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Abstract

Red-purple and blue-purple woolen yarns excised from a 1,500-year old Late Roman Period textile were analyzed by an integrated physical and chemical approach. Microscopic examinations showed that the red-purple yarn consisted of homogeneously dyed fibers, whereas the blue-purple yarn contained different red-purple, blue-purple, and undyed fibers. Thus, the spinner of these purple yarns used a total of four differently colored woolen fleeces, one for the red-purple yarn and three different ones for the blue-purple yarn. The malacological provenance of the purple dyeings was established via HPLC dye analyses, which showed the substantial presence of MBI in all these samples. Hence, the Hexaplex trunculus mollusk was the primary snail used for all these dyeings. The other dyes detected in all the purple fibers were IND, DBI, and DBIR. Quantitative analyses indicated that a DBI-rich trunculus was used for the red-purple yarn, with probably a minor addition of another redder-producing Muricidae mollusk. The dissected blue-purple yarn contained blue-purple fibers dyed with IND-rich trunculus snails, and red-purple fibers dyed with DBI-rich trunculus mollusks. This study is the first publication whereby a discrete polychromic yarn has been dissected into single fibers with each distinct color set individually chromatographed to produce a multicomponent dye analysis.

1 Introduction

The popular fascination with ancient purple dyeings produced from certain mulluskgs has seen a surge of interest particularly in the last two decades. This allure results from the considerable advances that chemical analyses have made in identifying a few rare cases where real purple has been found in colorful textiles. It is well known that these red-purple and blue-purple textiles were the privilege of kings, emperors, caesars, as well as military generals and high priests. The scientific art of dyeing textiles with the purple pigment produced from certain Muricidae mollusks originated about four millennia ago in the Mediterranean basin, probably first in the Aegean and then later further developed and exported by the Levantine Phoenicians. The name of their major city of Tyre, combined with their famous merchandise, produced the expression “Tyrian Purple”, which refers to the red-purple woolen textiles dyed with this sea snail pigment. These dyeings have also been referred to as Royal Purple and Imperial Purple. In the Mediterranean basin, the three most popular snails for producing purple pigments were Hexaplex trunculus (also known as Murex trunculus), Bolinus brandaris, and Stramonita haemastoma.

The chemistry of this purple pigment has been reviewed1 and analytical methods have been developed for multi-component identifications of Muricidae pigments via chromatography and spectrometry.2-12 Recent advances in the study of the molluskan dye have been published.13 The malacological pigments consist of about 10 brominated and un-brominated colorants, which can include isatinoids, indigoids, and indirubinoids, and the molecular structures and UV/Visible spectra of these dyes are widely available in the literature.10,12 However, archaeological samples have shown that
the three indigoids are generally the dominant dyes. These are 6,6’-dibromoindigo (DBI), which produces red-purple colors on woolen textiles, the violet dye 6-bromoindigo (also known as “monobromoindigo”, MBI), and the blue indigo (IND) colorant. Often, the fourth dye also found is the reddish isomer of DBI, 6,6’-dibromoindirubin (DBIR).

Archaeological textiles dyed with a molluskan purple pigment have been reported in the literature. Examples include a 3rd - 5th century AD purple-dyed Coptic textile,14,15 2000-year old Roman Period purple-dyed textiles,16-21 a 4th century BC Pazyryk textile from the Siberian desert,22,23 and a 2nd millennium BC textile from the royal palace of ancient Qatna.24

Purple-dyed textiles have special historical significance and meticulous analyses are warranted for such important cultural heritage objects. This paper reports on an integrated micro-physical (microscopic) and micro-chemical (chromatographic) approach for the study of purple dyeings. The methodology is applied to a highly decorated and multicolored textile (inventory number KTN 1475) in the Katoen Natie Collection in Antwerp, Belgium. This combined methodology would assist in determining the malacological provenance of these dyes.

2 The Ancient Textile, KTN 1475

2.1 The Physical State

The textile from which the purple wool yarns were excised for this study was previously briefly described25,26 and is shown in Figure 1. It arrived in the Katoen Natie collection from an antiques dealer in 2005. The provenance is unknown but it can be assumed that the textile originated in Egypt as the weave technique of the piece is typical Egyptian, all S-spun threads, the traditional spin direction in ancient Egypt. Radiocarbon tests performed at the Royal Institute for Cultural Heritage (KIK/IRPA, Brussels) yielded the following dates:27

68.2% probability: 430 – 540 AD
95.4% probability: 420 – 550 AD

Thus, this 5th – 6th century AD textile can be considered to be from the Late Roman Period.

Textile KTN 1475 consists of two fragments woven in tapestry technique that were sewn together in recent times (sewing thread: green wool Z2S), but the attachment is not the original composition. Each part has a dimension of 6.5 cm in width and 19 or 19.5 cm in length. These fragments seem to be part of a larger fabric because in one fragment a narrow border of 6 warp threads in plain yellow color is connected during weaving at one side by dovetailing, and the other fragment has a similar band, with remains of a narrow plain yellow border, but now in weft direction with 4 red and 8 golden yellow picks. These narrow plain stripes also appear in other more complete textiles. These fragments can be part of the border of a square tapestry panel (20-30 cm) of which the central square is missing. The pattern of lozenges in different colors is exceptional. The warp is green S-spun wool (11/cm), and all wefts are S-spun (38/cm). The woolen wefts consist of the following colors: beige-yellow, red, turquoise, pink, green (2 shades), and blue-purple wefts that are very loosely plied S2Z or can be a paired S-spun thread (2S). For the white details, undyed S-spun linen weft is used.

In other collections, there are fabrics with a pattern and dimensions comparable to KTN 1475, but these textiles have a linen warp. One textile in a private collection28 has similar features having warp threads of S-spun wool, wefts of S-spun wool and linen. It is a large square fabric of 27 cm long and 24 cm wide, with a border of multicolored acanthus leaves. The dark purple center part in this fabric, reported to be dyed with mollusk purple in combination with vegetable indigoid and madder,29 depicts an Eros harvesting grapes. These square fabrics belong to a group of multicolored tapestry ornaments with wool warps and plain outer frames that appear to have been woven separately for application to a base cloth by sewing.28

Textiles with S-spun wool warp threads and S-spun wefts dyed with mollusk purple are rare. Additionally, the functional purpose of textile KTN 1475 is difficult to deduce. There are five textiles that have been reported to be dyed with mollusk purple in the Katoen Natie collection. Only the textile belonging to a private collector,28 has technical features comparable to KTN 1475.

2.2 Previous Dye Analyses

Dye analyses on textile KTN 1475 were previously performed in 2005 at the KIK/IRPA via HPLC-PDA. The dye components detected in the red-purple and blue-purple yarns from the textile (Figure 1) were reported as...
follows, with their respective relative peak areas measured at 288 nm:

Red-purple dye in the small squares placed in cross form in the diamond-shaped pattern consists of 21.5% IND and 78.5% MBI.30

Blue-purple dye in the hook-shaped swirl design of the half-diamond composed of 93% IND and 7% MBI.31

In the case of purplish-colored yarns, the presence of a brominated dye indicates that the origin of the pigment is from a purple-producing sea snail source because plant dyes do not contain any bromine-containing colorants. This would then imply that the fibers from these purple yarns were dyed with real molluskan-derived pigments, which would automatically render special importance to such a textile, as this was a dye used by royalty, high priests, military generals, and others of especially high nobility. However, the reported results of the dyestuffs detected were puzzling as no molluskan purple pigment analyzed by the first author—modern or ancient—has ever been found where the sole brominated indigoid is MBI. All real purple pigments possess DBI, with or without MBI, but DBI is always present in varying compositions. Any reddish indirubinoids detected so far in archaeological samples are, at most, minor components, and thus visually they would not shade the color to the reddish side of purple. Thus, the primary source of the reddish shade in a red-purple yarn must originate from the red-purple DBI dye, which was not detected in the previous report.

The discrepancies between the results reported in this study and the ones previously published are not due to the different samples that were analyzed because the same respective areas were sampled in both studies. Further, the lack of detection of DBI by the previous work is not due to degradation of this ancient molluskan purple pigment to non-detectable levels caused by ageing. Archaeological purple samples that are about 2,000 and even 2,500-year old, which are 1,000 years older than the textile that is discussed in the current study, have been found to contain DBI together with other related components.5,12,14-16,18 In addition, archaeological pigments from about four millennia ago from Thera have been analyzed and found to contain DBI.8 Hence, ageing does not significantly degrade DBI.

The details of the analyses that were previously performed have not been published. However, it can be conjectured that the previous study probably utilized the HCl/methanol combination for the extraction of the purple dyes, as it was used in other similar studies.20,21,32 This solvent system is effective in extracting mordant dyes, but is mostly ineffective in dissolving the various indigoid vat dyes as it is a poor solvent for these colorants. The solubility of IND is very low in acidic aqueous methanol (even when hot), and the solubility decreases even more so for MBI, and DBI is nearly insoluble. Thus, the utilization of methanol diluted with aqueous HCl solution will in general not extract DBI to a detectable level.

It has been known for more than two decades that the effective solvents for dissolving indigoid pigments are pyridine at 100 °C2,3 and DMF at near-boiling temperatures,33 while the most optimal solvent for this purpose is DMSO at 100 or 150 °C,15 depending on the quantity of dye to be extracted. The DMSO method utilized in the current paper produces a blue solution as it completely extracts all the dye components from a purple dyeing, which can be clearly observed from the remaining fibers. In HCl/methanol, an extracted solution from a purple dyeing will at best appear a very pale blue color due to some dissolved IND and, much less so, MBI, but the remaining fibers would still have most of the original color on them. Because any complete dye analysis must be quantitative, the entire amount of the dye, not just part of it, must be extracted from the fibers in order to perform a valid quantitative analysis.

Thus, as a purple-dyed textile is of such special historical significance, it was deemed worthy to re-analyze the blue-purple and red-purple yarns by means of an integrated physical (microscopic examination) and chemical (micro-chromatographic detection) approach.

3 Experimental

3.1 Close-Up Images

Prior to the chemical dye analyses, close up views of the yarns were needed in order to determine the physical composition of the color observed. Photographic images were obtained of segments from this textile via a Zeiss stereo microscope and are shown in Figure 2.

Figure 2: Photomicrographic images of various segments from textile KTN 1475.

3.2 Yarns Sampled

Yarn samples for analyses were removed from three areas labeled as "Red-Purple", "Blue-Purple", and "Turquoise" in Figure 3. Due to the extreme difficulty of excising micro-samples from this textile without damaging it, only one red-purple yarn and one turquoise yarn were sampled, while two blue-purple yarns were removed. One blue-purple yarn was analyzed whole, while a second sample was dissected under the microscope into individual fibers and each set of distinct colors was also individually analyzed.

3.3 Photomicrography

Microscopic analyses of the excised yarns and fibers were performed with a Zeiss STEMI SV8 stereo micro-
3.4.2 Chromatographic System

A Waters High-Performance Liquid Chromatography (HPLC) system was used for the reverse-phase chromatographic analyses, which included a 600E Controller, a 996 Photodiode array (PDA) detector, and 20-µL sample loop. The stationary phase consisted of a Waters C-18 5-µm particle size Symmetry column (Part No. WAT054200). The stepwise linear gradient elution method consisted of a binary methanol/water mobile phase with a constant flow rate of 0.6 mL/min according to the following times and increasing methanol percentages:

0 min, 20%; 3 min, 70%; 6 min, 70%; 20 min, 84%; 30 min, 100%.

3.4.3 Dye Extraction and Filtration

For the chromatographic analyses, a micro-sample consisting of either a small yarn (< 50 µg) or single fibers (< 5 µg) was placed in a 2-mL glass vial with 200 or 100 µL, respectively, of DMSO and placed in a dry block heater set at 150 °C for 5 min. The hot solution was immediately placed in a micro-centrifuge tube filter assembly consisting of a polypropylene body and a 0.45-µm nylon filter membrane (Grace Davison Discovery Science, Catalog No. 24139) and centrifuged for 3 minutes. From this filtered dye solution, 80 or 10 µL were then immediately injected into the HPLC, depending on whether the dye was extracted from a yarn or single fibers, respectively. All these steps were performed under subdued light, as required, in order to eliminate the undesired photo-debromination of the dyes in solution.

4 Results and Discussion

4.1 Turquoise Yarn

The microscopic analysis of the woolen turquoise yarn sample of Figure 4 shows that its greenish-blue coloration is relatively uniform along each fiber as well as among the fibers. Chromatographic analysis of the DMSO-extracted dye solution showed only the presence of the indigo dye (Figure 7) without the presence of any other yellow dye or decomposition product of indigo, such as isatin, examined at the appropriate UV and Visible wavelengths for such dyes. Hence, the greenish tint that is now visible in the turquoise yarn is probably due to the combination of the yellowing of the aged wool fibers together with the blue indigo dye, thus producing the resultant turquoise hue. The absence of a brominated indigoid indicates that the source of the dye is of plant origin, which in the Near
East in that period probably originated from woad (*Isatis tinctoria*).

### 4.2 Red-Purple Yarn

Microscopic views of the sample excised from a red-purple square are depicted in Figure 5. These photomicrographic pictures show that the dye density along the length of each red-purple fiber is relatively uniform and the same coloration exists among all these fibers. This is indicative of an exceptionally high quality of dyeing that is still visible after a millennium and a half. The red-purple yarn was thus chromatographed as a whole yarn and the HPLC result is shown in the chromatogram of Figure 8, where the wavelength chosen for depiction (570 nm) is only for qualitative visualization purposes as at this wavelength all the detected dyes can be clearly observed. The four dye components are as follows: IND (indigo), MBI (6-monobromoindigo), DBI (6,6'-dibromoindigo), and DBIR (6,6'-dibromoindirubin). These are the typical dyes identified in archaeological textile dyeings performed with molluscan purple pigments. The relative compositions of these dyes are discussed below in Section 4.4.

### 4.3 Blue-Purple Yarn

Two samples of the blue-purple yarn removed from the hooked swirl (see Figure 3) were analyzed, and one was chromatographed as a whole yarn (see Figure 6), while the other sample was dissected into single fibers. The chromatogram of an extract from the whole blue-purple yarn is shown in Figure 9, where the same four dyes were detected as in the red-purple yarn mentioned above, but with different relative dye compositions, as discussed in Section 4.4 below.

The microscopic pictures of the blue-purple yarn of Figure 6 clearly show that it is actually composed of three different colored woolen fibers: reddish, bluish, and, to a lesser degree, yellowed (undyed). From these images it can be discerned that the reddish fibers in this yarn are of a different shade — less red — than the red-purple fibers constituting the red-purple squares, seen in Figure 5. Thus, the other blue-purple yarn sample was carefully and painstakingly dissected into individual single fibers and grouped into separate reddish, bluish, and undyed fibers. This was accomplished by use of a needle-pointed tweezers with the aid of the stereo microscope, and the resulting images are seen.
The column values shown in the figure for the peak-area compositions of modern molluskan purple pigments are based on the data obtained from extractions of the pigments performed at elevated temperatures with appropriate solvents. These values were obtained from Table 4 of Reference 12 and from unpublished results of additional dye analyses on snail pigments performed by the first author of this paper.

It is important to note that significant variations in the dye compositions are possible and that these values are non-statistical as it would require a significantly large population size of snails to be sacrificed for such a study. The variations in the calculated compositions of molluskan pigments from the same species can be due to numerous factors involving the sea snails, such as, environmental (sea water conditions, e.g., temperature, pH, salt content, and water depth, and the season), geographical location, and biological (sex and size). In addition, differences in the computed compositions can be due to various experimental conditions associated with the analyses, which include sample preparation and the HPLC elution method used. In preparing samples for analysis, the final dye composition is influenced by the extracting solvent, the temperature of extraction, the length of time the dye resides in the solvent, and whether the extraction is performed in the dark or in a lit environment. Similarly, the spectrometric detection of the dissolved colorant occurs at a certain dye concentration, which is dependent on the mobile phase used and its pH. Hence, all these multiple factors can yield different relative peak areas for the same snail species, and calculating a strict average of values obtained from different experimental conditions is irrelevant. Thus, the values reported in the literature for the dye compositions of the purple pigments must be critically evaluated in order to determine if they are based on the same technique and if a complete quantitative extraction was performed.

With all the limitations that have been mentioned above, within the gamut of the relevant purple components determined to date, these sets of values have been found to be representative of the pigments from these snails.

4.4 Integrated Peak Areas

In order to quantify all the results and base them on a standard scale, all the integrated peak areas of these four detected dye components were evaluated at the standard wavelength of 288 nm. This standard wavelength was originally used for the relative quantifications of the dye components of purple pigments as solutions of all these components show considerable absorption at this wavelength. The peak-area values are not the actual mass compositions of the dyes as these need to be weighted with the respective absorptivity coefficients of the dyes. However, these area percentages, normalized to 100 % for each sample, can nevertheless be used for semi-quantitative comparative studies, and are depicted in Figure 13.

The first four columns of Figure 13 refer to the relative peak areas of the red-purple and blue-purple yarns of textile KTN 1475 of this study. The last four columns relate to the typical relative dye compositions found in the purple pigments produced from the three above-mentioned mollusks inhabiting the Mediterranean: *H. trunculus*, *B. brandaris*, and *S. haemastoma*. Within the *H. trunculus* species, as shown in the figure, two varieties have been found, where irrespective of the amount of MBI present, one is richer in DBI than in IND, and the other is richer in IND.12
4.5 Malacological Provenance of the Purple Dyeings

All purple pigments produced from sea snails possess the common red-purple DBI dye; however the malacological source of this purple dye can be ascertained from the presence or absence of an abundant amount of the MBI dye. Koren has previously established that only the Hexaplex trunculus molluskan species produces significant amounts of MBI, whether it is a DBI-rich or IND-rich pigment, as can also be seen from the last four columns of Figure 13. From the first four columns of Figure 13 it can be seen that all the red-purple and blue-purple samples of the archaeological textile of this study have a substantial amount of MBI, ranging from about 35–50%. Hence, all the red-purple and blue-purple molluskan dyeings were produced with the use of the H. trunculus species. Whether an additional species was also used in some of the dyeings is discussed below.

4.5.1 Red-Purple Yarn

The strong reddish color of this yarn (Figure 5) is evident from the very large contribution of the reddish dye components (Figure 13), mostly DBI with some DBIR, which together total about 44%. The violet MBI amounts to about 54%, with only about 2% of IND. Such dyeings, which contain a sizable quantity of MBI and a minimal amount of IND, can be mostly obtained from a DBI-rich H. trunculus snail alone. It is to be noted that the variation of IND in DBI-rich trunculus snails can range from less than 1% to as much as nearly 20%. Hence, the IND in the red-purple of the archaeological textile falls within this range. Based on the dye compositions of the red-purple yarn there would not be a need to use an additional species; however, if there was a need to increase the red coloration, some minor amount of B. brandaris or S. haemastoma may have also been used (see the discussion below).

4.5.2 Reddish Fibers Dissected from the Blue-Purple Yarn

The dissected blue-purple yarn shows reddish fibers as well as bluish ones (Figures 6 and 10). A comparison of these dissected reddish fibers with the previously discussed whole red-purple yarn fibers of Section 4.5.1 and Figure 5, both from a visual microscopic view as well as from a chemical perspective, clearly confirms that the two reddish samples were differently dyed. Visually, the reddish fibers from the blue-purple yarn (Figure 6) are seen to be less red, and bluer, than the fibers from the whole red-purple yarn (Figure 5). This difference is also borne out chemically (as seen in Figure 13) by the relatively large IND content of the reddish fibers from the blue-purple yarn, which is more than 20 times that in the whole red-purple yarn. Thus, to produce such a reddish dyeing in the blue-purple yarn (Figure 6) with such a large blue-character in its color, it is obvious from Figure 13 that a DBI-rich H. trunculus species was used without the need for any additional snail species.

Further, it can now be extrapolated that since the dye composition of the previously discussed whole red-purple yarn (Figure 5) is much redder, it thus indicates that minor usage was probably made of the other snails, B. brandaris and/or S. haemastoma, which produce redder pigments than even the DBI-rich H. trunculus species.

4.5.3 Bluish Fibers Dissected from the Blue-Purple Yarn

The dye composition (Figure 13) of the bluish fibers removed from the blue-purple yarn clearly indicates that these bluish fibers were produced from an IND-rich H. trunculus, without the use of any other sea snail species.

4.5.4 Whole blue-purple yarn

The dye analysis of the whole blue-purple yarn (second column of Figure 13), without dissecting it into its individual fibers, is thus seen to be an average of the compositions of the two fiber color types (third and fourth columns).

5 Conclusions

Table 1 summarizes the results of the physical and chemical examinations of the purple yarns via microscopy and chromatography, respectively.

<table>
<thead>
<tr>
<th>Yarn Color</th>
<th>Color of Fibers</th>
<th>Malacological Dye Source</th>
<th>Fleeces Spun</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red-purple</td>
<td>Red-purple</td>
<td>DBI-rich H. trunculus + probably minor use of B. brandaris and/or S. haemastoma</td>
<td>1</td>
</tr>
<tr>
<td>Blue-purple</td>
<td>Reddish (less red than above)</td>
<td>DBI-rich H. trunculus</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Bluish</td>
<td>IND-rich H. trunculus</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yellowed</td>
<td>(undyed)</td>
<td></td>
</tr>
</tbody>
</table>

The summary table shows that two varieties of the H. trunculus were used as well as probably a minor quantity of B. brandaris and/or S. haemastoma for the various colors desired. Further, the spinner of these purple yarns used a total of four differently colored fleeces, one for the red-purple yarn and three distinct fleeces for the blue-purple yarn: a reddish-purple dyed fleece, a bluish-purple one, and a slight amount of undyed (now yellowed) woolen fleece. Perhaps the purpose of spinning together undyed fibers together with the intensely dyed ones is to produce a lighter shade of blue-purple, whereas just using the colored fibers would have produced a darker shade.

This study is the first publication where a single polychromic yarn was dissected into separate fibers, and each different fiber color group was individually chromatographed. The methodology employed by this investigation, which integrated the usage of microscopic and chromatographic analyses, must be a caveat for any future dye analyses: First, a microscopic examination of the yarn must be performed, and if it is composed of differently colored fibers, then the yarn
must undergo dissection into individual color groups whereby each is individually chromatographed. Further, only the HPLC method can provide the full spectrum of dyes used in a dyeing, and no other technique can provide such a complete qualitative and quantitative “chromatic fingerprinting” essential for the determination of the specific malacological provenance of purple dyes.

The microscopic and chromatographic analyses performed in this work shed further light on the mastery of the ancient textile dyer and weaver. The fact that this textile contains fibers produced from a molluskan source renders the fabric to be of special importance. However, the ultimate question that this study has posed is thus: Why did the weaver use such expensive and beautiful molluskan dyes for such narrow details – the very small red-purple squares and the miniature blue-purple hooked swirls – that are difficult to distinguish in the highly multicolored motif? This is a mystery in which the weaver and dyer have colluded and still remains unknown after a millennium and a half of history.

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7 References

6. R. Clark, C. Cooksey, Monobromoindigo: a new general synthesis, the characterization of all four isomers and an investigation into the purple colour of 6,6'-dibromoinindo, New J. Chem. 1999, 23, 323-328.
8. I. Karapanagiotis, Identification of indigoid natural dyestuffs used in art objects by HPLC coupled to APCI-MS, Aper. Lab. 2006, 38, 36-40.
23. N. Polosmak, L. Kundo et al., Textiles from the “frozen” tombs in Gorny Altai 400-300 BC, an integrate study, Russian Academy of Sciences, Siberian Branch, Novosibirsk, 2006, 34-37, 108-109, 111, 249.
24. M. James, N. Reifarth et al., High prestige royal purple dyed textiles from the Bronze Age royal tomb at Qatna, Syria, Antiquity 2009, 83, 1109-1118.
26. B. Evans, The past made present, Halli Carpet, Textile and Islamic Art, 2012, 171, 95 (Figure 16).
27. KIK/IRPA, Report KIA-28757(1475).