reconstruction of an optimal method for the all-natural purple woolen dyeing utilizing only fresh *Hexaplex trunculus* [*Murex trunculus*] snails 'in-the-shell' that have just expired as a result of the extraction process. It is based on experiments conducted at the author's laboratory during an eight-year period,<sup>39</sup> a paper on which was delivered in 2001.<sup>40</sup>

## Experimental

The experimental nature of this work consisted of the following procedures: collection of *Hexaplex trunculus* snails from the sea; dye extraction from these fresh snails; vatting (reduction) of the extracted purple pigment; and dyeing of a sample of woolen fleece. The overall ratio of the constituents used for the vatting and dyeing stages was:

1 g wool: 3 snails: 200 mL total volume (including snails in their shells + alkaline solution).

### *Snail collection*

Live *Hexaplex trunculus* snails were collected from the relatively shallow (<2 m) rocky and sandy Mediterranean seabed off the north central coast of Israel at Mikhmoret. They were brought to a seawater aquarium in the laboratory and kept for about a month until ready for processing.

### *Dye extraction*

The snails were processed in the laboratory under normal room lighting conditions. The shells were carefully broken with a hammer blow such that the gland was punctured deliberately (Plate 15.1 in the color plates). The entire broken shell with the animal was then immediately placed in a glass jar (total volume 200 mL). Seconds after this puncture, as the snail was expiring, a white mucus-like fluid was observed oozing out of the gland and, within a few minutes, a violet ink-like fluid began forming in the mixture. A jar containing three snails was then sealed loosely, covered from all light sources, and left for three days in order to insure that all the dark violet pigment would be formed. This and the other experimental stages are summarized in Table 15.1.

### *Dye vat*

The dye vat was then prepared by adding aqueous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution (pH 9.00 at 25 °C) as shown in Plate 15.2. The jar was topped off by the alkaline solution, just submerging the snails, and loosely covered. This was done in order to minimize the amount of air entering the solution so as to allow for the reduction of the pigment and to prevent the premature oxidation of the dissolved pigment. This mixture was maintained continuously in a thermostatted water bath at 50°C to provide the necessary conditions for thermophilic fermentation. Twice each day, the mucky mixture was stirred very gently, in order to avoid introducing

**Table 15.1** Dye extraction and reduction stages.

Day	Time	Action taken	pH (at 45 °C)		Color of liquid
			Unadjusted	Adjusted	
1	Thurs. 11:00	Hammered snail shells to puncture the gland deliberately			Blue-violet beginning
4	Sun. 15:30	Added sodium carbonate solution (pH =9.00 at 25 °C)			Dark blue-violet (before addition of solution)
5	Mon. 09:30	Measured and adjusted the pH	6.70	9.01	Mucky blue-green with reddish tint
6	Tues. 12:20	Measured and adjusted the pH	7.67	9.01	Olive-green
7	Wed. 11:00	Measured and adjusted the pH	8.86	9.00	Clearer olive-green
8	Thurs. 09:30	Measured the pH	8.97	(not adjusted)	(unchanged)

an excessive amount of atmospheric oxygen. The pH was checked after each day with the container removed from the bath, and, when needed, adjusted to a value of 9.0 at 45°C by adding a small amount of saturated sodium carbonate solution. The daily pH readings resulting from the acid-producing fermentation of the snail flesh are given in Table 15.1.

After four days of fermentation in the alkaline solution, and a total of seven days since the glands were punctured, the pH of the mixture had not decreased, indicating the cessation of fermentation. The color of the dark, muddy mixture was green, as shown in Plate 15.3, clearly indicating that reduction of a brominated or unbrominated indigoid to its soluble alkaline *leuco*-form had occurred.

### Dyeing

The first dyeing was performed with a woolen fleece (1.0 g) for four hours at 50°C. Immediately upon the removal of the wool, its hue was green, but, after about 20 seconds in the air, oxidation of the *leuco*-indigoid components in the wool commenced and the purple color began to develop (see Plates 15.4a-d). The dye-bath was completely exhausted by two more consecutive dyeings, each with 1.0 g samples of fleece; the second dyeing was also performed at 50°C for 4 hours, but the third and last dyeing was at 70°C for 2 hours. So efficient were the reduction and the subsequent dyeings that, after the mixture in the container had been

disposed of, no noticeable bluish or purplish indigoid residue adhered to the container walls or to the shells.

After the woolen dyeings had been allowed to dry for two days, they were rinsed thoroughly with cold running tap water. These dyeings, which range in color from light purple to pale blue to light greenish-yellow, are shown in Plate 15.5.

### Colorimetric characterization

The colorimetric properties of the three dyeings were characterized by means of an ICS – TEXICON Spectraflash 500 Spectrophotometer and compared with those of undyed wool. The instrument settings chosen were the following: D65 daylight illuminant; 10° observer, UV radiation and specular (gloss) component of the measurement included; ultra-small aperture. The percent reflectance (% R) and resulting Kubelka-Munk (K/S) absorption-type spectra were obtained between 390 and 750 nm at 10 nm intervals. In addition, the CIELab coordinates L\* (lightness), a\* and b\* (defined below), and C\* (chroma) and h\* (hue) were also produced.

### Results and discussion

The results of the fermentative dyeing experiment and of the colorimetric characterizations of the dyeings are presented in the sections below.



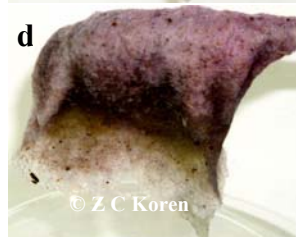
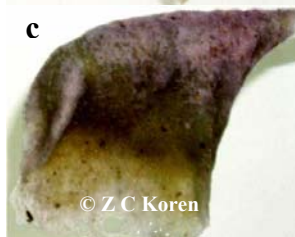
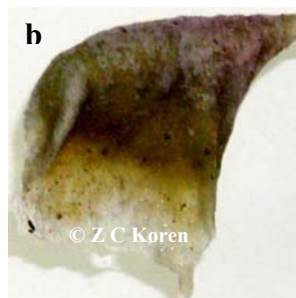
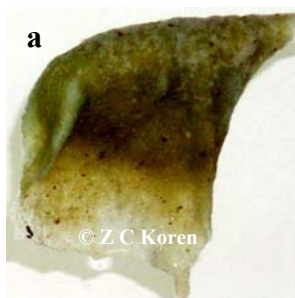
**Plate 15.1** Hammering the *Murex Trunculus* snail to extract the dye.



**Plate 15.2** Purple alkaline mixture with snail pigment.



**Plate 15.3** The greenish fermentative dye vat characteristic of an indigoid reduction



**Plate 15.4a-d** The air oxidation of the *leuco* dyes in the wool as it is removed from the dye vat: the color changes from green to purple.



**Plate 15.5** The three exhaust dyeings from the fermentative dye vat

### *Vatting and dyeing*

The dyeing method utilized in this work takes advantage of the fact that not only does the murex snail supply the precursors to the dye components, and ultimately to the purple pigment itself, but also the bacterial reducing agent necessary for the dissolution of the pigment. The murex snails themselves constitute a self-contained, built-in, all-in-one system, which therefore does not necessitate the use of an external reductant – effective or not – as, for example, the metal tin, the sulfur groups in wool or in the glandular precursors, or another molluskan species foreign to this ‘Club Med’ area. The complexity of this puzzle, which waited nearly a millennium and a half to be completely deciphered, lay in its simplicity!

The results of this work show that good purple coloration can be obtained on 1 g of wool with just three snails, even though darker hues and a more uniform dyeing can obviously be produced by using a more concentrated dye solution and/or less wool. In subsequent experiments performed by the author, excellent uniformity of dyeing was obtained by utilizing three successive 1-g samples of wool, 20 medium-sized snails (total weight with shells about 360 g), and about 200 mL net alkaline solution volume, which was enough to just cover all the snails. It should therefore be possible to produce uniform purple dyeings with the following ratio:

1 g wool: 7 medium snails: 70 mL alkaline solution.

Sodium carbonate, also known as soda ash or washing soda, the alkaline medium used in this study for maintaining the proper alkaline pH for the reduction and dissolution of the pigment to be effective, is a *natural* ingredient. As a mineral, it occurs in nature as the hydrate, thermonatrite, and as the decahydrate, natron or natrite.<sup>41</sup> The consonantal letters ‘ntr’ of this substance's name are found not just in this modern nomenclature, but also in very ancient languages. This compound was referred to as *neter* in biblical Hebrew,<sup>42</sup> and was always in

use as a cleansing material, both physical and spiritual. That this compound is an alkaline substance used for washing can be seen from the following biblical analogy:

For though you wash yourself with *neter*, and use much *borit* [probably soapwort], yet the stain of your iniquity is before Me, says the Lord God.<sup>43</sup>

Similarly, in ancient Egyptian, Ntr signifies God or pure.<sup>44</sup> From that etymological root, the Greeks derived their word *nitron*, as well as the other classical form *natron*,<sup>45</sup> and this word construct was passed on to the Talmudic Hebrew of the Roman and Byzantine periods. Interestingly, the Talmud – a multivolume treatise embodying Jewish civil and religious laws and customs and dating from the first five centuries AD – discusses two types of *neter*: Alexandrian *neter* and Antipatrisian *neter*.<sup>46</sup> The former is the mineral form available from Alexandria, Egypt, and paralleling that citation are the statements by both Forbes<sup>47</sup> and Brunello,<sup>48</sup> indicating the importance of *natron* in ancient Egypt. The second-mentioned *neter* is the one obtainable from the ashes of plants (‘soda ash’), which does contain carbonates of sodium and potassium. It was produced in the ancient town in Israel named Antipatris, situated during Talmudic times north-northwest of Jerusalem, which was founded by King Herod the Great and named after his father.<sup>49</sup> Although ashes of plants were widely used elsewhere as a cleaning agent in place of the mineral form of sodium carbonate, they were probably not in use in ancient Egypt, as the mineral was easily collected in great quantities and, as raw alkaline material, was purer than ashes.<sup>50</sup> Thus, the biblical and Talmudic *neter* and the Greek *nitron*, which are used in the context of a washing and cleaning material, refer to sodium carbonate, and not to the similarly sounding word ‘nitre’ (British spelling)<sup>51</sup> or ‘niter’ (American spelling),<sup>52</sup> which refers to the nitrate of potassium (or sodium), and possesses no detergent properties.

The reduction itself must have undoubtedly occurred as a result of bacterial



action on the indigoidal pigment; these bacteria would be present in the flesh of the snail and breeding on its fleshy meat. This reducing species is possibly a *Clostridium* bacterium, as in the reduction of indigo from woad leaves.<sup>53</sup>

Thus, all the ingredients used in this reconstructed murex dyeing experiment were entirely natural. All that was needed was to control the pH of the dye vat to sustain the alkaline environment and to maintain tepid temperatures.

### **Color characterization**

The Kubelka-Munk K/S absorption-type spectra for the three dyeings are shown in Figure 15.1 (a,b,c). These values were obtained for each dyeing by measuring the % reflectance at different locations on the woolen fleece, and show the slight non-uniformity of each dyeing. The spectra were averaged and the resulting average spectrum for each dyeing is also shown in the appropriate figure and summarized in Figure 15.2. The comparable spectrum of a sample of undyed wool is also presented for comparison.

In the Kubelka-Munk equation,<sup>54</sup> for a given wavelength,

$$K/S = (1 - R)^2/2R,$$

where K is the absorption coefficient, S is the scattering coefficient, and R is the measured reflectance value presented as a numerical ratio between 0 and 1.

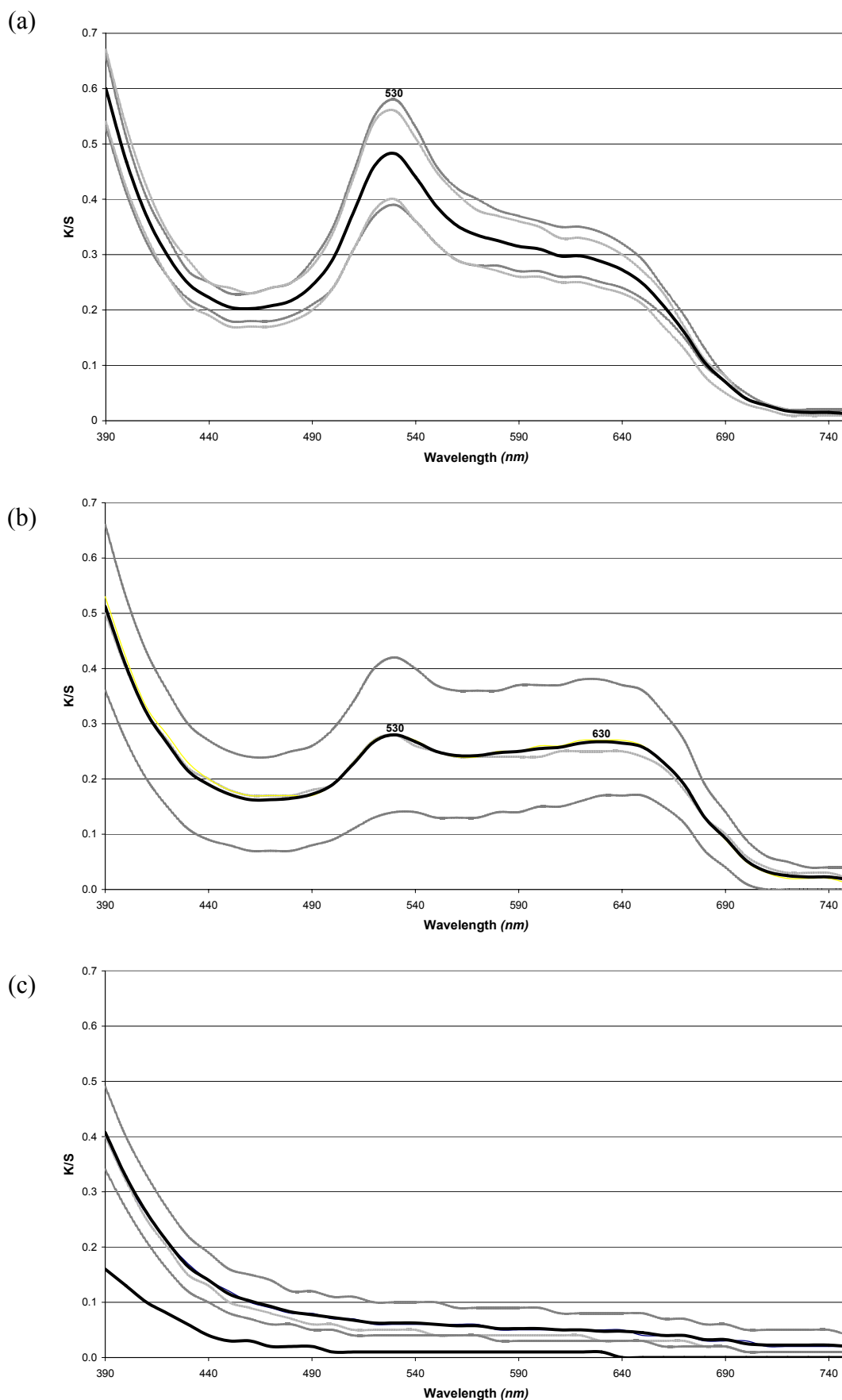
The spectrum of the first dyeing (Figs 15.1a and 15.2), as calculated using the Kubelka-Munk equation, clearly shows a strong absorption maximum at about 530 nm, which is the colorimetric signpost indicative of a significant presence of the reddish DBI dye in woolen dyeings.<sup>55</sup> There is only a shoulder present at about 620 nm, an area where the absorption due to the blue-violet indigo (IND) colorant in woolen dyeings would be expected. These spectrometric measurements cannot, of course, indicate the presence of the other dye components that may also be present together with DBI and

IND; this type of detailed information can be obtained from a chromatographic analysis,<sup>56</sup> which will be performed in the near future.

The Kubelka-Munk spectrum of the second dyeing (Figs 15.1b and 15.2) shows two nearly equal maxima, one at 530 nm, as in the first dyeing, and a second at 630 nm. The average absorption maximum at 530 nm is about half of that in the first dyeing. This indicates that while a significant amount of DBI was removed from the solution by the first dyeing, some DBI still remains. However, and this is an important phenomenon, the average absorption at the other maximum (630 nm) in the second dyeing is just slightly less than the absorption at this wavelength in the first dyeing. This clearly shows that the affinity of DBI to wool is much higher than that of IND to wool! This behavior was first seen in the case of dyeings resulting from photodebrominated *leuco-indigoids*.<sup>57</sup>

The third dyeing (Figs 15.1c and 15.2) is not illustrative as the dyeing took place at an elevated temperature (70°C) instead of 50°C, which may have resulted in the decomposition of the vat; that is, in the degradation of the dye components and/or their partial oxidation. The spectrum of the third dyeing is closely similar to that of undyed wool, which is also shown in Figures 15.1c and 15.2.

The Commission Internationale de l'Eclairage CIELab coordinates,<sup>58</sup> formally known as the 1976 CIE L\*a\*b\* Space, were also measured by the spectrophotometer, and the range of a\* and b\* values for the three dyeings and of the undyed woolen sample is depicted in Figure 15.3. The a\* scale, from -a\* to +a\*, is the green to red color axis. The b\* scale, which runs from -b\* to +b\*, is the blue to yellow color axis. From this figure, it is clear that the purplish first dyeing has both red and blue components. The first dyeing is much redder than the second, but the second is only a little less blue than the first. Both of these characteristics parallel those previously observed in the Kubelka-Munk spectra of Figures 15.1 (a,b,c) and 15.2. The third dyeing is only a little more yellow and green than an undyed sample.



**Figure 15.1** Kubelka-Munk K/S absorption spectra measured at different locations on each of the three dyeings and the average spectrum (middle solid curve) for each dyeing: (a) first dyeing; (b) second dyeing; (c) third dyeing and undyed wool (bottom solid curve).

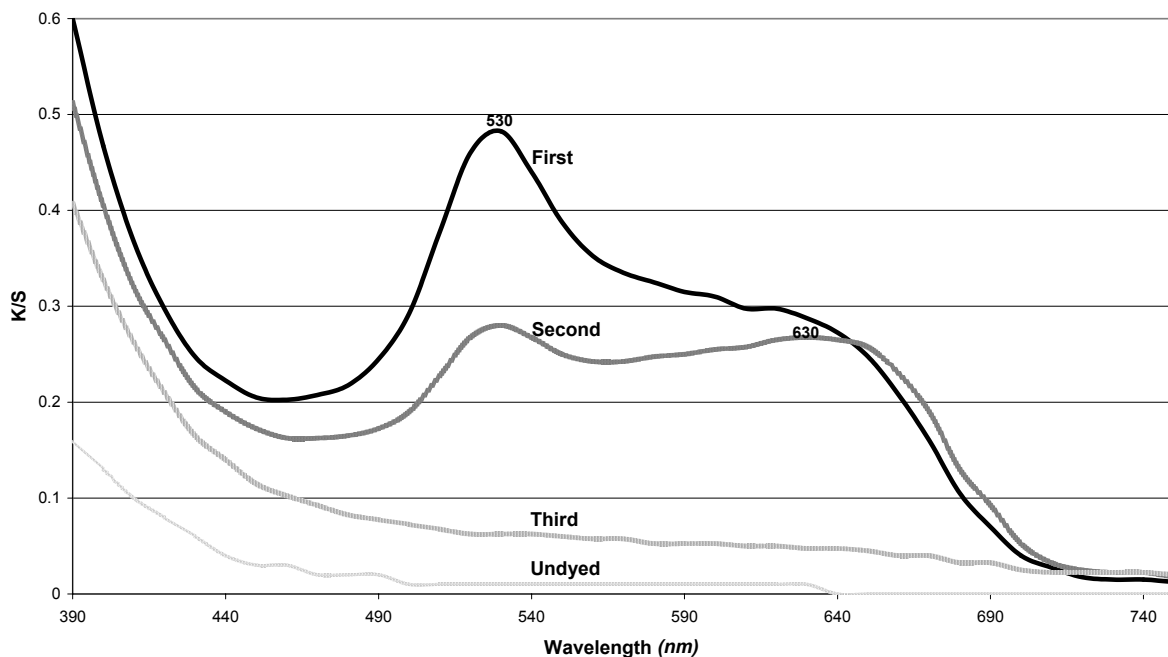


Figure 15.2 Average Kubelka-Munk K/S absorption spectra of the three dyeings and of undyed wool.

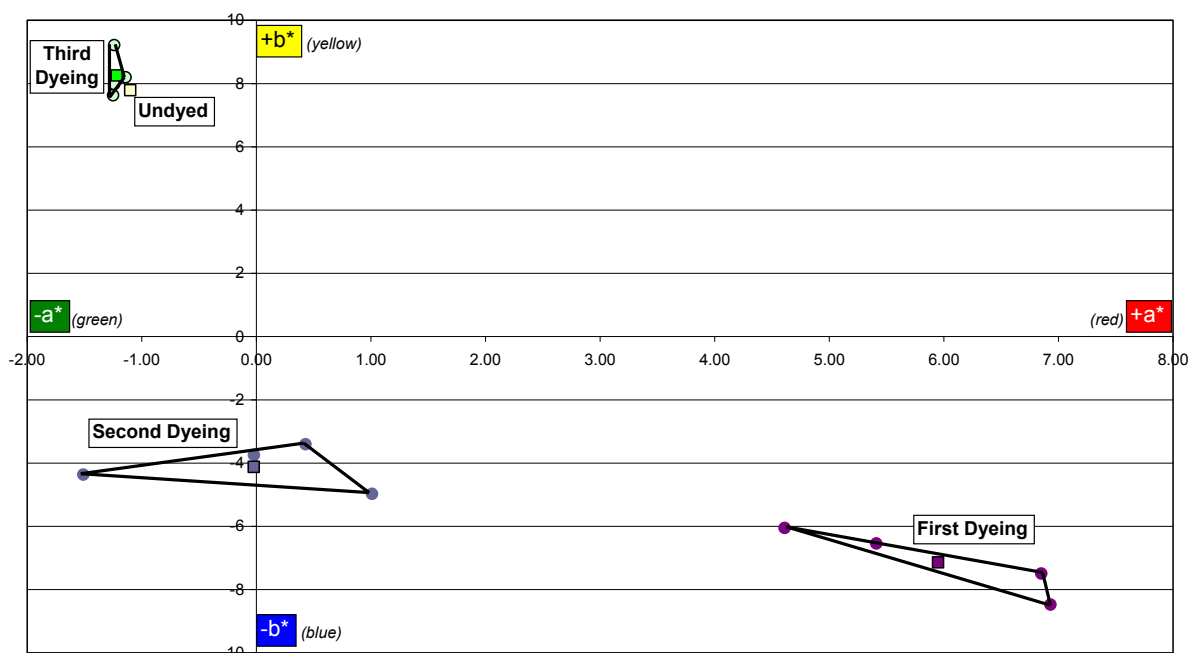


Figure 15.3 CIELab a\* and b\* coordinate values of the three dyeings, measured at different locations on the wool (circles) with respective average values (squares), and values of undyed wool.

### Conclusions

Although purple dyeing was a complex biochemical technology practiced by the ancient dyer, the ingredients needed for such a challenging task were surprisingly simple. These included a clay vessel, murex snails captured near the dyeing site, heat, and a natural alkaline medium such as sodium

carbonate, plant or wood ash, or lime, all widely available.<sup>59</sup>

The vatting and dyeing method used in this study represents a successful optimal reproduction of an ancient purple dyeing process. It consists of a fermentative reduction and air oxidation process utilizing the same ‘in-the-shell’ Mediterranean *Hexaplex trunculus* [*Murex*

*trunculus*] mollusks, which were alive just prior to the extraction process, as the source of both the dye and the reducing agent. For the first time since purple dyeing ceased along the shores of ancient Israel and environs, about a millennium and a half ago, this work has shown that the ancient eastern Mediterranean dyer possessed all the natural ingredients, tools and skills to produce such a maximal all-murex purple dyeing. In addition, this research has demonstrated that a one-gram woolen fleece can be dyed to a purple shade (although light in color) with just three snails.

While Pliny described his understanding of the Tyrian purple dyeing process performed in the Roman empire, the Talmud also contains a brief discussion of that process in connection with the related *tekhelet* dye. The following is the only passage in the Talmud that discusses the dyeing process, and, based on the life span of the two rabbis involved in that discourse, is dated to the early 4th century AD:

Abbaye said to Rabbi Samuel son of Rabbi Judah: 'That *tekhelet*, how do you dye it?' He said to him: 'We bring sea-snail blood and compounds, and put them into a vat (and we heat [literally 'boil'] the mixture). We then take out a little [of the liquid] into an egg-shell and test [the liquid] with a fleece of wool. We then throw away that egg-shell and burn the [trial sample of dyed] wool.'<sup>60</sup>

The royal and sacral recipes for producing purples and blues according to Pliny and the Talmud are thus remarkably similar and parallel the reconstructed, entirely natural, dye vat achieved in this work.

The beauty and grandeur of these purple, violet and blue hues were indeed destined for the monarchs, Caesars, emperors, generals, high priests, and temples. Calculations based on experiments in the author's laboratory, and mentioned above, show that the all-natural dyeing of 1 g of wool requires about seven or more snails, depending, of course, on the final shade desired. Hence, to dye a kilogram or more of one entire royal or priestly robe, cloak, mantle, toga or other garment ('from

head-to-toe') to a deep shade would require a total of about 10,000 snails! Indeed a mighty task, fit only for a king and high priest. During lean times, however, the kingdom would suffice with a 'mere' 5,000 snails to cloak his royal highness.

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## Editor's note

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## Notes and references

1. Herzog, I. (1987) 'Hebrew porphyrology', D.Litt. dissertation, University of London, 1913, in E. Spanier (ed.) *The Royal Purple and the Biblical Blue: Argaman and Tekhelet. The Study of Chief Rabbi Dr. Isaac Herzog on the Dye Industries in Ancient Israel and Recent Scientific Contributions*, Jerusalem, pp. 17-145; Karmon, N. (1993) 'The purple dye industry in antiquity', in C. Sorek and E. Ayalon (eds) *Colors from Nature: Natural Colors in Ancient Times*, Eretz-Israel Museum, Tel-Aviv, pp. 35\*-37\* (English), 80-95 (Hebrew); Karmon, N. and Spanier, E. (1987) 'Archaeological evidence of the purple dye industry from Israel', in Spanier 1987 (cited above), pp. 147-58; Spanier, E. and Karmon, N. (1987) 'Muricid snails and the ancient dye industries', in Spanier 1987 (cited above), pp. 179-92; Reese, D. R. (2000) 'Iron Age shell

- purple-dye production in the Aegean', Appendix 6.1, in J.W Shaw and M.C. Shaw (eds) *Kommos IV. The Greek Sanctuary, Part I*, Princeton, pp. 643-8; Reese D.S. (1987) 'Palaikastro shells and Bronze Age purple-dye production in the Mediterranean basin', *The Annual of the British School of Archaeology at Athens* 82, pp. 201-6; Reese, D. R. (1980) 'Industrial exploitation of Murex shells: purple-dye and lime production at Sidi Khrebish, Benghazi (Berenice)', *The Society for Libyan Studies 11th Annual Report* (1979-80), pp. 79-93; Stieglitz, R.R. (1994) 'The Minoan origin of Tyrian purple', *Biblical Archaeologist* 57, pp. 46-54; Thompson, D.W (1947) *A Glossary of Greek Fishes*, London, pp. 209-18; Ziderman, I.I. (1990) 'Seashells and ancient purple dyeing', *Biblical Archaeologist* 53, pp. 98-101; Rilov, G., Gasith, A. and Benayahu, Y (1996) 'Selected aspects of ecology of large predatory gastropods in rocky littoral habitats along the Israeli Mediterranean coast', in *Proceedings of the Sixth International Conference of the Israeli Society for Ecology and Environmental Quality Sciences. Preservation of Our World in the Wake of Change*, Vol. VI B, Jerusalem, pp. 608-13; Koren, Z.C. (1993) 'The colors and dyes on ancient textiles in Israel', in Sorek and Ayalon 1993 (cited above), pp. 15\*-31\* (English), 47-65 (Hebrew).
2. Fouquet, H. and Bielig, H.-J. (1971) 'Biological precursors and genesis of Tyrian purple', *Angewandte Chemie, International Edition* (English) 10, pp. 816-17; Fouquet, H. (1970) 'Bau und Reaktionen natürlicher Chromogene indigoider Farbstoffe bei Purpurschnecken', PhD thesis, University of Saarlandes, Saarbrücken; Baker, J.T. (1974) 'Tyrian purple. Ancient dye, a modern problem', *Endeavour* 33, pp. 11-17.
  3. Cooksey, C.J. (2001) 'Tyrian purple: 6,6'-dibromoindigo and related compounds', *Molecules* 6, pp. 736-69; Clark, R.J.H. and Cooksey C.J. (1999) 'Monobromoindigos: a new general synthesis, the characterization of all four isomers and an investigation into the purple colour of 6,6'-dibromoindigo', *New Journal of Chemistry* 23, 3, pp. 323-8; Verhecken, A. (1994) 'Experiments with the dyes from European purple-producing molluscs', *Dyes in History and Archaeology* 12, pp. 32-5; Verhecken, A. (1990) 'Experiences with mollusc purple', *La Conchiglia* 22, pp. 250-52; Verhecken, A. (1989) 'The indole pigments of mollusca', *Annales de la Société royale zoologique de Belgique* 119, pp. 181-97; Zollinger, H. (1989) 'Welche Farbe hat der antike Purpur?', *Textilveredlung* 24, pp. 207-12; Clark, R.J.H. and Cooksey, C.J. (1997) 'Bromoindirubins: the synthesis and properties of minor components of Tyrian purple and the composition of the colorant from *Nucella lapillus*', *Journal of the Society of Dyers and Colourists* 113, pp. 316-21; Cooksey, C.J. and Withnall, R. (2001) 'Chemical studies on *Nucella lapillus*', *Dyes in History and Archaeology* 16/17, pp. 91-6; Koren, Z.C. (1995) 'High-performance liquid chromatographic analysis of an ancient Tyrian purple dyeing vat from Israel', *Israel Journal of Chemistry* 35, pp. 117-24.
  4. Michel R.H., Lazar, J. and McGovern, P.E. (1992) 'The chemical composition of the indigoid dyes derived from the hypobranchial glandular secretions of Murex mollusks', *Journal of the Society of Dyers and Colourists* 108, pp. 145-50; McGovern, P.E., Lazar, J. and Michel, R.H. (1991) 'Caveats on the analysis of indigoid dyes by mass spectrometry', *Journal of the Society of Dyers and Colourists* 107, p. 2801; McGovern, P.E., Lazar, J. and Michel, R.H. (1990) 'The analysis of indigoid dyes by mass spectrometry', *Journal of the Society of Dyers and Colourists* 106, pp. 22-5; Daniels, V. (1989) 'Appendix 1. Analysis of the dyes', in H. Granger-Taylor, I.D. Jenkins and J.P Wild, 'From rags to riches: two textile fragments from Cyprus', in V Tatton-Brown (ed.) *Cyprus and the East Mediterranean in the Iron Age. Proceedings of the 7th [i.e. 12th] British Museum Classical Colloquium, April 1988*, pp. 153-4; Voss, G. (2000) 'The analysis of indigoid dyes as leuco forms by NMR spectroscopy', *Journal of the Society of Dyers and Colourists* 116, pp. 87-90; Voss, G. and Schramm, W. (2000) 'Selectively C-deuterated indigotins', *Helvetica Chimica Acta* 83, pp. 2884-92; Withnall, R., Clark, R.J.H., Cooksey, C.J. and Daniels, M.A.M. (1993) 'Non-destructive, *in situ* identification of indigo/woad and shellfish purple by Raman microscopy and visible reflectance spectroscopy', *Dyes in History and Archaeology* 11, pp. 19-24; Wouters, J. (1992) 'A new method for the analysis of blue and purple dyes in textiles', *Dyes in History and Archaeology* 10, pp. 17-21; Wouters, J. and Verhecken, A. (1991) 'High-performance liquid chromatography of blue and purple indigoid natural dyes', *Journal of the Society of Dyers and Colourists* 107, pp. 266-9;

- Koren, Z.C. (1994) 'HPLC analysis of the natural scale insect, madder and indigoid dyes', *Journal of the Society of Dyers and Colourists* 110, pp. 273-7; McGovern, P.E. and Michel, R.H. (1985) 'Royal purple dye: tracing the chemical origins of the industry', *Analytical Chemistry* 57, pp. 1514A-22A; McGovern, P.E. and Michel, R.H. (1984) 'Royal purple and the pre-Phoenician dye industry of Lebanon', *MASCA Journal* 3, pp. 67-70; Koren, Z.C. (1993) 'Methods of dye analysis used at the Shenkar College Edelstein Center in Israel', *Dyes in History and Archaeology* 11, pp. 25-33; Koren, Z.C. (2001) 'The purple question reinvestigated: just what is really in that purple pigment?', paper presented at the 20th Meeting of *Dyes in History and Archaeology*, Instituut Collectie Nederland, Amsterdam, November 2001. See also Clark and Cooksey 1997 (see note 3 above); Cooksey and Withnall 2001 (see note 3 above); Koren 1995 (see note 3 above).
5. Koren 2001 (see note 4 above).
  6. Pliny [Gaius Plinius Secundus] (1940) [*Naturalis Historia*] *Pliny Natural History*, transl. H. Rackham (Loeb Classical Library), 10 vols, Cambridge, Mass. (repr. 1950), Vol. III, IX.lx-lxiv.
  7. McGovern, P.E. and Michel, R.H. (1990) 'Royal purple dye: the chemical reconstruction of the ancient Mediterranean industry', *Accounts of Chemical Research* 23, pp. 152-8; Michel, R.H. and McGovern, P.E. (1987) 'The chemical processing of Royal purple dye: ancient descriptions as elucidated by modern science', *Archaeomaterials* 1, pp. 135-43; Michel, R.H. and McGovern, P.E. (1990) 'The chemical processing of Royal purple dye: ancient descriptions as elucidated by modern science, part II', *Archaeomaterials* 4, pp. 97-104.
  8. Edmonds, J. (2000) *The Mystery of Imperial Purple Dye* [Cover title: *Tyrian or Imperial Purple Dye*] (Historic Dye series no. 7), Little Chalfont (published by the author).
  9. Undergraduate dissertations, Shenkar College of Engineering & Design, Ramat-Gan, Israel: Edraki-Joop-Froessl, A. (1993) 'Color computer and high-performance liquid chromatographic quantifications of Royal purple and Biblical blue dyeings'; Hoetzel, P. (1994) 'Quantitative photochemical dyeings with the ancient purple dye'; Cohen, S. (1996) 'Reconstruction of the ancient dyeing technology of Tyrian purple in a natural reducing environment' (Hebrew); Eich, E. (1999) 'An HPLC and spectrometric analysis of the components of the Tyrian purple pigment'; Konstantini, E. (1999) 'HPLC and spectrometric analyses of the components of the Tyrian purple pigment' (Hebrew).
  10. Koren 2001 (see note 4 above).
  11. Benkendorff, K., Bremner, J.B. and Davis, A.R. (2001) 'Indole derivatives from the egg masses of Muricid molluscs', *Molecules* 6, pp. 70-78.
  12. Barash, A. and Zenziper, Z. (1991) *Mollusca of the Mediterranean Sea of Israel*, Tel-Aviv (Society for the Protection of Nature in Israel) p. 8 (Hebrew).
  13. Barash and Zenziper 1991 (see note 12 above), p. 61.
  14. Pliny 1940 (see note 6 above), IX.lx-lxi.
  15. Reese 2000 (see note 1 above); Reese 1987 (see note 1 above); Reese 1980 (see note 1 above); Stieglitz 1994 (see note 1 above).
  16. Koren 1995 (see note 3 above); McGovern and Michel 1985 (see note 4 above); McGovern and Michel 1984 (see note 4 above); Koren 1993 (see note 4 above).
  17. See notes 2 and 3 above.
  18. Pliny 1940 (see note 6 above), IX.lx.
  19. Koren 2001 (see note 4 above).
  20. Reese 2000 (see note 1 above); Reese 1987 (see note 1 above); Reese 1980 (see note 1 above); Stieglitz 1994 (see note 1 above).
  21. This translation of Pliny, Book IX, Section lxii, is based on the Latin version and English translation given by Rackham (see note 6 above), with certain etymological emendations and parenthetical remarks given by the author. The original names of the Roman weights and measures given by Pliny are retained in the citation. The Roman pint, which is about 1.2 times the modern pint, is equal to about 542-568 mL. The Roman pound is about  $\frac{3}{4}$  of a modern pound and equal to about 327-335 g. The Roman amphora is equal to about 6 gallons and 7 pints, about 26 L.
  22. Pliny 1940 (see note 6 above), IX.lx, lxxiii-lxiv.
  23. Exodus 25.4.
  24. *Encyclopaedia Judaica* (1974), ed. C Roth *et al.*, Jerusalem, Vol. 6: *Exodus*, pp. 1042-50.
  25. Bridgeman, J. (1987) 'Purple dye in late antiquity and Byzantium', in Spanier 1987 (see note 1 above), pp. 159-65.
  26. Frankel, Y. (1990) 'The early Arabic period (632-1099)', in B. Z. Kedar, T. Dothan and S. Safrai (eds) *P'rakim beToldot haMishar be'Eretz Yisrael* [Chapters in the History of Commerce in the Land of Israel], Jerusalem

- (Yad Yitzchak Ben-Zvi and the Israel Exploration Society), pp. 223-38 (Hebrew).
27. Frankel 1990 (see note 26 above).
  28. Herzog 1987 (see note 1 above).
  29. Koren 1995 (see note 3 above).
  30. Website: www.tekhelet.com.
  31. Author's translation of Numbers 15.38.
  32. Elsner, O. (1992) 'Solution of the enigmas of dyeing Tyrian purple and the biblical *tekhelet*', *Dyes in History and Archaeology* 10, pp. 11-16; Elsner, O. (1987) 'The past, present and future of *Tekhelet*', in Spanier 1987 (see note 1 above), pp. 167-77; Elsner, O. and Spanier, E. (1985) 'Dyeing with Murex extracts: an unusual dyeing method of wool to the Biblical sky blue', in M. Sakamoto (ed.) *Proceedings of the 7th International Wool Textile Research Conference, Tokyo 1985*, Tokyo (Society of Fiber Science and Technology), 5, pp. 118-30.
  33. Koren, Z.C. (1994) 'Photochemical vat dyeings of the Biblical purple *tekhelet* and *argaman* dyes', paper delivered at the 13th Meeting of *Dyes in History and Archaeology*, Royal Museum of Scotland, Edinburgh, 2 December 1994.
  34. Doumet, J. (1980) *Etude sur la couleur pourpre ancienne; A Study on the Ancient Purple Colour and an Attempt to Reproduce the Dyeing Procedure of Tyre as Described by Pliny the Elder*, Beirut (Imprimerie Catholique).
  35. Numbers 31.22.
  36. See note 32 above and personal communications.
  37. Michel and McGovern 1990 (see note 7 above).
  38. Edmonds 2000 (see note 8 above).
  39. See undergraduate dissertations cited in note 9 above.
  40. Koren 2001 (see note 12 above). Subsequent to this author's research, Inge Boesken Kanold of France has utilized the glandular excision method for the dye extraction: see I. Boesken Kanold, 'The purple fermentation vat: dyeing or painting parchment with *Murex trunculus*', in this volume, pp. 150-54.
  41. *The Merck Index: An Encyclopedia of Chemicals, Drugs and Biologicals* (1989) 11th edn, ed. S. Budavari *et al.*, entry 8541, p. 1359.
  42. Proverbs 25.20; Jeremiah 2.22.
  43. Jeremiah 2.22.
  44. Brunello, F. (1973) *The Art of Dyeing in the History of Mankind*, transl. B. Hickey, Vicenza, p. 45.
  45. Brunello 1973 (see note 44 above).
  46. *Babylonian Talmud, Tractate Shabbat*, p. 90a; A. Steinsaltz edn, Vol. 2 (1987) Jerusalem (Israel Institute for Talmudic Publications), p. 388.
  47. Forbes, R. J. (1964) *Studies in Ancient Technology*, Vol. IV, Leiden, p. 83.
  48. Brunello 1973 (see note 44 above), pp. 44-5, 54-5.
  49. Jastrow, M. (1992) *A Dictionary of the Targumim, the Talmud Babli and Yerushalmi, and the Midrashic Literature*, New York (The Judaica Press), pp. 83-4, 901, 946.
  50. Brunello 1973 (see note 44 above).
  51. Forbes 1964 (see note 47 above), p. 84; Brunello 1973 (see note 44 above), p. 54.
  52. *Webster's New World Dictionary of the American Language* (1976) 2nd College edn., ed. D.B. Guralnik, Cleveland-New York, entry 'niter', p. 963.
  53. Padden, A.N., John, P., Collins, M.D., Hutson, R. and Hall, A.R. (2000) 'Indigo-reducing *Clostridium isatidis* isolated from a variety of sources, including a tenth century Viking woad vat', *Journal of Archaeological Science* 27, pp. 953-6; Padden, A.N., Dillon, V.M., Edmonds, J., Collins, M.D., Alvarez, N. and John, P. (1999) 'An indigo-reducing moderate thermophile from a woad vat, *Clostridium isatidis* sp. nov.', *International Journal of Systematic Bacteriology* 49, pp. 1025-31; Padden, A.N., Dillon, V.M., John, P., Edmonds, J., Collins, M.D. and Alvarez, N. (1998) 'Clostridium used in mediaeval dyeing', *Nature* 396, p. 225.
  54. Billmeyer, F.W. and Saltzman, M. (1981) *Principles of Color Technology*, 2nd edn, New York, p. 140.
  55. Koren 1994 (see note 33 above).
  56. Koren 1993 (see note 4 above).
  57. Koren 1994 (see note 33 above).
  58. Billmeyer and Saltzman 1981 (see note 54 above), pp. 62-5, 87, 101, 103-5.
  59. Koren 1995 (see note 3 above).
  60. *Babylonian Talmud, Tractate Menahot*, p. 42b. Translation and remarks in square brackets are the author's.

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