


Review

A Review on the Archaeological Chemistry of Shellfish Purple

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Abstract: Shellfish purple, also known as Tyrian purple and royal purple, has a long history, which has been revealed and documented in recent years through valid physicochemical studies using sophisticated techniques. The aim of the work was to summarize the conclusions of these studies and to describe the results of two unpublished investigations regarding the (i) identification of shellfish purple in a textile (4th century BCE) from ancient Macedonia and (ii) dramatic effect of the dyeing conditions on the composition of the purple dye. Moreover, a critical discussion is included about the discovery of the shellfish pigment and dye based on the available scientific evidence. Previously published reports describing the identification of the shellfish colorant in objects of the cultural heritage were carefully summarized. Shellfish purple was not used only as colorant, but it served other purposes as emphasized in this review. In particular, examples for the use of shellfish purple in medicine, grave goods and fillers and plasters in walls, were described. Examples of materials and methods that were used in the past to produce “fake” purple, imitating the aesthetic result of the valuable royal marine material were summarized. Finally, the solubility of indigoids was discussed using modern approaches of physical chemistry.

Keywords: purple; shellfish; mollusk; Tyrian purple; indigo; pigment; dye; cultural heritage; HPLC

1. Introduction

Identification of the materials of cultural heritage objects is important to develop and apply effective conservation strategies, which ensure the preservation of the valuable historical and archaeological objects. Conservation and preservation are probably the most important conditions towards a sustainable market for cultural heritage, along with appropriate policies aiming at promoting the human civilization through the multidisciplinary area of archaeometry and other disciplines [1]. Moreover, the characterization and identification of cultural heritage materials leads to useful insights regarding the technological skills of civilizations and reveals economic, social and historic aspects [2]. For these reasons the application of physicochemical methods and instruments to archaeological research has increased substantially over the last half-century and today represents a major methodological subfield within archaeological science [3].

Ever since the beginning of human existence, humans made use of materials to color virtually everything they used or had: Bodies, caves, pottery, sculpture, stone structures, parchment, paper, clothing and other textiles [4]. The important role of color in human civilization becomes dominant for painting art and textiles. The former is essential for human nature, as evidenced for example by the Lauscax cave paintings, dated from about 17,000 BCE and the hundreds of other paleolithic cave paintings e.g., in Altamira, Chauvet and Cáceres. The astonishing findings of abalone shells that were used to hold ochre mixtures 100,000 years ago suggest that pigments were utilised from the very early days [5]. The vital, timeless and universal power of painting and, more general, pictorial art is

evidenced in many different ways. For example, icons have been used for centuries by the Orthodox Church as a window to communicate with the unseen divine reality whereas the Pioneer plaques are pictorial messages for potential extraterrestrial life. Organic materials such as textiles and their colorants (dyes) are sensitive to degradation effects developed through ageing. Consequently, early known-identified use of dyes dates back to at around 6000 years ago [6], which falls short compared to the iron and manganese pigments found in the aforementioned prehistoric caves.

Among the various colorants, which have been used since the prehistoric times, shellfish purple originating from marine mollusks holds a prominent position [7–9]. Shellfish purple (in Greek, *porphyra* = *πορφύρα*) is known also as Tyrian purple, because of the significant deposits of shells found in the area of Tyre and the important role of the purple dye in the Phoenician history. The material is also known as royal purple and imperial purple, as the expensive purple-dyed textiles were status symbols. Shellfish purple is connected with the incredible story of tekhelet, the elusive sky-blue color mentioned throughout the Bible and the clothing of emperors and high priests in civilizations, which had scattered all around the Mediterranean basin.

The goal of this review is to summarize the current state of the art provided by the Natural Sciences for the shellfish purple in archaeology. Examples of historical written sources are briefly presented; biological mollusk sources and the chemical composition of shellfish purple are described. Critical discussions are included associated with the discovery of the shellfish pigment and dye based on the available scientific evidence. Previously published reports describing the identification of shellfish purple in objects of cultural heritage are carefully summarized, revealing the pros and cons of the physicochemical instruments employed for analytical purposes. Emphasis is placed on the results of shellfish purple in the prehistoric Aegean. Two unpublished studies are included (i) describing the identification of shellfish purple in a textile from ancient Macedonia and (ii) demonstrating the dramatic effect of the dyeing conditions on the composition of the purple dye. Shellfish purple was not used only as a paint and dye, but it served other purposes as described in the present review. Materials and methods that were used in the past to produce “fake” purple, imitating the aesthetic result of the valuable imperial marine material are discussed. Finally, the solubility of indigoids is discussed using modern approaches of physical chemistry.

2. Historical Written Sources and Legends for Shellfish Purple

The first inscription referring to the royal color is revealed in Amarna letters, dated to the 14th century BCE, in which blue-purple wool objects are described [10]. Another important written source comes from the Mycenaean Linear B clay tablets of Knossos dated to the 13th century BCE [11]. The masculine (po-pu-re-jo) and the feminine (po-pu-re-ja) adjectives are cited in tablets KN X976 and KN L474, respectively [11]. According to the Acts of the Apostles (Chapter 16), Lydia of Thyatira, who was baptized by St. Paul and is the first documented convert to Christianity in Europe, was in the purple-dye trade. Purple produced from mollusks is mentioned several times in the Bible as well as by Homer, Aristotle, Herodotus, Aeschylus and several others [12]. An impressive written example for the use of purple in Byzantine times is the inscription of the mosaic of the Byzantine Emperor, John II Komnenos (*Ἰωάννης Β' Κομνηνός*) in Hagia Sophia (= Holy Wisdom), which was the cathedral and the spiritual center of the Byzantine empire, as it was the Parthenon for Athens, which was dedicated to the Goddess of Wisdom, Athena. The mosaic in Hagia Sophia is dated to the 12th century CE and the inscription reads: “John faithful in Christ God, emperor of the Romans the Komnenos and king born in the purple”.

The history of shellfish purple is full of legends with the most famous being the one describing the discovery of Murex shellfish by Hercules' hound. The scene is represented in the exergue of coins with the ambrosial rocks [13,14], as well as in paintings, such as the oil on panel artwork by the 17th century Flemish master Peter Paul Rubens [8]. Murex shells have been represented in various objects since antiquity, as shown for instance in the Geek krater and coin of Figure 1 [15,16].



Figure 1. (a) Pottery krater painted with red bands and row of parallel murex shells (13th century BCE). (b) Silver coin with the Head of Demeter (obverse) and barley-ear with murex (reverse; 4th century BCE). Both objects were found in Greece [15,16]. © The Trustees of the British Museum. Shared under a Creative Commons Attribution–NonCommercial–ShareAlike 4.0 International (CC BY–NC–SA 4.0) license.

3. Biological Sources and Chemical Composition

Shellfish purple originates from marine mollusks of the Muricidae family, such as *Hexaplex trunculus* L. (*Murex trunculus*), *Bolinus brandaris* L. (*Murex brandaris*) and *Stramonita haemastoma* (*Thais haemastoma*). These three species live in the Mediterranean basin where the use of the purple pigment/paint in prestigious archaeological findings has been revealed. In the Aegean Sea, *M. trunculus* is the most abundant followed by *M. brandaris* and finally *T. haemastoma* species. However, it should be noted that the mollusk populations have been affected by the recent effects of sea pollution and global warming [17]. Surprisingly, *T. haemastoma* mollusks once described in the taxonomic literature as common in the Levant basin were not found in a recent survey [17]. In the same investigation, a decrease in the population of *M. trunculus* was reported. These observations are schematically presented in Figure 2.

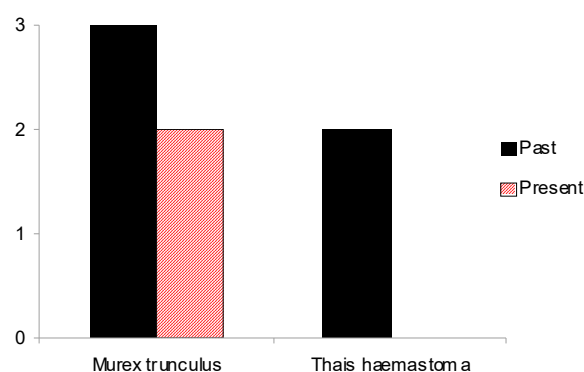


Figure 2. Past and present abundance categories for *Murex trunculus* and *Thais haemastoma* populations in the Levant basin [17]: 0 = not found; 1 = rare; 2 = common; 3 = very common.

Photographs of *M. trunculus* mollusks, which were collected in the Thermaic (Thessaloniki) gulf in the Aegean Sea, are shown in Figure 3a. The coloring compounds do not exist in the living mollusks, but they are produced by precursors that are called chromogens. The latter are present in hypobranchial glands of the mollusks and undergo spontaneous chemical reactions under exposure to light and air thus yielding to the coloring components of shellfish purple [9,18]. For example, the reaction series for the conversion of tyrindoxyl sulfate (precursor) to 6,6'-dibromoindigotin, DBI (coloring compound) is schematically illustrated in Figure 3b [9,18]. The conversion is fast and it takes about 5–10 minutes after exposure to air and sunlight. By analogous reaction series, the other coloring compounds of shellfish

purple are produced: Indigotin (IND), 6-bromoindigotin (MBI), indirubin (INR), 6'-bromoindirubin (6'MBIR) 6-bromoindirubin (6MBIR) and 6,6'-dibromoindirubin (DBIR).

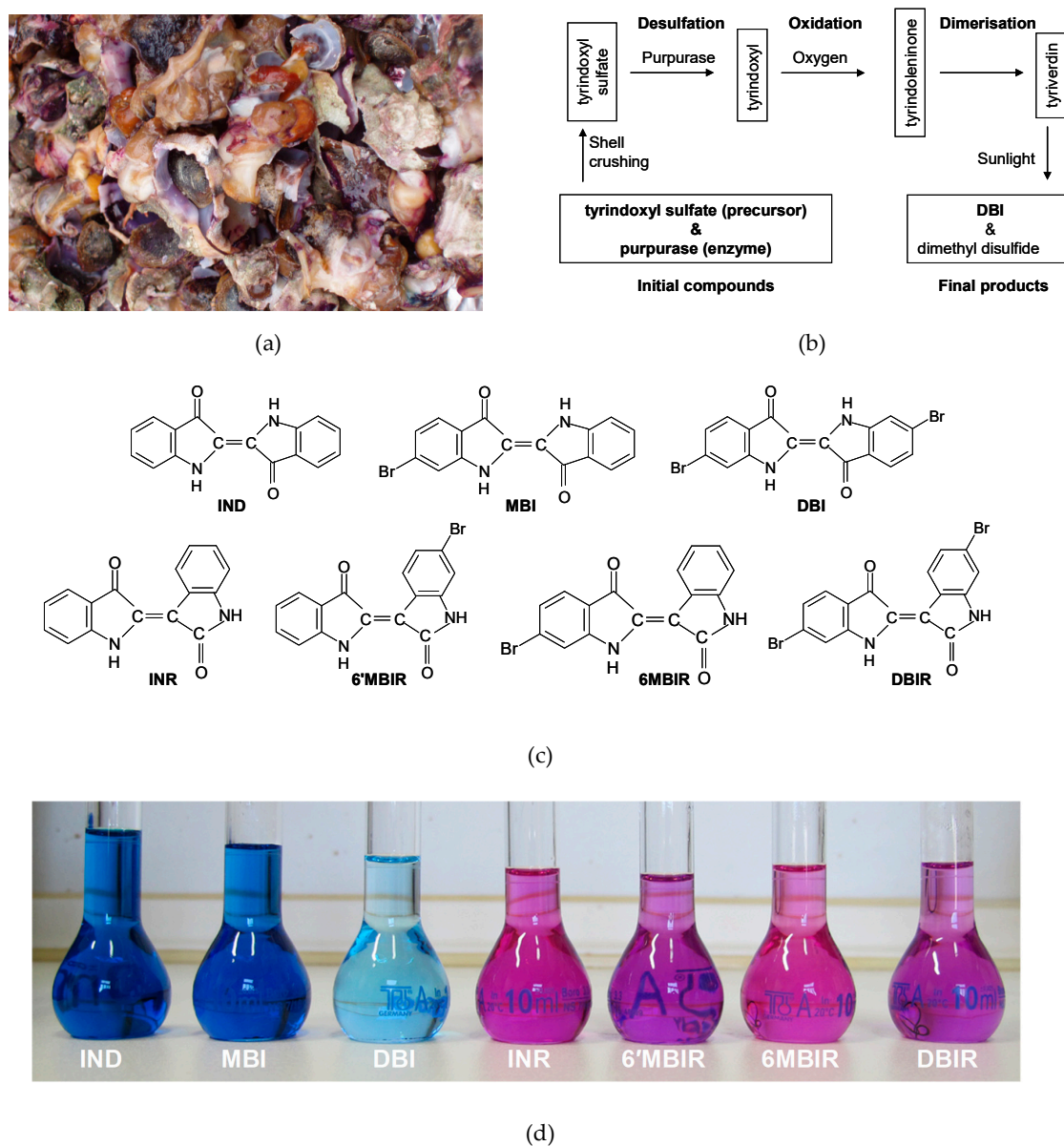


Figure 3. (a) *M. trunculus* mollusks. (b) Conversion of tyrindoxyl sulphate to DBI. (c) Structures of the coloring compounds of shellfish purple: Indigotin (IND), 6-bromoindigotin (MBI), 6,6'-dibromoindigotin (DBI), indirubin (INR), 6'-bromoindirubin (6'MBIR) 6-bromoindirubin (6MBIR) and 6,6'-dibromoindirubin (DBIR). (d) Solutions of the compounds in dimethyl sulfoxide (DMSO), 20 $\mu\text{g mL}^{-1}$.

The compounds of Figure 3c were detected in extracts of *M. trunculus* [19–21] and *M. brandaris* [22]. However, only MBI, DBI and DBIR were detected so far in extracts of *T. haemastoma*. Four more analogues of brominated and unbrominated indirubins, which were detected in *M. trunculus* extracts, were not included in Figure 3c [23]. These isomers have been scarcely reported, as they were found in extremely small amounts [23]. In early reports, DBI was considered to be the marker for the identification of shellfish purple, as this was the first compound isolated from the raw purple pulp [24]. However, none of the brominated molecules of Figure 3c is found in any colorant other than the shellfish purple and therefore any of these molecules can be considered as markers for the presence

of shellfish purple. Moreover, DBI is not necessarily the most abundant component of the purple extract. Chromatographic results have shown that in some *M. trunculus* extracts, MBI is found in larger amounts than DBI [19–21].

Today, the compounds of Figure 3c can be produced in pure forms and in relatively large amounts following synthetic routes [20,25–27]. Photographs of standard solutions of synthesized shellfish components are provided in Figure 3d. Solutions of indigoids (IND, MBI, DBI) are bluish whereas solutions of indirubinoids (INR, 6'MBIR, 6MBIR, DBIR) are reddish. The latter are usually found in shellfish extracts in small amounts. Focusing now on the indigoids it is observed that the DBI solution has a bluish-purple color whereas the MBI and particularly the IND solutions are blue. Consequently, the color of a painted/dyed object can vary, depending on the relative composition of the fixed purple pigment/dye. For example, it was shown that wool dyed with (i) IND is blue, (ii) DBI is purple and (iii) MBI is in between blue-purple [28,29]. Microscopic and chromatographic studies in a 1500-year-old textile dyed with shellfish purple, showed that blue-purple and red-purple fibers were rich in IND and DBI, respectively [30]. In other studies on archaeological textiles, it was suggested that shellfish purple in antiquity was sometimes combined with red anthraquinones, when high proportions of IND were attached on dyed textiles [31–34]. High proportions of IND may have resulted because of the composition of the source mollusk or the dyeing conditions, as both affect the resulting color [28,29]. High proportions of IND may have resulted in purple dyes that looked too blue and therefore mixing with a red colorant was probably necessary to adjust the color and to make it look more purple [31].

4. The Discovery of the Purple Colorant

The origins of the purple dyeing or pigment production industry could have been in the Persian Gulf [9]. P. G. Moatsos wrote in 1932 that probably the Sumerians discovered the use of shellfish purple as a dye for textiles [35]. However, to date, there is no archaeological or scientific evidence to support this hypothesis. The earliest scientific evidence suggesting purple dyeing in the Gulf area goes back to only 3rd–5th century CE [36]. Fragments of pottery vessels used as dyed baths were analyzed revealing the presence of shellfish purple [36].

The first confirmed use of shellfish purple in wall paintings comes from the analyses of samples found in the islands of Santorini and Rhodes in the Aegean Sea [37–43]. The samples are dated to the 18th–17th century BCE. Among the findings in which the presence of shellfish purple was revealed by chemical analysis was a lump of pigment (Santorini). Chromatographic studies showed that the relative chemical composition of the pigment was similar with the compositions of purple paints removed from local wall paintings, proving indisputably the use of the pigment in the local painting art and suggesting pigment production in the Aegean in the Late Bronze Age [42,43]. The pigment was rich in chalk-aragonite and was presumably prepared by immersion of the chalk in the vat serving for the dyeing of textiles [43]. The procedure for the preparation of the pigment purpurissum, documented by Pliny the Elder [44], is reported to occur in the same dye bath, which also served for the dyeing of purple textiles [45]. It has been therefore suggested that the production of organic pigments in ancient times was probably carried out within the existing dyeing workshops using white inorganic substrates, which gave body to the purple pigment [43,45]. This argument is supported by the chemical results reported for samples that were extracted from a painted burial klinai and a textile fragment, both found within the same tomb, in Daskyleion (5th century BCE) [46]. The relative compositions of the shellfish purple pigment and dye used in the two objects were similar according to chromatographic results [46], thus offering support to the scenario that pigment production and dyeing were probably carried out within the same batch reactor-vessel. If this is true, then it serves as indirect evidence for the presence of a shellfish dyeing textile industry in the prehistoric Aegean where the purple pigment production has been confirmed.

The oldest textile fragments dyed with shellfish purple were found in archaeological sites in Syria and particularly in Chagar Bazar (18th–16th century BCE) [47] and in a tomb complex in Tell Mishrife (Qatna), which had remained sealed since the 14th century BCE, at the time of the Hittite conquest

of Syria [48]. The earliest scientific result supporting the development of a shellfish dyeing industry was achieved by analyzing samples of pottery vessels from a Minoan facility (ca. 1800/1700 BCE) in Alatsomouri–Pefka, in the island of Crete in the Aegean Sea [49]. These Cretan findings are earlier than the discovered Phoenician pottery sherds, suggesting that the *Murex* purple of the Minoans became the Tyrian purple of the Phoenicians and later the imperial purple of Byzantium [50]. Consequently, the findings in Chagar Bazar and Alatsomouri–Pefka are the earliest textile fragments and dyeing facilities associated with shellfish purple.

The discussion now focuses on the shell deposits found in the Mediterranean. In the eastern shores of the basin, significant deposits of shells have been discovered in various sites in the Aegean islands, which are dated to the 18th century BCE [51,52]. The earliest archaeological evidence comes from Crete and corresponds to the Old Palace Period and particularly in 19th–18th century BCE [53–55]. There is no evidence suggesting that the famous heaps of mollusk fragments found in Tyre are associated with a dyeing industry, which is dated earlier than the 17th century BCE [56]. Consequently, the available scientific and archaeological evidence suggest that the Minoans in the Aegean and probably the Hurrians in Syria have pioneered the extraction of shellfish purple centuries before the Tyrians.

On the other hand, there is no doubt that the purple dye industry of the Phoenicians became famous and dominated the market from the Homeric times (9th–7th century BCE) onwards [54]. The Phoenicians spread their trade and founded cities, ports and bases up to the Black Sea and across the Mediterranean basin and beyond the Pillars of Hercules. For example, the Phoenicians founded Gadir (Cádiz, Spain) and probably had visited the Canary Islands. In fact, the word “Phoenician” comes from the Greek word “Phoenix” (φοῖνιξ) meaning “red-purple”. Consequently, the Greeks had associated the purple pigment/dye with the Phoenicians. However, based on the available archaeological and scientific data, the shellfish purple industry was developed by the Minoans and probably the Hurrians before the Phoenicians.

Finally, it should be stressed that thousands of *M. trunculus* shells were found in Coppa Nevigata, Italy [56–59]. The accumulations of shells are present in the Early Proto-Apennine layers [58,59]. In particular, the collection of *Murex* began in the 19th–18th century BCE and continued throughout the entire Bronze Age, reaching its highest peak in the 15th and 14th centuries BCE [59]. The large quantity and the condition of the shells in Coppa Nevigata suggest that they were likely to have been used for the extraction of purple [57–59]. This may be the earliest known for the industry of purple, predating that from the Aegean islands [56,58]. It is interesting to note that excavation data indicate the existence of trading activities between Coppa Nevigata and the islands of the Aegean Sea [57].

5. Identification of Shellfish Purple in Archaeological Objects

5.1. Paints, Pigments and Identification Methods

The goal of this section is twofold: (i) To summarize the scientific identifications of shellfish purple pigments applied as paints on wall paintings and some other objects and (ii) to briefly discuss the analytical techniques used for identification purposes. Both, previously reported identifications and analytical techniques are summarized in Table 1 [37–43,46,60–74]. The latter shows that shellfish purple was used in different objects for painting purposes, uninterrupted by all major pre-Roman civilizations of the Aegean, starting with the Minoan period of the Late Bronze Age up to the Hellenistic period. The use of shellfish purple was disrupted abruptly with the conquest of Constantinople by the Ottomans (1453 CE). At that time the capital of the Byzantine Empire was the major processing center of the valuable material. Around the same time in the West, a decree (1464 CE) of Pope Paul II, stipulated the replacement of shellfish purple by kermes to dye ecclesiastical robes. The two events combined, brought the historical use of shellfish purple to an end. According to Table 1, the most recent historical object painted with true purple is a wall painting in France dated to the 12th century CE [74]. It was suggested that probably the purple pigment was transported there from the eastern coast of the Mediterranean Sea during the time of the Crusades [74].

Table 1. Identifications of shellfish purple in pigments/paints corresponding to various historical periods and geographical locations. The techniques used for identification purposes are included.

Date	Provenance	Location	Object/Samples	Technique ¹	Reference
18 th –17 th c. BCE	Minoan	• Akrotiri, Santorini, Greece	Pigment and wall paintings	XRF, HPLC–DAD, LC–APCI–MS, Raman, FTIR	[37–43]
		• Raos, Santorini, Greece	Wall painting	HPLC–DAD, Raman, FTIR	[41,42]
		• Trianda, Rhodes, Greece	Pigment	HPLC–DAD, Raman, FTIR	[41,42]
13 th c. BCE	Mycenaean	Nestor Palace, Peloponnese, Greece	Wall paintings	XRF, XRF–imaging	[60]
6 th –2 nd c. BCE	Archaic–Hellenistic	Cave of Koroneia, Greece	Painted astragalos	SEM–EDX	[61]
5 th BCE	Persian	• Daskyleion, Turkey	Painted klinai	FTIR, FTIR–imaging, SEM–EDX, HPLC–DAD	[46]
486/485 BCE		• Bible Lands Museum, Israel	Painted jar	HPLC–DAD	[62]
4 th c. BCE	Classical	• J. Paul Getty Museum, USA	Greek marble vessel	XRF	[63]
336 BCE		• Tomb of Philip II, Vergina, Macedonia, Greece	Mask (?)	FTIR	[64]
4 th c. –3 rd c. BCE	Daunian	Sansone Collection, Italy	Ceramics (vases, kraters)	IR, MCT	[65]
4 th –2 nd c. BCE	Hellenistic	• Macedonian Tomb III at Agios Athanasios, Greece	Wall painting	XRF, HPLC–DAD	[66–68]
		• Macedonian Tomb of the Palmettes, Greece	Wall painting	HPLC–DAD	[67–69]
		• Crete, Greece	Figurines	FTIR, XRF	[70]
		• Macedonian Tomb of Philosophers, Pella, Greece	Wall painting	SEM–EDX	[71]
		• Arch. Museum of Delos, Greece	Pigment	XRF	[72]
2 nd half of the 4 th c. BCE	Etruscan	Sarcophagus of the Amazons, Arch. Museum of Florence, Italy	Sarcophagus (from Tarquinia)	n.a.	[68]
1 st CE	Roman	Pompeii, Italy	Pigment	DE–MS	[69,73]
12 th c. CE	French	Church of Sainte Madeleine, France	Wall painting	HPLC–DAD, LC–APPI–MS	[74]

¹ DE–MS: direct exposure–mass spectrometry; FTIR: Fourier transform infrared spectroscopy; HPLC–DAD: high performance liquid chromatography–diode array detector; IR: infrared spectroscopy; LC–APCI–MS: liquid chromatography with atmospheric pressure chemical ionization–mass spectrometry; LC–APPI–MS: liquid chromatography with atmospheric pressure photoionization–mass spectrometry; MCT: Microchemical testing; Raman: Raman spectroscopy; SEM–EDX: scanning electron microscopy (SEM) coupled to energy dispersive x-ray (EDX) spectroscopy; XRF: X–ray fluorescence; n.a.: not available.

As described in Table 1 a large variety of techniques were used to identify paints and pigments of shellfish purple. The presence of bromine (Br) in the composition of the purple material (Figure 3c) offers the option to apply elemental analysis techniques, such as X-ray fluorescence (XRF) and scanning electron microscopy (SEM) coupled to energy dispersive x-ray (EDX) spectroscopy (SEM–EDX). The results should be carefully interpreted considering that lichens can contain significant amounts of Br. An example of a SEM–EDX study is provided in Figure 4, which shows the results for a purple painted sample extracted from a burial klinai [46]. The detection of Br is indicative for the use of true purple. Furthermore, the presence of an aluminosilicate compound and gypsum is supported by the results of Figure 4, as Al, Si, Ca and S are included in the detected elements of the EDX spectrum. FTIR measurements confirmed the presence of shellfish purple, kaolinite and gypsum in the archaeological sample [46]. Interestingly, the use of kaolinite in painting techniques of shellfish purple were previously reported in the analyses of the Darius I stone painted jar [62] and the pigment powder of Pompeii [73]. According to Table 1, vibrational spectroscopy, and particularly FTIR and Raman spectroscopy, is another set of techniques which was effective to identify purple pigments and paints in objects of the cultural heritage.

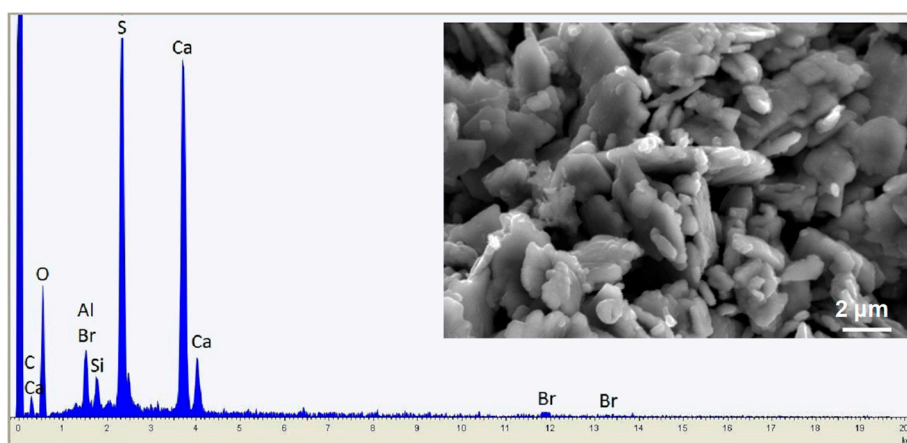


Figure 4. SEM–EDX analysis of a purple painted sample, which was extracted from a burial klinai, in Daskyleion, Turkey. Reprinted with permission from reference number [46].

High performance liquid chromatography–diode array detector (HPLC–DAD) is the most efficient among the techniques listed in Table 1 for the analysis of shellfish purple, as it provides: (i) Detection and identification of all seven components within a single measurement–chromatogram, (ii) semi-quantitative results relative to the composition of the detected purple pigment and (iii) complete quantitative results. Examples for these valuable sets of HPLC results are provided next.

The chromatogram for a purple pigment that was found in the Akrotiri settlement is shown in Figure 5. The sample was included in a previous study and labeled Ak3 [42]. The chromatogram is presented herein for the first time. INR was not detected in the sample extract. The other six components of shellfish purple are identified by HPLC, which therefore provides very rich results in terms of detected compounds.

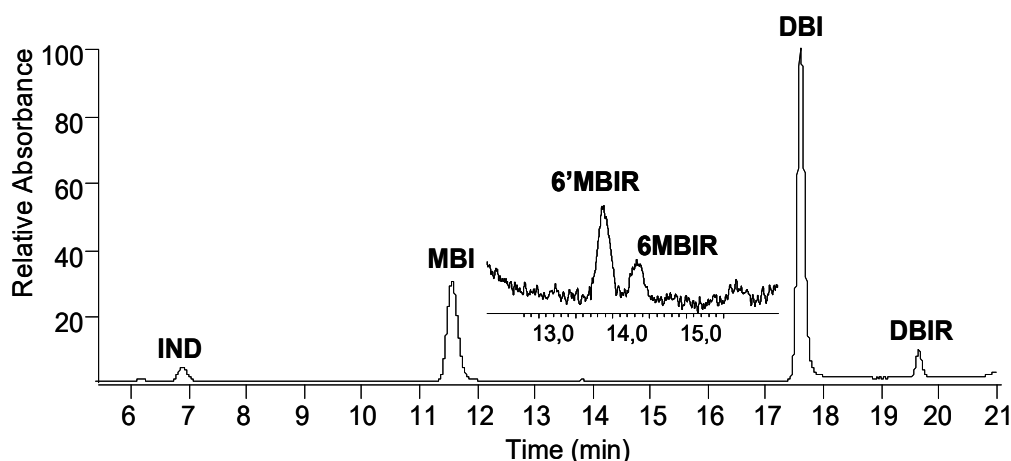


Figure 5. Chromatogram of a purple pigment from Akrotiri at 288 nm (Ak3 in [42]).

The HPLC peak areas (semi-quantitative results) are extremely useful to compare shellfish purple pigments from different samples. HPLC peak areas of purple components were reported in the literature for the samples of Minoan [42] and Persian origin [46,62] of Table 1 and these are summarized in Figure 6. In particular, relative integrated HPLC peak areas measured at 288 nm and normalized to the highest value (taken as 100%) are shown in Figure 6 for seven archaeological samples: Ak1 (pigment), Ak2 (wall painting), Ak3 (pigment) come from Akrotiri–Santorini, Ra (wall painting) from Raos–Santorini and Tri (pigment) from Trianda–Rhodes [42]. Samples Dar and Dask were extracted from the Darius I jar [62] and the burial klinai in Daskyleion [46], respectively. The HPLC peak areas for INR, 6'MBIR and 6MBIR were extremely small and therefore the sums of these areas are included in each sample column of the graphs of Figure 6.

The results of Figure 6a show that DBI is the dominant compound in the chromatograms of the five Minoan (Ak1, Ak2, Ak3, Tri and Ra) samples. The HPLC graphs gave moderate areas for MBI and small areas for IND and DBIR. The sum, INR + 6'MBIR + 6MBIR, is negligible or even zero (Ak2 and Ra) as revealed in Figure 6b. A similar HPLC profile was collected for the Dar sample [62], which, as shown in Figure 6, does not have any major difference compared to the Minoan samples. Trade routes between the southern Aegean islands, such as Santorini and Rhodes, and the Phoenician coast were developed since the prehistoric times and this may be depicted in the similar results of the Dar and the Minoan samples. However, the Dask sample is different: The HPLC peak area of DBI is small whereas the areas of IND, MBI, DBIR and the sum of INR + 6'MBIR + 6MBIR are large compared to the Minoan and the Dar samples. Consequently, a different processing method and/or molluscan sources should have been developed/used in Daskyleion, which is located close to the Marmara Sea, in the mainland of Turkey.

The relative peak areas reported in Figure 6 are not actual mass compositions of the samples. As mentioned previously, HPLC can provide complete quantitative results provided, however, that a HPLC calibration method is developed. The coloring components of interest should be available in pure form to be used as standards for quantitation purposes. A calibration procedure for shellfish purple pigment was previously developed and showed that the relative percentage of IND reported commonly using the HPLC peak areas at 288 nm (e.g., Figure 6) is in fact an overestimation of the actual mass content of IND [75]. On the other hand, the corresponding relative percentage of DBI, which is calculated using the HPLC peak areas at 288 nm, is an underestimation of the actual mass content of DBI in the shellfish pigment [75]. Moreover, the calibration process showed that low limits-of-detection (LODs) can be achieved with HPLC for the seven components of shellfish purple, ranging within 0.02 to 0.05 $\mu\text{g mL}^{-1}$ [75].

Finally, as described in Table 1, other methods employed to analyze and identify shellfish purple pigments/paints in objects of the cultural heritage are mass spectrometry (LC–MS, direct exposure–mass

spectrometry—DE-MS) as well as imaging techniques including FTIR and XRF imaging. The latter are useful to reveal the distribution of shellfish purple on a painted surface, which, in turn, is sometimes useful to understand the applied painting technique.

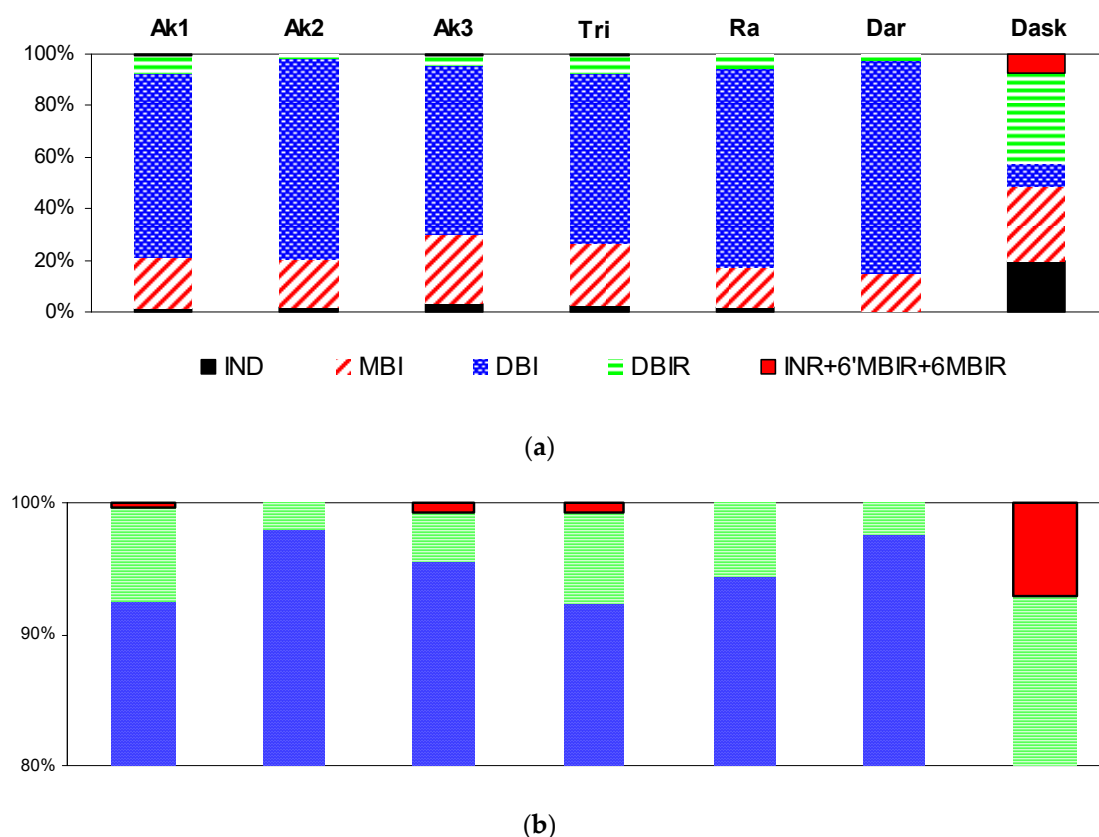


Figure 6. (a) Relative integrated HPLC peak areas measured at 288 nm and normalized to the highest value (taken as 100%) are shown for seven archaeological samples. The 18th–17th century BCE samples come from the Minoan sites in Akrotiri–Santorini (Ak1, Ak2, Ak3), Raos–Santorini (Ra) and Trianda–Rhodes (Tri) [42]. Samples Dar and Dask were extracted from the Darius I painted jar [62] and the burial klinai in Daskyleion [46], respectively, both dated to the 5th century BCE. The sums of the HPLC peak areas of INR, 6'MBIR and 6MBIR are included in the graph. (b) The upper (80%–100%) part of the (a) graph is enlarged.

5.2. Textiles

As mentioned previously, the earliest direct scientific evidence of the shellfish dyeing industry were reported for textile fragments unearthed in Chagar Bazar (18th–16th century BCE) [47] and Tell Mishrife [48] and pottery vessels from Crete (ca. 1800/1700 BCE) [49]. The most recent historical textile dyed with shellfish purple is a Byzantine epitaphios, which is dated to the 14th century CE [42] i.e., roughly about the time of the fall of Constantinople.

Shellfish purple has been identified in several textiles and objects related to the textile industry of antiquity e.g., post sherds [7,30–34,36,42,46–49,58,76–104]. As summarized in Table 2, it has been scientifically proved that the valuable dye was used by the Minoans, Hurrians, Phoenicians, Persians, Greeks (in various periods), Etruscans, Jews, Romans, Sarmatians, Copts-Egyptians, Arabs (pre-Islamic period) and Byzantines. These results show that the shellfish purple dye has a long established history of use that spans roughly 3.5 millennia, as it was used uninterrupted from the prehistoric up to the Byzantines times.

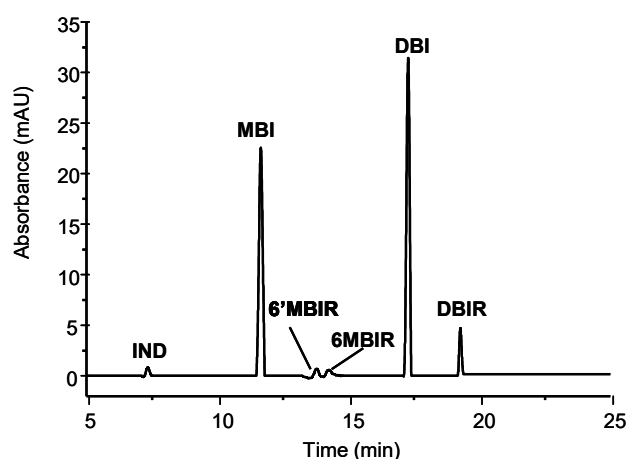
Table 2. Identifications of shellfish purple in textiles corresponding to various historical periods.

Provenance	Reference
Minoan (Crete)	[49]
Hurrian (Chagar Bazar, Qatna)	[47,48]
Phoenician	[76–81]
Phoenician–Punic	[82]
Submycenaean/Protogeometric (Greek)	[83]
Orientalising/early Archaic (Etruscan)	[84]
Archaic (Greek)	[85]
Persian	[46]
Classical (Greek)	[7,86–88]
Hellenistic (Greek & Etruscan)	[58,89–91]
Jewish	[92]
Roman	[31–33,93–96]
Sarmatian	[97,98]
Coptic–Egyptian	[34,97,99–104]
Arab (pre–Islamic period)	[36]
Byzantine	[7,30,42]

Case Study: Identification of Shellfish Purple in a Hellenistic Textile

In 1987 an excavation was carried out in a burial mound in the area of Lakkoma (Macedonia, Greece), which revealed a large cist tomb dating in the last quarter of the 4th c. BCE (Hellenistic period) [89]. Lakkoma is located around 60 km east of Aigai (Vergina), where the Royal Tomb of Philip II, the father of Alexander the Great, was found. The aforementioned dating of the burial is supported by a golden quarter stater of Philip II [89]. Textile purple residues and other organic materials were found within the tomb and investigated in the past using microscopic techniques [89].

A small piece of the textile residues was treated with hot dimethyl sulfoxide (DMSO) to extract the purple dye, which was analyzed using an established HPLC–DAD method [42,75]. This is the first reported HPLC analysis of a purple textile found in the mainland of Macedonia. The chromatogram is presented in Figure 7. The HPLC peaks corresponding to MBI, DBI and DBIR are dominant in the graph. IND, 6'MBIR and 6MBIR correspond to very small peaks, whereas INR was not detected.

**Figure 7.** Chromatogram of a purple textile sample from the Lakkoma tomb at 288 nm.

It is interesting to note that the HPLC profile in Figure 7 is not very different from that of Figure 5, which is representative of the Minoan purple paints and pigments. Consequently, based on the results of the present study it is reported that no major difference is observed in the chemical compositions of the shellfish purple materials used by the Minoans (Figure 5) and the Macedonians (Figure 7).

Apparently this is not a general conclusion; it is an observation based on the chemical results of the tested samples.

5.3. Manuscripts

The scientific investigation of historical manuscripts is a challenging task. While samples can be removed from large-scale objects with relatively little impact on the integrity of the object, the removal of even tiny samples from manuscripts is practically prohibited. Consequently, the study of historical manuscripts is limited to non-sampling techniques, such as, for instance, XRF [105–108], fiber optics UV-Vis diffuse reflectance spectrophotometry with optical fibres (FORS) [106,108] and Raman spectroscopy [108,109]. Recent advances in the development of non-sampling methods to identify shellfish purple offer new perspectives for the investigation of historical manuscripts, artworks and other objects of the cultural heritage [110,111]. In any case, the limitation to use only non-sampling techniques increases the degree of difficulty in studying manuscripts.

The results reported in the literature do not suggest a widespread use of shellfish purple in historical manuscripts. In particular, the use of shellfish purple has been suggested in very few objects such as, for instance, in a Byzantine (6th century CE) [105], Italian (6th century CE) [106] and Anglo-Saxon (8th century CE) [107] manuscript. The use of shellfish purple was suggested according to XRF results, which revealed the presence of Br [105–107]. FORS results, however, did not confirm the presence of shellfish purple. Analyses yield the information that the chromatic features of manuscripts are dominated by the presence of inorganic and organic colorants other than shellfish purple [105–112].

5.4. Other Uses of Shellfish Purple

In a recently published report, shellfish purple was identified by XRF and HPLC in a mass of clay material, which was stored within a compartment of a small case [113]. The lidded box was found in the grave B of Derveni (Macedonia, Greece) dated to the 4th century BCE, together with other goods, including the famous Derveni krater and a gold coin of Philip II. Based on the current archaeological data, related with other metal cases that have been unearthed in Macedonian burials, it is estimated that the content of the Derveni metal case was probably used for medical purposes [113]. If true, then this is the first scientific evidence about the medical use of shellfish purple in antiquity. It is noteworthy, that recent studies revealed that mollusks from the family Muricidae produce biological active compounds with anti-inflammatory, anti-cancer, muscle-relaxing and pain relieving properties as well as steroidogenic activity [114,115]. Some of these properties are found in the Murex extracts and have been known since antiquity [116].

The finding in Derveni is not the only one revealing the use of shellfish purple as grave good. Shellfish purple was identified by DE-MS, Raman spectroscopy and HPLC in residues collected from a Gallo-Roman burial (Naintré, France) dated to the 3rd century CE [117]. Purple was widely spread after the deposition of the body for burial, suggesting that the valuable purple grave good was part of the funeral practice [117].

Murex snails and shells have been probably used in jewels, tools and foods [118], as well as in fillers and plasters as discussed next. It was previously described that the chalk base of the Akrotiri–Santorini pigment was rich in aragonite, indicating that this was probably obtained from crushed Murex shells [43]. Shell fragments of mollusks are sometimes visible in plaster surfaces, dated from the Middle Bronze Age onwards [118,119]. Murex shells in the perimeter of the 5th century BCE wall of Hermione, Greece are shown in the photograph of Figure 8. Moreover, results provided from experimental archaeology demonstrated that Murex shells can be used as a raw material for lime making, but that this is not necessarily visible in its end product if done thoroughly and properly [118]. Consequently, the use of Murex shells in the lime plaster production process can be older than the reported visible archaeological evidence. Murex species might have been used to add color in plaster, as suggested by XRD analysis in painted plaster samples from Gla, Greece [120]. XRD lead to the

identification of aragonite in the investigated plaster samples, but the presence of Murex was not confirmed by SEM–EDX [120] or Raman [121] results.



Figure 8. Murex shells used as binder in the wall of Hermione, next to the Bisti area where the famous local dyeing workshops were located (photograph by V. Gatsos).

6. Purple but not True Purple

Shellfish purple was held in high esteem, as it is hard to be produced in large amounts from the molluskan raw source. In his pioneering work, Friedländer collected 12,000 *M. brandaris* extracting only 1.4 g of dry pigment [24]. It is estimated that 10,000 *M. trunculus* mollusks are needed to dye a kilogram and a half of wool [122]. Consequently, shellfish purple had always been an expensive material, which was sparingly used. Alternative procedures to mimic true purple had been developed and therefore “not all purples were equal, and not all purple was purple” [123].

For example, mixtures of Egyptian blue with red pigments were used in painting plasters to achieve a purple hue [124]. For the same reason, blue pigments and paints of Lapis lazuli [125] and indigo/woad [121] had been used in painting backgrounds since the Mycenaean period. Egyptian blue mixed physically with a red lake, which however is unidentifiable, was revealed in wall paintings fragments in Egypt [63]. Mixture of Egyptian blue and a red-pink lake was also found in 3rd century BCE oinochoe (British Museum) [45]. According to HPLC results, the lake was derived from purpurin-rich madder, cochineal (*Porphyrophora* spp.) and, unexpectedly, lac (*Kerria Lacca* Kerr) [45]. Mixtures of purpurin-rich madder and Armenian cochineal *Porphyrophora hamelii* Brandt were found in funeral figurines dated to 3rd–2nd century BCE [126,127].

A common practice for the Egyptian dyers was to mix madder and indigo/woad [8,34,93] achieving a remarkable purple hue. The purple mixture was sometimes enriched with a coccid dye, such as, kermes [128]. An analogous practice was revealed in Roman-Egyptian mummy portraits (2nd century CE) in which mixtures of madder lakes and indigo were identified and were probably applied as cheaper substitutes for shellfish purple [129]. Kermes in mixture with indigo/woad—but not madder—was identified in purple parts of a textile from the Topkapi Palace [130].

Folium and particularly orchil were widely used as alternatives to shellfish purple in the coloring of parchments in which the use of true purple was extremely rare [112,131,132], as discussed previously. Orchella weeds, when properly processed, provide a bright purple, which has been often detected in illuminated manuscripts [108,133].

7. Dyeing with Shellfish Purple: From Purple to Blue

Dyeing with shellfish is complicated. The colored water-insoluble extract must be chemically reduced in the dye vat to give the water-soluble and colorless leuco-forms of the compounds of Figure 3c. Reduction is induced by bacteria according to the mechanism that was elucidated for the reduction of woad [134]. The dyeing process can have an enormous effect on the composition and therefore the color of the attached dye considering that several parameters have to be adjusted in the vat (treatment time, temperature, pH, etc.). Moreover, sunlight can induce debromination of the leuco forms, which, moreover, do not have the same affinity for textile fibers [29].

The dramatic effect of the dyeing conditions on the composition of the attached dye is demonstrated in the following experiment. *M. trunculus* mollusks were collected by V. Gatsos from the sea of Hermione, Greece. The city of Hermione was famous for the fine dyeing with shellfish purple, an industry that had been flourished for more than 1000 years, from 6th century BCE to 6th century CE [12]. It was the Hermione purple that caused the admiration of Alexander the Great when he took Susa in 331 BCE and found purple garments in the palace of Darius III [7,12]. Wool and cotton were dyed by V. Gatsos following two recipes. Large mollusks (*M. trunculus*) were collected at a depth of 2–3 m, from the sea, just next to the ancient wall of Hermione.

Recipe I: The shells were crushed using a stainless steel tod at the third helix where the gland of the mollusk could be easily reached. The glands were quickly removed to preserve the secretions and placed in a flask containing 30 ml of water and 2 g of common salt. The flask was left open and was rigorously agitated 3–4 times per day for 15 days. After this process the pulp became purple. For the dyeing process, the purple pulp was transferred to a glass container. Ten (10) g of honey and 3 g of salt were added. The container was airtight sealed, agitated and remained into a water bath which was heated at 45 °C for two days. Then a 1 cm × 3 cm piece of fabric (wool or cotton) was immersed into the mixture and additional amounts of honey (2 g) and salt (1 g) were added. The container was airtight sealed, agitated and remained into a water bath which was heated at 45 °C for one day. The fabric was removed and washed with warm water (70 °C) and soap solution.

Recipe II: The shells were crushed and the glands were placed in a flask containing 80 mL of water and huge amount (20 g) of common salt. The flask was left in the sunlight for five days. Then, the dyeing procedure described in recipe I was followed.

Consequently, in recipe II, extreme conditions related to the quantity of salt and the duration of sunlight exposure were selected. The possible role of salt in the dyeing process is critically discussed in detail by C. Cooksey [18]. The four samples, two wools and two cottons, dyed with the two recipes, were analyzed using HPLC. A DMSO bath at 80 °C was used to extract the purple dyes [42]. The % relative integrated HPLC peak areas were measured and the results are provided in Table 3. The two recipes gave totally different results, as a dominant debromination process was developed in recipe II, resulting in reduced amounts of brominated indigoids (MBI and DBI) attached to the fibers. IND is clearly the major coloring compound in the samples, which were prepared using recipe II. On the contrary, large amounts of MBI were attached to fibers dyed with recipe I. The difference of the two recipes in the dyeing results was visible by naked eye, as samples prepared using recipe I were purple whereas samples that were dyed using recipe II were blue.

Table 3. Relative (%) integrated HPLC peak areas measured at 288 nm for wool and silk, which were dyed with two recipes, as described in the text.

Compound.	Recipe I		Recipe II	
	Wool	Cotton	Wool	Cotton
IND	11.9	8.5	70.3	94.4
MBI	56.5	44.7	16.0	3.3
DBI	29.1	4.5	8.8	1.7
INR	–	–	–	–
6'MBIR	0.2	0.2	–	–
6MBIR	0.2	0.1	1.2	–
DBIR	2.0	1.9	3.7	0.6

8. Solubility Issues

Solubility data is available in the open literature for indigo, which contains indigotin and indirubin but not their brominated derivatives. Table 4 shows the solubility of indigo in ten solvents [135]. The results of Table 4 were calculated using the COSMO–RS (conductor-like screening model for real solvents), which is a quantum-mechanical approach [135]. The best solvent found is sulfuric acid, in which COSMO–RS predicts complete miscibility with indigo. On the other hand, water practically does not dissolve indigo.

Table 4. Results of the conductor-like screening model for real solvents (COSMO–RS) solubility screening for indigo. The results were adapted from elsewhere [135].

Recipe I		Recipe II	
Sulfuric acid	100.0000	Pyrrole	4.1934
Dimethyl sulfoxide	11.9093	Chloroform	1.6337
Phenol	10.4013	Diethylether	1.4813
Propanone	6.5225	Ethanol	0.4694
Pyridine	4.3329	Water	0.0001

Efficient extraction of dyes from fiber samples is important for successful HPLC analysis of textiles of the cultural heritage. Among the solvents included in Table 4, DMSO [42,62] and pyridine [42,97] were suggested for the extraction of shellfish purple from archaeological samples. Moreover, N,N-dimethylformamide (DMF), which is not included in Table 4, was also used for the extraction of the purple material [42,78]. DMSO and DMF have similar solubility properties considering that they have comparable Hansen solubility parameters [136]. The latter are summarized in Table 5 for the three aforementioned solvents.

Table 5. Hansen solubility parameters: δ_d , δ_p and δ_{hb} are the dispersion, polar and hydrogen bonding parameters, respectively [136].

Solvent	δ_d	δ_p	δ_{hb}
Dimethylsulfoxide	18.4	16.4	10.2
N,N-dimethylformamide	17.4	13.7	11.3
Pyridine	19.0	8.8	5.9

The efficiencies of DMSO, DMF and pyridine to solubilize shellfish purple were compared using HPLC [42]. The experimental results showed that DMSO and pyridine result in very good and poor yields, respectively [42], which is in agreement with the prediction for indigo provided by the COSMO–RS (Table 4). Moreover, the experimental study showed that DMSO and DMF have comparable efficacy in solubilizing shellfish purple [42], which is in agreement with the similar Hansen solubility parameters of these two solvents (Table 5).

9. Conclusions

The conclusions of the review are summarized as follows:

- From the Minoan period to the cease of the Byzantine empire with the conquest of Constantinople by the Ottomans, shellfish purple had a significant role in painting art and textile industry, as suggested by chemical analyses (Tables 1 and 2; Figures 4–7) and depicted in various objects of cultural heritage (Figure 1).
- Not all purples were true purple, as procedures to mimic the purple hue had been developed by mixing blue and red pigments, lakes or dyes. Imitation of true purple was a common practice in purple manuscripts, as physicochemical analyses do not suggest a widespread use of the shellfish material on codices and manuscripts.
- Other past uses of shellfish purple in medicine, grave goods and wall construction (Figure 8) are supported by the literature.
- Dyeing conditions, such as sunlight and salt concentration, can have a dramatic effect on the composition of the purple dye and can therefore affect the color of the dyed textile, which can range from blue to purple (Figure 3; Table 3).
- The first HPLC analysis of a purple textile dated in the Hellenistic period was reported, herein. The textile fragment was found in the Macedonian tomb of Lakkoma (Northern Greece). The chromatogram was dominated by the peaks, which corresponded to 6-bromoindigotin, 6,6'-dibromoindigotin and 6,6'-dibromoindirubin (Figure 7).
- Dimethylsulfoxide and dimethylformamide are good solvents for indigoids dyes as suggested by experimental studies and theoretical predictions based on statistical mechanics (Tables 4 and 5).
- Marine species, including the mollusks of the Muricidae family are threatened by sea pollution and global warming (Figure 2). Action is needed to protect the shellfish, which for so many centuries have offered so much to us.

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