Reprint

Archaeological Chemistry

A Multidisciplinary Analysis of the Past

Edited by Mary Virginia Orna
and Seth C. Rasmussen

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ARCHAEOLOGICAL CHEMISTRY AND COLORING MATERIALS

CHAPTER 13

ARCHAEOLOGICAL SHADES OF PURPLE FROM FLORA AND FAUNA FROM THE ANCIENT NEAR EAST

ZVI C. KOREN*

Abstract

This chapter presents an analytical and historical study of the production of the color purple in the Ancient Near East that is based mostly on my own original research over the course of the past three decades. A colorful picture emerges that reveals how the dyer and weaver succeeded in creating variegated shades of purple – from reddish to bluish. For potentates, the powerful, and the priestly, the most prominent purples were produced from the *Muricidae* family of sea snails. The main molluskan species used for such colors was *Hexaplex trunculus*, with one variety of this species producing reddish-purple pigments, and similarly colored woolen dyeings, while another type of the same species produced bluish-purple pigments and dyeings. It was also probable that the two varieties of *H. trunculus* species were mixed to produce intermediate colors. The use of the other purple-producing Mediterranean mollusks (*Bolinus brandaris* and *Stramonita haemastoma*) was very likely as "color additives" to the red-purple producing *H. trunculus* species in order to produce even redder purple dyeings. For the more common folk who desired purple embellishments on their garments, the most common method of producing such purple colors – the "people's purple" – was by combining different non-molluskan dyes. A cornucopia of purple shades was then produced from the well-known red-madder and blue-indigo double-dyeing method. However, other surprising chemical and physical combinations were also utilized to produce purple colorations. These examples include mordanting madder with an iron salt, using entomological sources (Ararat cochineal and kermes insects) alone or

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in chemical and physical combinations with indigo or even with a malacological source. These and other insights regarding the dyeing process in antiquity could only be obtained from the detailed chromatographic and spectrometric analyses of archaeological dyeings that the HPLC technique provides and by understanding the various chemical steps that were performed by the skillful ancient dyer.

What's in a Name? Or, The Problem with "Purple"

Shakespeare's Juliet enlightens her Romeo that an object is still the same entity even if we give it different names:[1]

> *What's in a name? That which we call a rose by any other name would smell as sweet.*

However, the situation with the color "purple" is quite the opposite, so that the same name, "purple", can refer to a diverse range of colorations. Purple is not a pure color of the ROYGBV colors of the rainbow,[2] and as such, "purple" can connote different shades to different people. A purple-colored pigment can be produced by the subtractive mixing of red and blue colors. Thus, this color composite can range from reddish-purple (including bordeaux, burgundy, maroon, crimson, *etc.*) with a preponderance of the red component in the mixture, and conversely to a bluish-purple or violet color when blue is the dominant constituent. Cultural definitions of colors are quite varied,[3] and purple, with its wide-ranging possibilities, is no exception. This diversification of colors is markedly exemplified by the definition that the *Encyclopedia Britannica* proffers to the "purple colour" as "a shade varying between crimson and violet".[4] This popular notion of the extensive color span of "purple" from reddish to bluish can also be clearly visualized in the Wikipedia website under the entry "purple", which

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[1] William Shakespeare, *The Tragedy of Romeo and Juliet, Act II, Scene II,* https://www.gutenberg.org/files/1513/1513-h/1513-h.htm, accessed December 14, 2019.

[2] Red, Orange, Yellow, Green, Blue, Violet

[3] Guy Deutscher, *Through the Language Glass: Why the World Looks Different in Other Languages* (London: Arrow Books /Cornerstone, 2011), https://archive.org/stream/ThroughTheLanguageGlass/Through%20the%20Language%20 Glass_djvu.txt, accessed December 14, 2019.

[4] Michael Ray and The Editors of Encyclopaedia Britannica, "Purple Colour," https://www.britannica.com/science/purple-colour#ref1261236, accessed December 14, 2019,

shows images of the wide variety of what can be denoted as "purple" from brownish-red to blue-violet (as seen in Figure 13-1).[5]

Figure 13-1. A sampling of the images from Wikipedia, entry "purple", showing the wide range of "purple" colors – from brownish-red to bluish-violet (all images from Wikimedia Commons).

The visual perception of color is in the eye of an observer and is not objective. The subjective aesthetics of color and beauty are intertwined, and throughout history much of what has been said about beauty can also be applicable to colors. This subjectivity is poignantly expressed by the famous

[5] Wikipedia, *Purple,* https://en.wikipedia.org/wiki/Purple, accessed December 14, 2019.

statement about beauty, coined by the Irish novelist, Margaret Wolfe Hungerford, in 1878:[6]

Beauty is in the eye of the beholder.

Hungerford's phrasing was also used a short time later, in 1893, by Lewis Wallace, an American general, politician, and author, who wrote:[7]

Thou flatterer! Do I not know beauty is altogether in the eye of the beholder, and that all persons do not see alike?

Of course, from then on, as the saying goes, "the rest is history" and this phrase has been widely used. Previous to these 19th century writers, the philosophical sentiments regarding one's taste about beauty – and by association regarding colors – were also prevalent. Thus, in the mid-18th century, in one of his famous essays on the taste of beauty, the Scottish philosopher David Hume wrote:[8]

Beauty in things exists merely in the mind which contemplates them.

Similarly, in his Poor Richard's Almanac, Benjamin Franklin wrote:[9]

For, Beauty, like Supreme Dominion, is best Supported by Opinion.

Even earlier, Shakespeare in the 1590s wrote of beauty in "Love's Labour's Lost", wherein the Princess of France states:[10]

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[6] Margaret Wolfe Hamilton (aka The Duchess), *Molly Bawn* (New York: Hurst and Company Publishers, 1878), accessed December 14, 2019, https://www.gutenberg.org/files/22214/22214-h/22214-h.htm.

[7] Lew Wallace, *The Prince of India Or Why Constantinople Fell, Volume 1, Book 3, Chapter VI: What Do The Stars Say?* (New York: Harper & Brothers Publishers, 1893).

[8] David Hume, *Four Dissertations. Dissertation IV. Of the Standard of Taste* (London: A. Millar, 1757).

[9] Richard Saunders (aka Benjamin Franklin), *Poor Richard, 1741. An Almanack ["Poor Richard's Almanac"], May* (Philadelphia: B. Franklin, New Printing Office near the Market, 1741), http://www.rarebookroom.org/Control/ frapox/index.html, accessed December 15, 2019,

[10] William Shakespeare, *A pleasant conceited comedie called, Loues labors lost ["Love's Labour's Lost"]* (London: W. W. for Cutbert Burby, 1598), https://luna.folger.edu/luna/servlet/view/search?os=0&q=MFHD_Repository_Number%3D%22STC+22294+Copy+1%22&pgs=250&res=2&cic=FOLGERCM1%7E6%7E6&sort=MPSORTORDER1%2CAuthor%2CCD_Title%2CImprint, accessed December 15, 2019,

Beauty is bought by judgement of the eye.

At about the same time, John Lyly expressed one's "fancy" – or personal taste – to beauty in the following way:[11]

And as rare it is too see the Sunne with-out a light, as a fayre woeman without a louer, and as neere is Fancie to Beautie, as the pricke to the Rose, as the stalke to the rynde, as the earth to the roote.

Going further back into history, the 3rd century BCE Greek poet Theocritus, going against the general grain of his fellow philosophers, wrote in one of his Idylls:[12]

For truly in Love's eyes, often, O Polyphemus, what is not fair seems fair.

There is a comparable similarity to this ancient ocular imagery in various biblical passages, wherein grace, charm, favor, fairness, and fancy is in the eyes of the beholder. One of many biblical examples is the discourse between Ruth and Boaz, where Ruth asks if she "found grace (favor) in his eyes,"[13] or in the Book of Esther, where Esther also uses the same phrasing to beseech her husband, the Persian King Ahasuerus (probably Xerxes I).[14]

As with beauty, the perception of color too is literally in the eye of the beholder. The various scientific reasons for colors have been well documented.[15-17] That different people see color differently can be attributed to various biological and environmental factors. These are differences in sensitivities in retinal cone cells, an observer moving from one lighting condition to another (*e.g.*, from darkness to light, or vice-versa), lighting

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[11] John Lyly, *Euphues and His England Containing his voyage and aduenture, myxed with sundry pretie discourses of honest Loue, the discription of the countrey, the Court, and the manners of that Isle* (London: Gabriell Cawood, 1580), https://archive.org/details/in.ernet.dli.2015.503398/page/n91, accessed December 15, 2019.

[12] R C. Trevelyan, *A Translation of the Idylls of Theocritus* (Cambridge: Cambridge University Press, 1947), https://archive.org/details/in.ernet.dli.2015.86553/page/n37, accessed December 15, 2019.

[13] Book of Ruth 2:10.

[14] Book of Esther 7:3.

[15] Mary Virginia Orna, *The Chemical History of Color* (Heidelberg: Springer, 2013).

[16] Kurt Nassau, *The Physics and Chemistry of Color: The Fifteen Causes of Color. 2nd ed. Wiley Series in Pure and Applied Optics, Volume 38* (New York: Wiley, 2001).

[17] Heinrich Zollinger, *Color Chemistry: Syntheses, Properties, and Applications of Organic Dyes and Pigments. Third, Revised Edition* (Zurich: Wiley-VCH, 2003).

conditions on objects, induced concept changes (as to seeing one color frequently and then seeing a different, but similar, one afterwards).[18] On this topic, Mary Virginia Orna writes:[19]

> *The most important detector when discussing color is the human eye because perceived color is nothing more than the subjective personal evaluation of the light reflected or transmitted to the eye.*

Also, socially, certain cultures may not have a full range of words to describe the colors, as for example, in ancient Greece, Homer did not use "blue" to describe the color of the sea, but used the Greek term to describe it as "wine-colored."[20] Recently, the problems with the naming of colors were addressed, as exemplified by the following sentence:[21]

> *One of the fundamental problems in cognitive science is how humans categorize the visible color spectrum.*

In 1810 the German writer, statesman, and color aficionado, Johann Wolfgang von Goethe, while arguing with Isaac Newton's scientific basis, contended in his seminal work on color theory that perhaps the perception of color is inside the mind.[22] In the 16th century, John Lyly, who was also mentioned above, addressed this color problem, as has been noted in the following comment:[23]

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[18] Koos Looijesteijn, *How We All See Colors Differently - Color Theory in Design*, January 10, 2019, https://www.kooslooijesteijn.net/blog/how-we-all-see-colors-differently, accessed December 15, 2019.

[19] Orna, *The Chemical History of Color*, 23-24.

[20] Guy Deutscher, *Through the Language Glass: Why the World Looks Different in Other Languages* (London: Arrow Books / Cornerstone, 2011), https://archive.org/details/ThroughTheLanguageGlass, accessed December 15, 2019.

[21] Vittorio Loreto, Animesh Mukherjee, and Francesca Tria, "On the Origin of the Hierarchy of Color Names," *Proceedings of the National Academy of Sciences* 109 (18): 6819-6824.

[22] Johann Wolfgang Goethe, *Zur Farbenlehre [Goethe's Theory of Colours. Translated from the German: With Notes By Charles Lock Eastlake]* (London: John Murray, 1840), https://theoryofcolor.org/Theory+of+Colors, accessed on December 15, 2019.

[23] Armelle Sabatier, "Colour as an Art of Illusion in John Lyly's Campaspe (1584)." *E-rea* 12.2 (2) (2015), https://journals.openedition.org/erea/4281, accessed December 15, 2019.

Right from the opening lines of one of the prologues to his first comedy, John Lyly deliberately chooses to attract the spectators' and readers' attention to the problematic issue of the perception of colours.

This brings us back, full circle, to the equivalent aesthetics of color and beauty – both being in the eyes of the beholder.

To close out this section on color perceptions and specifically the "Purple Problem", there is an extreme eye-catching puzzling poem in the English literature, a literal "poetic license" approach on the historical "purple" color. This ambiguity is uniquely expressed in an unusual manner by the famous English poet, Robert Browning, in his 1855 poem titled "Popularity." This work disdained the fact that those who toiled very hard at their craft – the ancient Tyrian dye-makers as well as the "true" poets of his period, both groups noted as skillful craftspeople – did not achieve the "popularity" of those who easily lived off their labors without the necessary hard work.[24] The last two stanzas (XII and XIII) read as such in mentioning the "extract" from the murex snail:[25]

And there's the extract, flasked and fine,
And priced and saleable at last!
And Hobbs, Nobbs, Stokes and Nokes combine
To paint the future from the past,
Put blue into their line.

Hobbs hints blue,–Straight he turtle eats:
Nobbs prints blue,–claret crowns his cup:
Nokes outdares Stokes in azure feats,–
Both gorge. Who fished the murex up?
What porridge had John Keats?

Within the poem's 13 stanzas, Browning invokes the "fisher," "Tyre," "Tyrian shells," "whelks," King "Solomon," "conchs," and "murex," all entities associated with the famous "Tyrian Purple" dyed textiles. However, not once does he mention the word "purple" in his poem about what he calls the "dye of dyes," but eight times refers to the color as "blue"!

This is the paradigm example associated with the "purple problem." I believe that the reason that Browning chose the word "blue" instead of "purple" is due to his Judaic studies. Browning was interested in Judaism

[24] Jerome Thale, "Browning's "Popularity" and the Spasmodic Poets," *The Journal of English and Germanic Philology* 54 (1955): 348-354.
[25] Humphrey Milford, *Robert Browning Poetry & Prose* (London: Oxford University Press, 1945).

and wrote a number of poems with Jewish themes, as is well-known.[26- 30] His "Popularity" poem invokes King Solomon's Temple in Jerusalem and the cedar wood that Solomon used for parts of the structure, as well as the textile hangings in his Temple. Browning was undoubtedly taught that the most sacred of the trilogy of biblical colors is *Tekhelet* and that the dye is extracted from certain *Murex* species of sea snails and is a bluish color (actually blue-purple or violet).[31,32] It is the bluish *Tekhelet* that takes Browning's center stage, while not mentioning the biblical red-purple *Argaman* dye at all. That was probably the "blue" – the more revered biblical "purple" – that Browning wanted to convey.

Geography, Chronology, Methodology

This chapter will not be an encyclopedic account of all the different shades of purple found on archaeological textiles from all parts of the world. It will address the representative types of purples that were produced in antiquity by physical and chemical methods in the Ancient Near East, a region roughly corresponding to the modern Middle East. Chronologically, the oldest textile dyeings yet found were the indigo-dyed yarns in 6,000-

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[26] Judith Berlin-Lieberman, *Robert Browning and Hebraism: A Study of the Poems of Browning Which Are Based on Rabbinical Writings and Other Sources in Jewish Literature* (Jerusalem: Azriel Printing Works, 1934).

[27] Professor Barnett, "Browning's Jews and Shakespeare's Jew," *Browning Studies Being Select Papers by Members of the Browning Society* (1895): 253-266, accessed on December 15, 2019, https://archive.org/details/cu31924013444504/page/n271.

[28] Rowena Fowler, "Browning's Jews," *Victorian Poetry* 35, no. 3 (Fall 1997): 245-265.

[29] David Goldstein, "Jews and Robert Browning: Fiction and Fact," *Jewish Historical Studies* 30 (1987-1988): 125-134.

[30] Mary M. Cohen, "Browning's Hebraic Sympathies," Poet-Lore 3 (3) (1891): 250-254, accessed on December 15, 2019, https://babel.hathitrust.org/cgi/pt?id=mdp.39015025931273&view=1up&seq=264.

[31] Zvi C. Koren, "Dyeing with Sea Snails for the Production of Tekhelet and Argaman in Antiquity," in *Out of the Blue Exhibition Catalog*, ed. Ori Meiri, Yigal Bloch, and Yehuda Kaplan (Jerusalem: Bible Lands Museum Jerusalem, 2018), 87-97,190.

[32] Zvi C. Koren, "New Chemical Insights into the Ancient Molluskan Purple Dyeing Process," in *Archaeological Chemistry VIII, ACS Symposium Series 1147*, ed. Ruth Ann Armitage and James H. Burton (Washington D.C.: American Chemical Society, 2013), 43-67.

year old Peruvian textiles.[33] Approximately contemporaneous with these findings, and on the other side of the world, dark-brown colors on yarns from a large linen burial shroud found in the "Cave of the Warrior" in Israel's Judean Desert, were produced from a dye consisting of an organic acidic macromolecule to which a soluble iron salt was probably added.[34]

As for "real purple" colorations, the detailed chemistry of the production of shellfish purple has been given,[35] as well as a recent thorough review of this pigment.[36] Clay vessels that were used for dyeing began appearing about three and a half millennia ago when potshards from Phoenician dyeing vats used for molluskan-purple dyeing, dated to that period, have been excavated.[37] Furthermore, purple-dyed textiles have also been chromatographically determined to have been dyed with a molluskan source from 16th–18th centuries BCE Chagar Bazar,[38] which are the oldest purple-dyed textiles yet recorded, and in 14th century BCE Qatna,[39] both in today's Syria. Though it was reported that based on GC-MS analyses evidence was found for the use of murex purple on samples of pottery vessels from a Minoan facility (*ca.* 18th century BCE) in Alatsomouri–Pefka, on the island of Crete in the Aegean Sea,[40] nevertheless, that publication did not provide the necessary experimental data to support that claim. In addition, though

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[33] Jeffrey C. Splitstoser, Tom D. Dillehay, Jan Wouters, and Ana Claro, "Early Pre-Hispanic Use of Indigo Blue in Peru," *Science Advances* 2 (9) (2016): e1501623.

[34] Zvi C. Koren, "Color Analysis of the Textiles," in *The Cave of the Warrior. A Fourth Millennium Burial in the Judean Desert, IAA Reports, No. 5*, ed. Tamar Schick (Jerusalem: Israel Antiquities Authority, 1998): 100-106.

[35] Christopher J. Cooksey, "Tyrian Purple: 6,6'-Dibromoindigo and Related Compounds," *Molecules* 6 (2001): 736-769.

[36] Ioannis Karapanagiotis, "A Review on the Archaeological Chemistry of Shellfish Purple," *Sustainability* 11 (2019): 3595.

[37] Koren, "New Chemical Insights", 43-67.

[38] Catherine Breniquet, Sophie Desrosiers, Witold Nowik, and Antoinette Rast-Eicher.. "Les textiles découverts dans les tombes de l'âge du Bronze moyen à Chagar Bazar (Syrie)," in *Chagar Bazar (Syrie) VIII. Les tombes ordinaires de l'âge du Bronze ancien et moyen des chantiers D-F-H-I (1999-2011). Études diverses. Mission archéologique de l'Université de Liège en Syrie*, ed. Önhan Tunca and Abd el-Massih Baghdo (Leuven: Peeters, 2018): 11-47.

[39] Matthew A. James, Nicole Reifarth, Anna J. Mukherjee, Matthew P. Crump, Paul J. Gates, Peter Sandor, Francesca Robertson, Peter Pfalzner, and Richard P. Evershed.. "High Prestige Royal Purple Dyed Textiles from the Bronze Age Royal Tomb at Qatna, Syria," *Antiquity* 83 (2009): 1109-1118.

[40] Andrew J. Koh, Philip P. Betancourt, Marie Nicole Pareja, Thomas M. Brogan, and Vili Apostolakou.. "Organic Residue Analysis of Pottery from the Dye Workshop at Alatsomouri-Pefka, Crete," *Journal of Archaeological Science: Reports* 7 (2016): 536-538.

significant shell deposits of *Murex* snails have been discovered in various sites in the Aegean islands, some dating as early as the 19th century BCE from Crete,[41] however, there is no archaeo-chemical evidence that these snails were in fact used for the production of purple-dyed textiles. The purple could have been extracted from these mollusks for use only as a paint pigment.

Most of the textile dyeings discussed in this work date to the Roman Period of two millennia ago since during this period the quality and ingenuity of dyeing reached an apex of development. The most prominent geographical region encompassing this period is the Ancient Near East, and within this area, extensive research into ancient dyeings have been undertaken for almost three decades in the region of Ancient Israel.[42] This geographical area is representative of what can be gleaned from a general study of purple-shaded textiles and will be the focus of this study.

The molecular structures of the main dyes from flora and fauna sources discussed in this chapter are shown in Table 13-1. The roots of the madder plant (*Rubia tinctorum*) can contain as many as nearly 20 components.[43] However, in extractions of madder dyeings needed for further instrumental analyses, the main components are the hydroxy-anthraquinones alizarin (abbreviated as AL) and purpurin (PU).[44] Interestingly, the main components from red-dye producing scale insects are also hydroxy-anthraquinones. Two entomological species – scale insects – have been found on archaeological textiles from the Ancient Near East (see below). The main component of a cochineal insect (*Porphyrophora hamelii*) that breeds on the upper roots of grassy weeds found in the Mount Ararat region is carminic acid (CA). Based on the geo-political nature of this insect, its various names are Ararat, Armenian or Turkish cochineal, which recalls the above-mentioned remarks made by Shakespeare's Juliet, "what's in a name?". The two main dye components of Kermes insects (*Kermes vermilio*

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[41] D. S. Reese. "The invertebrates," in *Palaikastro, Building 1. Supplementary Volume I*, ed. J. A. Macgillivray and L. H. Sackett (Athens, Greece: The British School of Athens, 2019): 387-409.

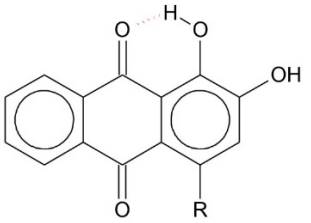
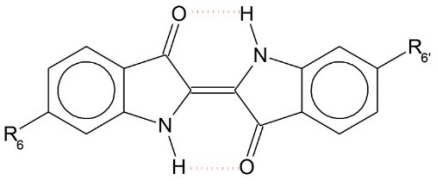
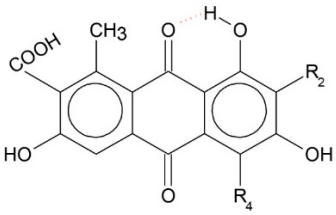
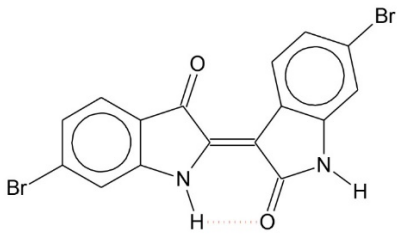
[42] Zvi C. Koren, "Investigating Dyes in Archaeological Textiles: Chemical Technology in the Service of the Ancient World," *Yalkut - Israel Textile Journal* 129 (1992): 20-23.

[43] Lauren Ford, Robert L. Henderson, Christopher M. Rayner, and Richard S. Blackburn, "Mild Extraction Methods Using Aqueous Glucose Solution for the Analysis of Natural Dyes in Textile Artefacts Dyed with Dyer's Madder (*Rubia tinctorum* L.)," *Journal of Chromatography A* 1487 (2017): 36-46.

[44] Pseudopurpurin can also be present in the roots, but in strong acidic extractions used for quantitative analyses, the dye undergoes decarboxylation to purpurin.

and similar species), which breed on certain oak trees found at relatively high altitudes, are flavokermesic acid (FK) and kermesic acid (KA).

Table 13-1. Molecular Structures of the Two Main Dye Classes Discussed in This Chapter

<table>
<tr><th>Hydroxy-Anthraquinones</th><th>Indigoids</th></tr>
<tr><td>Madder
 
<table>
<tr><th>R</th><th>Name</th><th>Abbreviation</th></tr>
<tr><td>H</td><td>Alizarin</td><td>AL</td></tr>
<tr><td>OH</td><td>Purpurin</td><td>PU</td></tr>
</table></td><td> 
<table>
<tr><th>R₆</th><th>R_{6'}</th><th>Name</th><th>Abbrev.</th></tr>
<tr><td>H</td><td>H</td><td>Indigo</td><td>IND</td></tr>
<tr><td>Br</td><td>H</td><td>6-Monobromoindigo</td><td>MBI</td></tr>
<tr><td>Br</td><td>Br</td><td>6,6'-Dibromoindigo</td><td>DBI</td></tr>
</table></td></tr>
<tr><td>Insects
 
<table>
<tr><th>R₂</th><th>R₄</th><th>Acid Name</th><th>Abb.</th></tr>
<tr><td>glucosyl</td><td>OH</td><td>Carminic</td><td>CA</td></tr>
<tr><td>H</td><td>H</td><td>Flavokermesic</td><td>FK</td></tr>
<tr><td>H</td><td>OH</td><td>Kermesic</td><td>KA</td></tr>
</table></td><td> 
6,6'-Dibromoindirubin DBIR</td></tr>
</table>

The indigoid group consists of the main indigo molecular skeleton and its brominated derivatives. The indigo pigment itself – also referred to as indigotin[45] – can be produced via reduction-oxidation processes from the leaves of various plants, such as woad (*Isatis tinctoria*), native to Europe

[45] Sometimes the indigo dye or pigment is referred to as "indigotin" from the etymological combination of indigo + tinct or tincture, in order to distinguish between the pigment and the plant name, which is also referred to simply as indigo.

and the Near East, or the indigo plant itself (*Indigofera tinctoria*), native to India and environs, as its name implies, and from other plants. Interestingly, the indigo pigment is also naturally produced from a molluskan source, specifically the *Hexaplex trunculus* sea snail species – also known as *Murex trunculus* (see below). About ten different indigoids and their isomers – the indirubinoids – and related isatinoids can be produced from these malacological sources.[46]

In order to detect these and other dye components, the optimal methodology for such a study of natural dyestuff sources, which contain a number of dye components, is the well-known separation technique, high-performance liquid chromatography (HPLC) coupled to a Photo-Diode Array (PDA) detector.[47] It provides two important properties – chromatographic and spectrometric – for the identification of each individual component. The chromatographic property is the unique retention time (t_R) of each substance before it is swept out of the stationary phase by the mobile eluents. Figure 13-2 shows a chromatogram[48] for the separation of madder and insect hydroxy-anthraquinones, and displaying the separation of the "kermes doublet." A chromatogram showing the separation of ten malacological components of a purple pigment has been previously published.[49]

The spectrometric property that the PDA detector produces is the resultant ultraviolet-visible (UV/Vis) spectrum, which can be seen in Figure 13-3 for some selected dyes. Though some of the dyes may have similar spectrometric profiles, such as carminic and kermesic acids, however, their retention times are significantly different. For the determination of unknown components, a mass spectrometer (MS) can also be coupled to the HPLC-PDA in order to obtain the molecular mass of each substance, which adds a third property for the identification of this dye.

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[46] Zvi C. Koren, "HPLC-PDA Analysis of Brominated Indirubinoid, Indigoid, and Isatinoid Dyes," in *Indirubin, the Red Shade of Indigo*, ed. Laurent Meijer, Nicole Guyard, Leandros A. Skaltsounis, and Gerhard Eisenbrand (Roscoff, France: Life in Progress Editions, 2006): 45-53.

[47] Zvi C. Koren, "Editorial: Extracting Thousands of Years of Colorful Dye History Through Analytical Science," *Palestine Exploration Quarterly* 143 (1) (2011): 1-3.

[48] A chromatogram is a graph of the relative absorption of irradiated light (measured in absorbance units, AU) by the components of a solution moving through a stationary medium, as a function of time.

[49] Zvi C. Koren, "Modern Chemistry of the Ancient Chemical Processing of Organic Dyes and Pigments," in *Chemical Technology in Antiquity, ACS Symposium Series Vol. 1211*, ed. Seth C. Rasmussen (Washington, DC.: American Chemical Society, 2015): 197-217.

The textile dyeings discussed in this paper are the ones that have undergone rigorous HPLC analyses and are generally from the Roman Period, as noted above. Though, a lichen ("*phycos*") has been described by the Roman historian Pliny the Elder as a dye for purple colors ("the *phycos* growing on rocks round the island of Crete is also used for a purple dye"), it has not yet been found on such antique textiles, but on much later illuminated manuscripts. Thus, it will not be discussed in this work.

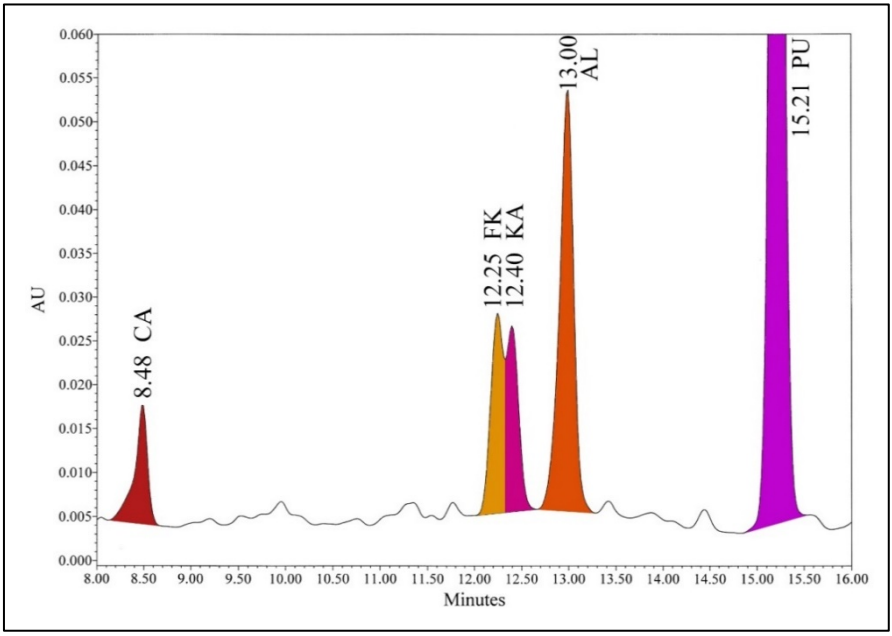

Figure 13-2. HPLC–PDA chromatogram with corresponding retention times of reddish hydroxy-anthraquinone dye components from cochineal (CA = carminic acid) and kermes (FK = flavokermesic acid, KA = kermesic acid) insects and madder roots (AL = alizarin, PU = purpurin).

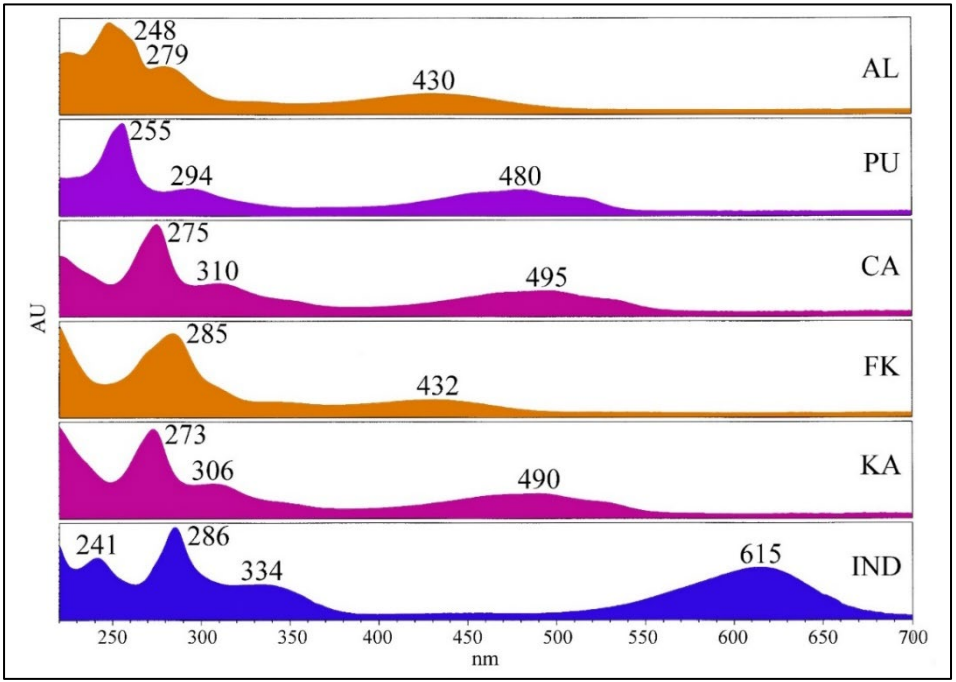

Figure 13-3. UV/VIS spectra generated by the PDA detector of the HPLC of acidic methanolic solutions of alizarin (AL), purpurin (PU), carminic acid (CA), flavokermesic acid (FK), kermesic acid (KA), and a solution of indigotin (IND) in dimethyl sulfoxide (DMSO); also shown are the wavelength values at maximum absorption, λ_{max}, as well as the general color of each dye in solution.

The Ancient Dyer as an Advanced Materials Scientist

The dyer's expertise in being able to work with various materials – both organic and inorganic – is astounding. The colorful crafter in the Ancient Near East knew that the optimal fibrous material to use for dyeing was wool with its protein structure possessing polar charged sites, as we now know, and hence the ability to attach itself – directly or indirectly – to the dye molecules. While flax and other cellulosic plant fibers were common in this region, the cellulosic nature of linen textiles does not possess the necessary molecular sites for producing strong chemical bonds with the natural dyes in use at the time. Thus, while there are archaeological examples of dyed linens, these show relatively inferior dyeings to the ones that were produced at the same time on woolens. Besides producing the three primary dye colors – red, blue, and yellow – as is already well-known, the dyer of the Roman period was especially interested in producing the most sought-after color – purple – in all of its different variations, and may have even produced more than "fifty shades" of purple.

In order to produce purple and other dyeings from non-molluskan sources, the dyer possessed the technological knowledge that many dyes from botanical or entomological sources, which we now know are hydroxy-anthraquinones, required a mordant. The role of the mordant (from the Middle French *mordre* and earlier from the Latin *mordēre* meaning "to bite"),[50] is to be a "matchmaker" – a bridging or bonding agent – that acts as a mediator to indirectly unite the dye to the fibers. The dyer also knew that different mordants with the same dye will produce different colors because, in modern terminology, differently colored metal-organic complexes are formed. The main mordant that was used was the potassium aluminum sulfate dodecahydrate salt, $KAl(SO_4)_2{\cdot}12H_2O$, known simply as alum, a mineral that was readily available. The expertise of the dyer is apparent from the choice of salt that was used. Ordinary salt, NaCl, will produce the univalent sodium ion, Na^+, which has a negligible ability to form the insoluble metal-dye complex necessary to fix the dye into the textile fiber. As any student of general chemistry knows, all sodium salts have relatively good solubilities in aqueous solutions and thus any possible sodium–dye complex will simply not form. However, the alum's trivalent Al^{3+} ion can form insoluble complexes via not only ionic bonding but also

[50] Merriam-Webster, *Mordant*, https://www.merriam-webster.com/dictionary/mordant, accessed on December 15, 2019.

coordinate-covalent bonds as the Al^{3+} ion also acts as a Lewis acid.[51,52] Thus, on one side, alum's aluminum ion can attach itself via these bonds to the oxygen and nitrogen atoms of wool's amino acids, as well as to water molecules, to produce chelate structures.[53] On the other side, the Al^{3+} ion can also form insoluble dye complexes (known as "lakes") via the same type of ionic and coordinate-covalent bonds, to produce the necessary insoluble Al–dye complex. In addition, the nature of the Al^{3+} ion is its octopus-like "tentacles" whereby each cation can wrap itself around several dye molecules. This complexation can, therefore, produce polymeric Fiber–Al–dyes–Al–dyes– *etc*. structures in the textile and thus increase the fastness – stability – of the resultant dyeing to washing and to the influence of light.

Botanical Purples

Madder + Iron mordant

Besides alum, another mordant that has been used, though less frequently, is a soluble iron-salt, which contains divalent Fe^{2+} and trivalent Fe^{3+} ions able to produce insoluble complexes similar to the Al^{3+} ion of alum. While alum-mordanted dyeings produce bright vivid colorations, the use of an iron-mordanted dyeing will result in a darkening of the dyeing to produce, *e.g*., chocolate-colored or purplish dyeings with madder. This iron-madder combination was reported by one of the early dye analysts, Judith Hofenk de Graaff, to be present in a textile (*ca.* late 1st century BCE – 1st cent. CE) excavated at Masada.[54] This famous archaeological site was the cliff-top palace and fortress built by King Herod the Great, overlooking the Dead Sea in Israel's Judean Desert. Iron mordants would have been readily accessible from muddy areas, and thus were used in what is known as "mud-dyeing." Although mud contains insoluble iron oxides and hydroxides – these iron compounds are not the ones that act as mordants; it is the soluble iron salts in the muddy water that are, in effect, the mordanting agents.

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[51] Koren, "Modern Chemistry," 197-217.

[52] A Lewis acid is a chemical species that is capable of accepting an electron pair from a Lewis base.

[53] Mohd. Yusuf, Shahid-ul-Islam, Mohd. Ali Khan, and F. Mohammad, "Investigations of the Colourimetric and Fastness Properties of Wool Dyed with Colorants Extracted from Indian Madder Using Reflectance Spectroscopy," *Optik* 127, no. 15 (2016): 6087–6093.

[54] Judith H. Hofenk de Graaff, *The Colourful Past: Origins, Chemistry and Identification of Natural Dyestuffs* (Riggisberg, Switzerland and London: Abegg-Stiftung and Archetype Publications, 2004).

Thus, with the use of the madder dye, the expert dyer could have also performed a dyeing by using both aluminum and iron mordants to produce the desired shade of purple.

Madder + Indigo

The most popular method by which non-molluskan purplish colors were produced in antiquity was the combination of red and blue dyestuff sources, as the ancient dyer was keenly aware of the "colorimetric trick" that the mixing of blue and red colorants produces purple. This combination was mostly performed by the "double-dyeing" or "over-dyeing" technique of using a dye bath containing the roots of a madder species, and with a separate dye solution containing the indigo dye produced from the leaves of certain plants. The dyer was obviously able to shade the final color that was produced, so that if a bluish-purple or violet coloration were desired then more blue would have been present, and if a reddish-purple color was required then more madder was used.

Prior to the indigo dyeing process, the indigo pigment needed to be reduced to a soluble dye. The dyeing was then performed by immersing the textile in this solution and later removing it from the dye bath and allowing the soluble dye molecules within the fibers to undergo air-oxidation. This type of dye – referred to as a "vat dye" – does not require a mordant in order to fix it into the fibers, and thus if only an indigo dyeing was desired, then no mordant was deliberately used for that.

The first step in the overall indigo dyeing process would have been performed with the reduction of indigo by means of the anaerobic, moderate thermophilic bacterium (*Clostridium* in woad) naturally present in the fermenting vat.[55,56] For this reduction to be effective, an alkaline pH of about 8 and a temperature of 50-60 ^{o}C are necessary. Under these conditions, it is considerably easier to reduce indigo (reduction potential of about –0.6 V)[57] than the Al–O bonds between the alum and the woolen

[55] A. Nikki Padden, Vivian M. Dillon, Philip John, John Edmonds, M. David Collins, and Nerea Alvarez, "*Clostridium* Used in Medieval Dyeing," *Nature* 396 (1998): 225.

[56] A. Nikki Padden, Vivian M. Dillon, John Edmonds, M. David Collins, Nerea Alvarez, and Philip John, "An Indigo-Reducing Moderate Thermophile from a Woad Vat, Clostridium isatidis sp. nov.," *International Journal of Systematic Bacteriology* 49 (1999): 1025-1031.

[57] Sonja K. Nicholson and Philip John, "The mechanism of bacterial indigo reduction," *Applied Microbiology and Biotechnology* 68, no. 1 (2005): 117-123.

fibers in mordanted wool; e.g., $Al_2(OH)_3$ has a standard reduction potential of -2.31 V.[58]

In this red-blue combination method to produce purple dyeings, it cannot be absolutely ascertained as to which came first – the madder dyeing or the indigo dyeing. However, it would be reasonable to presume that the probable order was indigo dyeing before the madder one. If the mordant-madder dyeing would have been performed prior to the indigo dyeing, then there is the possibility that the harsh chemical environment required for the following indigo dye bath – a reducing alkaline setting – would adversely affect a mordant-dye complex. Mordanting, which was needed for the last madder-dyeing stage, could have been performed either before or after the indigo dyeing. If the alum-mordanting of wool pre-staged the indigo dyeing, then indigo's reducing environment would have a negligible effect on the mordant in the fibers. Similarly, if the mordanting were performed after the indigo dyeing, then the presence of the solidified indigo molecules, which form intermolecular bonds with the textile fibers, should also have little effect upon the formation of Al–wool(O,N) bonds in the mordanting process. The third, last, stage would then be dyeing with a separate madder dye bath to form the Al–dye complex within the fibers.

In analyses that I performed on such double-dyed purples, typically both alizarin and purpurin were detected, which points to the use of a madder plant. However, it was surprising to find that generally, more purpurin was present than alizarin in these purples. The analytical extract from "Dyer's Madder" (*Rubia tinctorum*) typically contains more alizarin,[59] though, in a few cases, it was reported that these roots contain less alizarin than purpurin.[60] However, the main madder species available in the Levant that produces more purpurin than alizarin is "Wild Madder" (*Rubia peregrina*).[61] Alternatively, with international commerce existing two millennia ago between India and the Levant, it was also possible to have used "Indian Madder" (*Rubia cordifolia*) whose major component is

[58] Petr Vanýsek, "Electrochemical Series," https://sites.chem.colostate.edu/diverdi/all_courses/CRC%20reference%20data/electrochemical%20series.pdf, accessed on December 15, 2019.

[59] Jan Wouters, "High Performance Liquid Chromatography of Anthraquinones: Analysis of Plant and Insect Extracts and Dyed Textiles," *Studies in Conservation* 30 (1985): 119-128.

[60] Jan Wouters, "The Dye of Rubia Peregrina. I. Preliminary Investigations," *Dyes in History and Archaeology* 16/17 (2001): 145–157.

[61] Wouters, "The Dye of Rubia Peregrina," 145–157.

reported to be purpurin.[62] Thus, this adds an additional "feather in the cap" of the ancient dyer. If only a reddish – alizarin-rich – dyeing was desired by using a madder dyestuff then the *R. tinctorum* species was used. However, if the dyer were interested in producing a purple shade then he would have used a madder species, namely *R. peregrina*, which already by itself can produce a more purplish shade due to its purpurin-rich dye composition. This phenomenon of a purpurin-rich madder seems to be the norm in such double-dyed purple textiles. The possible use of two different madder species was reported when I prepared my 1994 publication on Masada textile dyeings.[63] One cannot preclude from this discussion the possibility that the ancient dyer was able to somehow process Dyer's Madder in a certain way so as to enrich it with purpurin.[64]

There are many examples of this type of purple, and two such examples are shown in Figures 13-4 and 13-5. Figure 13-4 is from King Herod's palatial fortress atop Masada in the Judean Desert.[65,66] The other example (Figure 13-5) is from 'En Raḥel (literally "the Spring of Rachel"), a Nabatean fort in the arid 'Arava Valley (in today's southeastern Israel bordering Jordan), and it was probably a way-station along the Spice Route from Petra to Gaza.[67] Both Roman Period examples are from about two millennia ago.

It is also interesting to note that probably the first reports of the use of a purpurin-rich madder-type dye plant was from the textile discoveries in the

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[62] Deepti Gupta, Shipra Kumari, and Mohan Gulrajani, "Dyeing Studies With Hydroxy-Anthraquinones Extracted From Indian Madder. Part 1: Dyeing of Nylon With Purpurin," *Coloration Technology* 117, no. 6 (2001): 328-332.

[63] Zvi C. Koren (Kornblum), "Analysis of the Masada Textile Dyes," in *Masada IV. The Yigael Yadin Excavations 1963–1965. Final Reports*, ed. Joseph Aviram, Gideon Foerster, and Ehud Netzer (Jerusalem: Israel Exploration Society, 1994), 257-264.

[64] Vincent Daniels, Thibaut Devièse, Marei Hacke, and Catherine Higgitt, "Technological Insights Into Madder Pigment Production in Antiquity," *Technical Research Bulletin of The British Museum* 8 (2014): 13-28.

[65] Avigail Sheffer, and Hero Granger-Taylor, "Textiles from Masada: A Preliminary Selection," in Masada IV. The Yigael Yadin Excavations 1963-1965. Final Reports, ed. Joseph Aviram, Gideon Foerster, and Ehud Netzer (Jerusalem: Israel Exploration Society, 1994), 151-250.

[66] Koren (Kornblum), "Analysis of the Masada Textile Dyes," 257-264.

[67] Zvi C. Koren, "Microscopic and Chromatographic Analyses of Decorative Band Colors on Nabatean 'En Rahel Textiles – Kermes and Shaded Bands," *'Atiqot* 38 (1999): 129-136.

Wâdī ed-Dâliyeh,[68,69] which is about 14 km north of Jericho, where it was suggested that the dye source was Munjeet (*Rubia cordifolia*), cultivated in India.[70] In addition, at a different site, it was found that red Nubian threads contained purpurin as the main constituent, and it was surmised that the source might have also been Munjeet (mentioned by the investigators as *Rubia munjista* or as *Rubia cordifolia*) or possibly *Rubia peregrina*.[71]

A typical chromatogram set that is obtained from archaeological purple dyeings produced from a madder-indigo combination is shown in Figure 13-6. The detected dyes from an HCl/DMSO extract from the madder dyestuff are alizarin and purpurin, and from indigo, the indigo dye is of course noticeable as well as indirubin (INR) and isatin (IS). In order to visualize the yellow to orange components, the low detector wavelength of 418 nm was used. In that chromatogram, the alizarin peak is clearly visible, as well as a trace of the yellow isatin dye. The latter colorant, if present, is always a minor component. For the visualization of the possible presence of indirubin, the higher detector wavelength of 540 nm was used, however, it too is usually of a much lesser quantity than indigo.

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[68] G. W. Midgelow, "Report on the Dyes," in Elisabeth Crowfoot, *The Textiles*, in *Discoveries in the Wâdī ed-Dâliyeh, The Annual of the American Schools of Oriental Research, Vol. 41*, ed. Paul W. Lapp and Nancy L. Lapp, (Cambridge, Massachusetts: American Schools of Oriental Research, 1974): 80.

[69] M. C. Whiting and Takeo Sugiura, "Additional Study of the Dyes," in Elisabeth Crowfoot, *The Textiles*, in *Discoveries in the Wâdī ed-Dâliyeh, The Annual of the American Schools of Oriental Research, Vol. 41*, ed. Paul W. Lapp and Nancy L. Lapp, (Cambridge, Massachusetts: American Schools of Oriental Research, 1974), 80-81.

[70] Midgelow, "Report on the Dyes," 80.

[71] L. Masschelein-Kleiner and L. Maes, "Ancient Dyeing Techniques in Eastern Mediterranean Regions," *Proceedings of the ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb* 78/9/3 (Paris: International Council of Museums, 1978): 78/9/3/1 - 78/9/3/10.

Figure 13-4. A 2,000-year old Masada woolen textile, probably from a mantle or other piece of clothing, showing a salmon-pink ground produced from the alizarin-rich Dyer's Madder (*Rubia tinctorum*) and a notched purple weft band produced from an over-dyeing with a purpurin-rich madder species (probably Wild Madder, *Rubia peregrina*) and an indigo-producing plant, probably woad (*Isatis tinctoria*).

Figure 13-5. Two adjoining shaded weft bands from ‘En Raḥel; the blue was produced only with the indigo dye (probably woad) and the purple-violet from a double-dyeing with a purpurin-rich madder (probably Wild Madder, *Rubia peregrina*) and the indigo-producing plant, as in Figure 13-4.

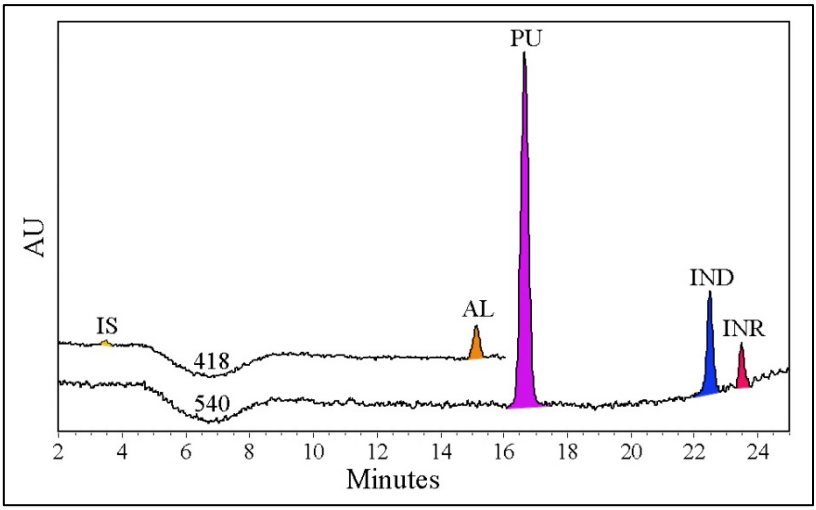

Figure 13-6. Typical chromatograms for the extracted dye solution from madder-indigo dyeings, at 418 and 540 nm (for visualization purposes).

Entomological Purples

All the entomological "scale insect" dyes have hydroxy-anthraquinone molecular structures, similar to madder (Table 13-1), and thus require a mordant in order to form stable dyeings, as mentioned above.

Ararat Cochineal

At the Late Byzantine fortress of 'En Boqeq ("the Spring of Boqeq"), a way-station close to one of the spice routes overlooking Israel's Dead Sea, a small reddish woolen patch was excavated (see Figure 13-7).[72] Today, the site sits a short walk across a highway from a luxury hotel located on the southwestern shore of that saltiest body of water.

[72] Zvi C. Koren, "Chromatographic Analyses of Selected Historic Dyeings from Ancient Israel," in *Scientific Analysis of Ancient and Historic Textiles: Informing, Preservation, Display and Interpretation*, ed. Rob Janaway and Paul Wyeth (London: Archetype Publications, 2005), 194-201.

Figure 13-7. Red patch on an undyed soiled textile from early 7th century CE 'En Boqeq, near the Dead Sea.

At first sight, this fragment seemed to belong to the many madder-type reddish dyeings found in the Middle East. However, this petite, and to the naked eye, "typical" ancient red dyeing, was in actuality of major importance. It showed the cleverness of the dyer and weaver, working together, to produce an economically rich product. After analyzing this red textile, as discussed below, it also reminded me of the famous adage coined by the prominent color scientist, and one of the early analysts of archaeological dyes, the late Max Saltzman, who stated:[73]

You can't tell a dye by its color.

Under the microscope, a whole new colorful world shines through, as the crimson-colored dyed weft yarns, reminiscent of certain similarly colored molluskan-based reddish-purple dyeings, are revealed (Figure 13-8). However, the warp yarns appear to be of a different coloration – dull red. Physically, this weave is "weft-faced" so that mostly the crimson weft side of the textile is visible, with the warp yarns serving as a kind of background – a "behind-the-scenes" color. The subsequent results of the HPLC analyses

[73] Max Saltzman, "Analysis of Dyes in Museum Textiles or You Can't Tell a Dye by its Color," in *Textile Conservation Symposium in Honor of Pat Reeves, 1 February 1986, Los Angeles*, eds. Catherine C. McLean and Patricia Connell (Los Angeles: Los Angeles County Museum of Art, 1986): 27-39.

of these two yarn types revealed the synergistic ingenuity of the dyer and weaver. The duller red warp yarn fibers were dyed with "ordinary" Dyer's Madder, described above. However, the majestic bright crimson weft yarns were dyed with the more valuable and prestigious insect dyes containing mainly carminic acid. Thus, the weaver, wanting to highlight the radiance of this textile showcased the crimson look at center stage, but yet, still wanting to maintain the overall reddish nature of the textile, chose the more ordinary madder dyestuff for the nearly imperceptible background.

This insect species is not native to the site where the dyed textile was found (very close to the Dead Sea), but from the geographical viewpoint, the closest habitat to Ancient Israel whereby this insect species breeds indicates that the "Ararat cochineal" is the most likely source of that dyeing. The conclusion is that either this insect was traded as a valuable commodity and made its way to the Dead Sea or environs where it was used for dyeing. Alternatively, it is possible that the actual dyeing was performed near to its breeding grounds and that this textile – or its owner – finally made its/his way to 'En Boqeq. Either way, this 1,500-km trip would have taken about 330 hours by foot (according to Google Maps) – or on a slow donkey – a doable journey in ancient times.

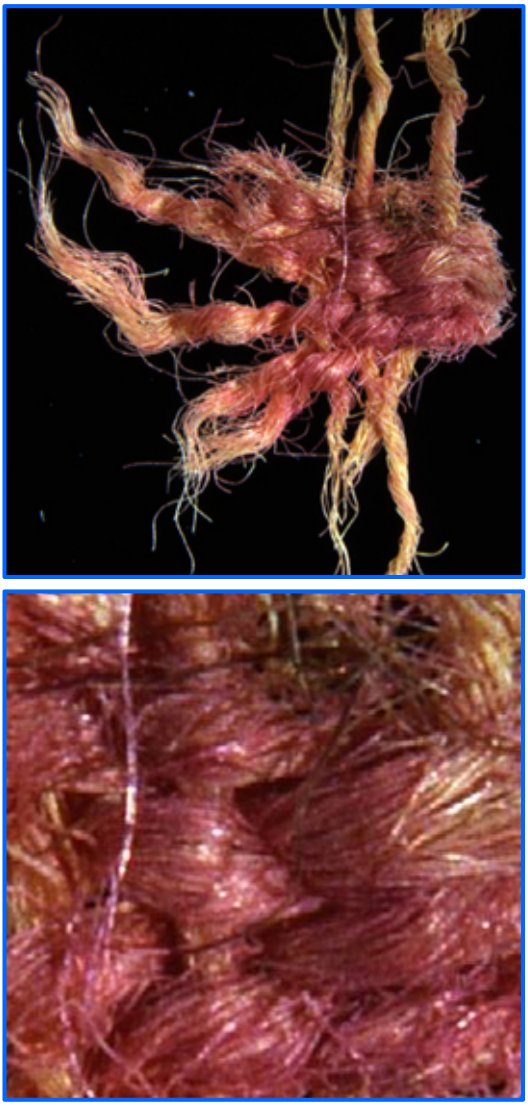

Figure 13-8. Highly illuminated microscope pictures of a sample from the red patch (of Figure 13-7) showing the bright-crimson weft yarns and the dull-red warp yarns *(top)*, and the details of the weft yarns *(bottom)*.

Kermes insect

The 2,000-year old Nabatean-Roman site of ‘En Raḥel (mentioned above) was the first site with findings of the use of a Kermes insect – perhaps the *Kermes vermilio* species[74] – for the dyeing of a purple color.[75] Kermes was found as the sole dyestuff in the purplish band shown in the textile fragment of Figure 13-9. Though their numbers may not be great, Kermes insects are still found in today’s Israel.[76]

In modern dye-producing *Kermesidae* species, such as *Kermes vermilio*, two main dye components are always present, yellow-orange flavokermesic acid (denoted as “FK”) and purplish kermesic acid (“KA”), as mentioned above. Interestingly, an alum-mordanted woolen dyeing with Kermes insects, which naturally contains both dyes, yields orange-red dyeings, and this is the *Shani* color (“scarlet”, not crimson) mentioned in the Bible as the third sacred colored dyeing, in addition to the previously discussed *Tekhelet* and *Argaman*.

In HPLC analyses, though both dyes are closely eluted from the HPLC column, nevertheless, they both can be clearly detected in the chromatogram in the “kermes doublet” (see Figure 13-2) as well as in their different UV/Vis spectra (Figure 13-3). However, in present day analyses of ancient dyeings with a kermes species, it appears that the FK dye is not stable over the archaeological timeframe, and after two millennia only the KA colorant remains in the dyeing.[77] This can be seen in the chromatogram set of Figure 13-10. Thus, ancient kermes-based dyeings found today would appear to be more purple than originally envisioned by the dyer of yore. This purple-colored sample of Figure 13-9 exemplifies the adage of “what we see today is not necessarily what was seen yesterday.” While it may be possible that perhaps the dyer used a kermes species that mainly has the KA dye, so far no such kermes insect has been found without the presence of both FK and KA.

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[74] Dominique Cardon, *Natural Dyes: Sources, Tradition, Technology and Science* (London: Archetype Publications, 2007).
[75] Koren, "Microscopic and Chromatographic Analyses,” 129-136.
[76] Malkie Spodek and Yair Ben-Dov, "A Taxonomic Revision of the *Kermesidae* (*Hemiptera*: *Coccoidea*) in Israel, With a Description of a New Species," *Zootaxa* 3781, no. 1 (2014): 1-99.
[77] Koren, "Microscopic and Chromatographic Analyses,” 129-136.

Figure 13-9. A 2,000-year old weave from ‘En Raḥel showing the purple band with the presence of the kermesic acid dye, indicating that it was dyed with a Kermes scale insect.

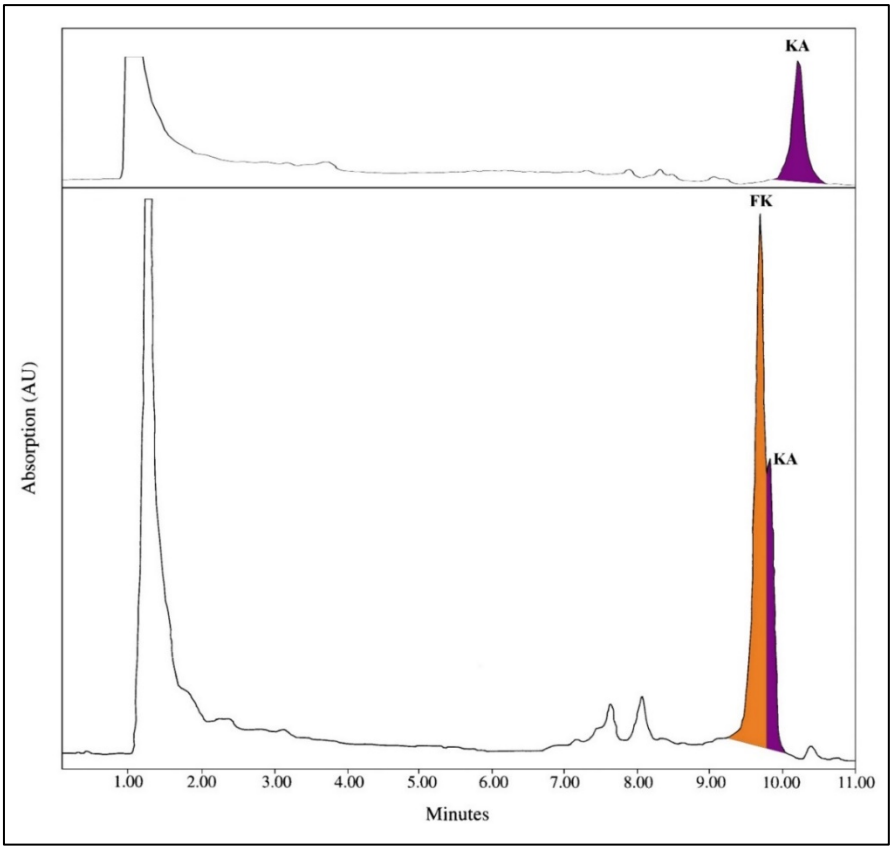

Figure 13-10. Chromatograms from a *Kermes* insect at 275 nm. *Bottom*: Modern insect sample. *Top*: Archaeological purple sample from ‘En Raḥel.

Mixed Entomological-Botanical Purples

Kermes + Indigo: Chemical combination

In another dyeing found at ‘En Raḥel, the dark-purple band was produced by means of an overdyeing with a Kermes insect and the indigo pigment, and is shown in Figure 13-11. The use of a relatively expensive insect dye from Kermes breeding on special oak tree species found only in certain regions, and which is to be combined with indigo, is a bit eccentric. The overall colorful purple look of this double-dyeing combination could

have been produced, as discussed above, with the red from madder, a much more economical dyestuff source, which can literally be grown in one's garden. Perhaps the owner of the textile believed that such an expensive dye, even in a combination, was more prestigious.

Figure 13-11. A 2,000-year old weave from 'En Raḥel showing the dark-purple band double-dyed with a Kermes scale insect and the indigo dye.

Kermes-Indigo + Madder-Indigo: Physical combination

A most unusual combination of a kermes insect dye together with the indigo and madder dyes appears in a textile from the 2,000-year old site of Masada. In this weave from a tunic (Figure 13-12), the purple color was achieved, in part, by the physical mixing of differently dyed yarns – a "trick on the eyes" – in contrast to the much more common double-dyeing technique – a chemical process.

The yarns in the border decoration in Figure 13-12 appear uniformly purple-colored on the macro level, but beneath the surface there's "much more to that than meets the eye." When I analyzed each whole purple yarn under the microscope, an unusual combination of yarns was revealed. Each whole yarn is actually composed of plying a total of 4 individual yarns according to the following mix: 2 identical blue-violet (BV) yarns were plied together and 2 identically colored reddish-purple (RP) yarns were plied with each other. These two pairs were then plied together to form one composite yarn. Performing HPLC analyses on each of these 4 dissected yarns yielded the following dye components:

RP: indigo >> indirubin, isatin. Purpurin >> alizarin.
BV: indigo >> indirubin. Kermesic acid.

The obvious implications are that each red-purple yarn was dyed with the familiar double-dyeing pattern with the indigo dye and the purpurin-rich madder mentioned above. Each blue-violet yarn was also double-dyed with indigo, but in this case, the red component was from the Kermes insect. Though the blue-violet (BV) yarn contained the purplish KA dye, nevertheless, the overall bluish coloration of this yarn is due to the preponderance of indigo in this dyeing. In the case of the dark-purple band of Figure 13-11 above, the major component in the kermes-indigo double-dyeing was kermesic acid and thus showing a pronounced purplish color.

The overall surprising discovery was that the two plied red-purple yarns, which were produced from flora sources alone, were physically twisted together with two blue-violet yarns, which contained an entomological dyestuff source.

Figure 13-12. A Masada woolen textile with purple yarns composed of kermes double-dyed with indigo and mixed with double-dyed madder-indigo yarns.

Malacological Purples

Of all the various combinations for producing purple colorations on textiles discussed above, it is the purple of a molluskan origin that is the "*pièce de résistance*", the "dye of dyes" in Browning's eyes. It was the regal and sacral color for potentates and priests, and known by a variety of names based on its geographical origins and its end-product use, including Tyrian Purple, Imperial Purple, Royal Purple, and Biblical Purple. The archaeological examples in this last section highlight the multifaceted diversity of "purple", as discussed in the opening section of this paper. Thus, we encounter two chromatic varieties of "purple" – reddish and bluish, and final shades that are in-between and beyond.

Red-Purple

There is a popular notion in the literature that the sea snail that produced the famous "Tyrian Purple" textile dyeings from the *Muricidae* family of mollusks was the *Murex brandaris* (renamed as *Bolinus brandaris*). See, for example, the websites of the Smithsonian[78] and the *Encyclopedia Britannica*,[79] as well as various journal articles,[80,81] which ascribe the Tyrian Purple to the *B. brandaris* species. Furthermore, the view was that the component of Tyrian Purple was DBI alone (see Table 13-1). The archaeochemical evidence regarding dyeing with marine snails shows that the situation is much more complex, as described below, and that the above perceptions are only "half-truths."

Ever since the Roman historian Pliny the Elder[82] discussed in detail the sea snail species that produced the purple pigment and its processing into a

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[78] Colin Schultz, "In Ancient Rome, Purple Dye Was Made from Snails," Smithsonian.com Smart News, October 10, 2013, https://www.smithsonianmag.com/smart-news/in-ancient-rome-purple-dye-was-made-from-snails-1239931, accessed on December 15, 2019.

[79] Virginia Gorlinski and The Editors of Encyclopaedia Britannica, "Murex - Mollusk Family," https://www.britannica.com/animal/murex-mollusk-family#ref227413, accessed on December 15, 2019,

[80] For example, Lloyd B. Jensen, "Royal Purple of Tyre," *Journal of Near Eastern Studies* 22, no. 2 (1963): 104-118.

[81] Fathi Habashi, "Indigo and Bromo Indigo. The Plant and Animal Kingdoms," *Latest Trends in Textile and Fashion Designing* 1, no. 4 (2018): 80-82, https://lupinepublishers.com/fashion-technology-textile-engineering/fulltext/indigo-and-bromo-indigo-the-plant-and-animal-kingdoms.ID.000119.php, accessed on December 15, 2019.

[82] Especially Book IX of Pliny's *Natural History*

dye, it is well-known that in the Eastern Mediterranean a purple pigment could be extracted from three species of the *Muricideae* family of mollusks. These are *Hexaplex (= Murex) trunculus*, *Bolinus brandaris*, and *Stramonita haemastoma*, and are shown in Figure 13-13. However, "not all snails were created equal." While the main colorant in the *B. brandaris* and *S. haemastoma* (and other sea snails from other oceans and seas) is the DBI colorant, the *H. trunculus* pigment can have as many as about 10 colorants.[83] The major components, though, from the *H. trunculus* species are red-purple DBI, violet MBI, and blue IND, where often in archaeological dyeings some reddish DBIR, DBI's isomer, is also detected (see Table 13-1). It is important to emphasize that these components could not have been deliberately and artificially produced during the natural dyeing process practiced in antiquity (even though with today's synthetic reducing reagents it can be done).[84]

The chemical detective work needed in order to determine that a molluskan source was used for a dyeing begins with finding DBI in the colorant. This dye is the common denominator of all purple-producing molluskan species from all parts of the marine world. It could still be that other botanical and/or entomological dyestuff sources were also used, but the presence of DBI is the "smoking gun" evidence needed to prove that a "real-purple" dyeing was performed.

In order to determine the zoological provenance of molluskan-purple dyeings, *i.e.*, identifying the specific marine species that was used for the dyeing, one needs to determine whether other indigoids besides DBI are also present in the dyeing. Though *H. trunculus* pigments contain IND, if that dye is detected in any real-purple dyeing, then one cannot be absolutely certain whether this IND dye was naturally obtained from this species or if it originated from a plant source and was added to the dyeing. This is because, of course, chemically the IND molecule from a malacological source is identical to one of botanical origin. However, a distinctive feature of all *H. trunculus* species – what sets them apart from all the others – is that only they have a significant quantity of MBI, and thus finding this dye in a molluskan purple dyeing would indicate that the *H. trunculus* was used.[85] If only minute amounts – or none at all – of MBI are present then any purple-producing sea snail could have been used for that dyeing. Thus, the chromatic bio-marker for determining whether *H. trunculus* was used is in the presence of MBI. What is most interesting is that to date, all

[83] Zvi C. Koren, "Archaeo-Chemical Analysis of Royal Purple on a Darius I Stone Jar," *Microchimica Acta* 162 (2008): 381-392.
[84] Koren "New Chemical Insights," 43-67.
[85] Koren, "Archaeo-Chemical Analysis," 381-392.

Figure 13-13. Purple-producing *Muricidae* mollusks. From bottom to top: *Bolinus (= Murex) brandaris*, *Hexaplex (= Murex) trunculus*, and *Stramonita (= Purpura) haemastoma*.

molluskan archaeological purples – as paint pigments or textile dyes – that have been properly analyzed via HPLC have shown the presence of an appreciable quantity of MBI, which could sometimes even be the major

component. This clearly indicates that all molluskan purple dyeings performed in antiquity used *H. trunculus* sea snails; sometimes alone and sometimes mixed with other sources (see discussion below). Further, I have discovered that there are two chromatic varieties of *H. trunculus* snails – perhaps even "subspecies" of the same *H. trunculus* species (see Figure 13-14). One type produces reddish-purple pigments that are richer in DBI than IND and, thus, exhaust dyeings produced with that pigment will have similar reddish-purple colors. The other variety produces bluish-purple (or violet) pigments that are IND-rich and thus similarly colored violet dyeings.

Figure 13-14. Two different chromatic varieties of modern *Hexaplex trunculus* sea snails. *Top:* Red-purple pigment that is DBI-rich; *Bottom:* Blue-purple (violet) IND-rich pigment oozing from the snail's aperture.

A majestic example of a Royal Purple dyeing[86] is from Masada and is archaeologically dated to the late 1st century BCE layer associated with King Herod I ("the Great"), the Rome-appointed sovereign of Judea from about 40 BCE until his death in 4 BCE (see Figure 13-15). Based on the physical structure of the weave – and the fact that the "Royal Purple" dye was found on it – this textile was probably a fragment from the royal mantle of the king. Further, the chromatographic signature shown indicates that a DBI-rich *H. trunculus* was used for this dyeing. Importantly, this reddish-purple textile was probably the biblical purple *Argaman* dye mentioned above.

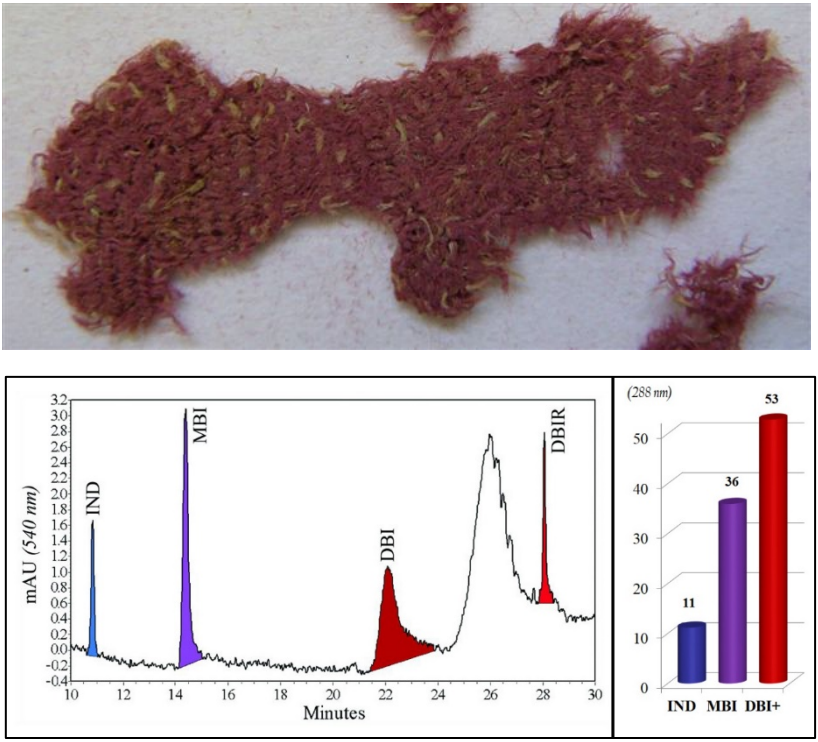

Figure 13-15. *Top:* Royal purple textile found at Masada and associated with King Herod I. *Bottom left:* An HPLC chromatogram (at 540 nm, for visualization purposes only) of a hot DMSO-extraction of the purple yarn. *Bottom right:* Relative integrated peak areas at the standard 288 nm wavelength for quantitative comparisons.

[86] Koren, "Dyeing with Sea Snails," 87-97, 190.

Blue-Purple

An example of an IND-rich dark blue-purple or violet dyeing produced from the other variety of *H. trunculus* sea snails, as mentioned above, was also excavated at Masada and can be seen on the embroidered yarns in Figure 13-16. This is an example of the biblical *Tekhelet*, the most sacred of biblical colors, and usually given somewhat incorrectly in many English translations of the Bible as simply "Blue."

Figure 13-16. Blue-purple (violet) embroidery yarns, dyed in the fleece with IND-rich *Hexaplex trunculus* snails, on an undyed yellowed woolen weave excavated at Masada.

Greenish-Blue "Purple"

The analytical results on an unusual greenish-blue textile (Figure 13-17) found at Wadi Murabba'at, a ravine south of Qumran, were recently published.[87,88] What was surprising was that the bluish yarns were dyed with marine snails. I re-analyzed the greenish-blue yarns via HPLC to obtain the necessary relative integrated peak areas at the standard wavelength of 288 nm, which at this value all the indigoids show strong absorptions. The results of the HPLC analysis show the presence of the three indigoids as depicted in Figure 13-18.

In light of the physical and chemical analyses of the dyed yarns, there are a number of possible causes for the appearance of this greenish-blue coloration. Firstly, the overall greenish nature of the dyed areas, as seen today, can be explained as an unintentional modern "trick on the eyes." Since wool yellows over the archaeological timeframe and if the quantity of the bluish dye is not relatively high, then the physical combination of yellowed fibers together with bluish fibers will visually combine to produce a greenish effect.

Secondly, how was this bluish dye, which has a molluskan basis, produced? The dilemma is further exacerbated because while the *H. trunculus* produces all three indigoids, and even for a type of *H. trunculus* that can produce more IND than DBI, such as in this case, the coloration would be a blue-purple or violet coloration (as shown above in Figure 13-16) but not simply blue alone. There are two possibilities for this molluskan blue-ness. Based on peak area values, which can be used as relative compositional parameters, there is a substantial quantity of IND in the dyeing, even considerably greater than MBI, which is not the typical chromatographic signature of IND-rich *H. trunculus* species. However, since the IND dye produced from a malacological source is molecularly identical to that produced from a plant source, as discussed above, it is therefore impossible to know whether the finding of IND in a molluskan dyeing is only from the marine source alone or also from a plant source. From the malacological components being IND > MBI >> DBI, it is possible that for whatever reason, the dyer may have added a plant-based

[87] Naama Sukenik, David Iluz, Orit Shamir, Alexander Varvak, and Zohar Amar, "Purple-Dyed Textiles From Wadi Murabba'at. Historical, Archaeological and Chemical Aspects," *Archaeological Textiles Review* 55 (2013): 46-54.

[88] Naama Sukenik, Alexander Varvak, Zohar Amar, and David Iluz, "Chemical Analysis of Murex-Dyed Textiles from Wadi Murabba'at, Israel," *Journal of Archaeological Science: Reports* 3 (2015): 565-570.

indigo dyeing to the IND-rich *H. trunculus* dye bath to produce bluer dyeings. Perhaps, originally,

Figure 13-17. Greenish-blue 2,000-year old textile from Wadi Murabba'at dyed with a molluskan source.

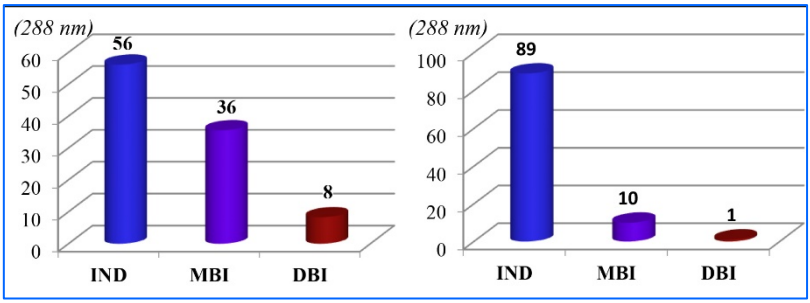

Figure 13-18. Relative integrated peak areas of molluskan components in Wadi Murabba'at textiles. *(left)* the greenish-blue textile of Figure 13-17, above. *(Right)* The red-purple textile of Figure 13-20, below.

the dyed textile was poorly, or insufficiently, dyed to a very light shade and then the dyer desired to produce a bluer dyeing. With all that, the overall appearance of the light-blue dyeing shows that the quantity of the indigo dye in it is relatively small. There are many other cases of archaeological textiles that were dyed with the indigo dye alone that are dark blue in appearance even today.

An alternative possibility for the production of this blue molluskan dyeing is that this was the result of a secondary dyeing from a molluskan dye bath that was already used for a first dyeing. The DBI dye has a stronger affinity to wool fibers than IND. This was observed in the reconstruction of the all-natural processing of molluskan purple that would have been practiced in antiquity.[89] While the first dyeing would have a significant reddish content (even from IND-rich snails, which still have DBI in them), dyeing of a fresh new woolen fleece in the same dye bath results in an overwhelming blue shade of this second fleece as IND was still left in solution. Thus, the Wadi Murabba'at sample could have resulted from the dyer not wanting to waste the dye bath that was already used, and in seeking to exhaust this dye solution, another woolen sample was immersed in this dye bath, which resulted in the light blue nature of this dyeing.

It is important to mention that based on the materials and opaque covered (air-free) clay vats required for this dyeing, more IND could not have been artificially created from the original dyestuff composition.

[89] Zvi C. Koren, "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 (London: Archetype Publications, 2015) 136-149, Color Plates 15.1-15.5.

Mixed Malacological species

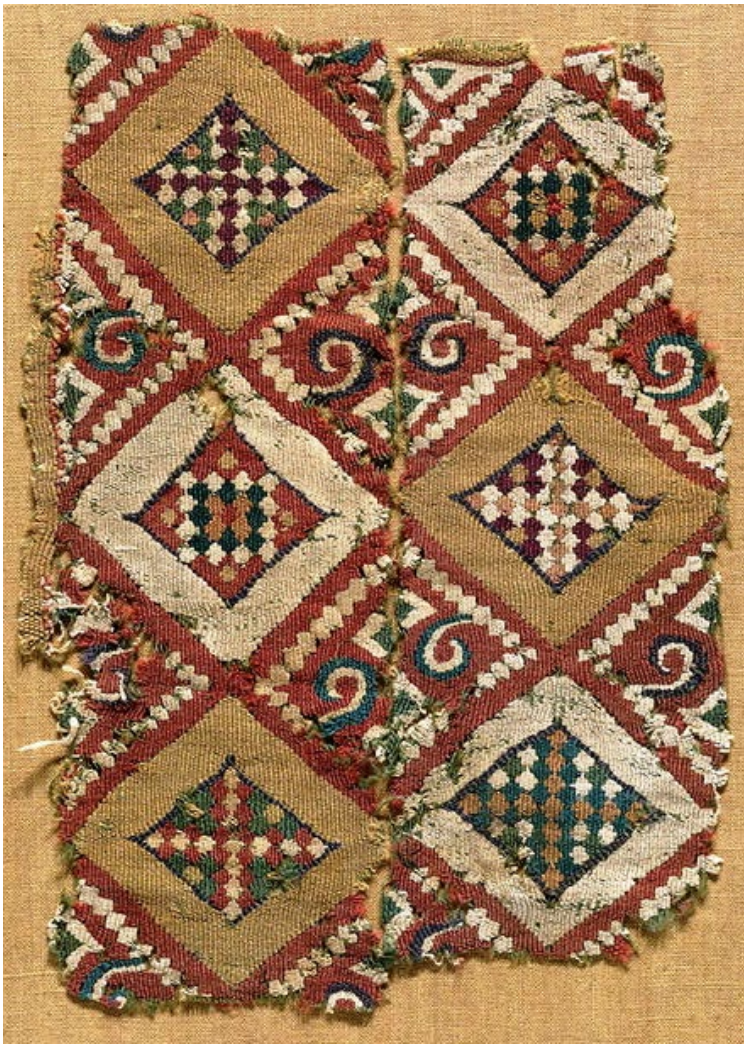

Figure 13-19. Polychrome textile from the Late Roman Period, 5th – 6th centuries CE, with the purple yarns dyed with different molluskan species.

The most direct chromatographic proof of the use of different marine snails for the production of a purple dyeing is from the polychrome textile from the Late Roman Period Egypt (see Figure 13-19).[90] This textile now resides at the Art Gallery HeadquARTers[91] of the Katoen Natie (Flemish for "Cotton Nation") company, in Antwerp, Belgium. In this one textile, various yarns were found to have been dyed with real purple, but they show different shades of purple – from bluer to redder purple. Since all of these dyeings contained a considerable amount of MBI, then they were all dyed with the *H. trunculus* species. The bluer-purple dyeings were produced from the *H. trunculus* species alone. However, the redder-colored purple yarns indicate that another sea snail species – such as, *B. brandaris* and/or *S. haemastoma*, which both produce redder dyeings containing mainly DBI – was added to the *H. trunculus* pigment.

Mixed Malacological-Entomological

At the same Wadi Murabba'at site where the greenish-blue textile (Figure 13-17) was found, another textile dyeing was discovered (see Figure 13-20) with a most unusual combination of dyes.[92] In my HPLC re-analysis of the purple yarns, the malacological nature of this dyeing was confirmed by the detection of the three indigoid dyes, as shown in Figure 13-18 (right) above. The presence of the significant amount of MBI again indicated that the marine provenance was the *H. trunculus* sea snail species. The surprising secondary dyestuff source for this dyeing was the Ararat cochineal (also mentioned above) since carminic acid was also detected.

There are several unusual aspects associated with this dyeing. If just the malacological source were used, then the dyeing would look blue to the naked eye as if it were dyed with a botanical indigo source alone because the indigoidal composition of the dyeing is mostly due to IND, as shown in Figure 13-18 (right). The most probable cause for the nearly 90% peak area of IND in the dyeing is, as discussed above, either much botanical indigo was also used, or this textile was the second – or even third – dyeing from the same dye bath that was previously used for an earlier dyeing, and thus leaving a significant amount of IND still in the dye bath.

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[90] Zvi C. Koren and Chris Verhecken-Lammens, "Microscopic and Chromatographic Analyses of Molluskan Purple Yarns in a Late Roman Period Textile," *e-Preservation Science* 10 (2013): 27-34.

[91] Cleverly spelled as "HeadquARTers" in order to emphasize the art displays at this site.

[92] Sukenik, "Purple-Dyed Textiles," 46-54.

Figure 13-20. The 2,000-year old Wadi Murabba'at textile with a blue malacological base made red with the addition of the Ararat cochineal.

The second unusual aspect is that the dyer, in desiring a red-purple coloration, continued with an additional fauna dyestuff source. Hence, to this blue-colored textile from a marine source, the red-producing Ararat

scale insect was added. The latter is of course the one responsible for the overall reddish nature of the dyeing and not the molluskan source. The discovery of the use of such an insect in the Levant in a 2,000-year old textile pre-dates the find from 7th century CE ‘En Boqeq, discussed above, by many centuries. Since this scale insect is not native to the territory around Ancient Israel, it is fascinating to note that international commerce between these regions existed even two millennia ago.

Conclusions

After 30 years of analyses of ancient dyes and pigments on archaeological textiles and on potshards from dyeing vats from the Ancient Near East, an awe-inspiring picture of the ancient dyer appears as a truly advanced empirical chemist. The exceptional quality of the dyeings – even after millennia have elapsed from the hoary past – is a testament to the dyer’s mastery of complex processes associated with botany, entomology, and malacology. Many of these dyeings appear today not as if they were dyed thousands of years ago, but only “yesterday”. This expertise of the heralded dyer of yore, working with “primitive” tools to produce a cornucopia of colors, is especially evident in the plethora of purple shades produced by the dyer and weaver by using a variety of organic sources from flora and fauna. Regarding this skilled master craftsperson, we can rephrase a divine declaration in Jeremiah and ascribe it to the ancient colorist: “Behold, like material in the hand of the crafter,”[93] the ancient dyer could elevate the foulest molluskan material to create the most majestic purple product; a testimonial to a truly divine “miracle worker”.

Acknowledgments

I would like to express my sincere appreciation for the support provided for this research by the Sidney and Mildred Edelstein Foundation over these many years and allowing me to continue the instrumental research into ancient dyes that was pioneered by Dr. Sidney M. Edelstein in the early 1960s.

[93] Jeremiah 18:6.

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