18. **Color Analysis of the Textiles**

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The sources of the beige, brown, and dark colors on the Chalcolithic 6,000-year old textiles found in the Judean Desert Cave of the Warrior were analyzed in microscopic, chemical, and chromatographic tests performed on threads composed of plied yarns. Dark (brown-black) colors were present on weft threads forming part of the decorative bands of the large and the smaller textiles and on the outer warp threads on both sides of the large textile. Dark colors were also present on sections near the corners of the large textile. Microscopic analyses indicated that the fibers in the dark yarns (and, to a lesser degree, in the brown yarns) adhered to each other due to the use of a gluey dark brown colorant. The dark colors of the decoration threads were the result of a very dark brown (nearly black) colorant applied to each individual thread. The analyses indicated that this adhesive colorant was an organic macromolecule with acidic groups and that the source of the colorant may be gum, resin, asphalt or bitumen, or collagen-like material. The textile is the earliest example of thread-dyeing yet discovered worldwide. The colors on even later third millennium textiles were produced by surface coloration – painting or smearing – of part or all of the bulk textile, and not by dyeing individual threads before weaving, as practiced in the Warrior textile.

**Introduction**

Beige, brown, and dark colors were present on the two 6,000-year old linen fabrics examined. The large textile (A) measured c. 7 × 2 m, and the smaller (B) c. 1.40 × 0.90 m. The decorative bands at the woven ends in each of these two textiles contained dark (brown-black) brown, and beige threads. Dark threads were also present as outer warp threads on both sides of Textile A. In addition, irregularly shaped dark brown areas occupy its four corners. Both fabrics were composed of a background of beige hues, resulting from the natural aging of the linen fibers, and of brown colors.

Textile A was found folded in four. In it were the skeletal remains of a male, accompanied by grave goods, such as a wooden bow, arrows, a flint knife, sandals, a basket, and a wooden bowl (Schick, this volume).

Reddish spots on the fabric (Color Pl. 3.4) have been identified as ochre (iron oxide) (Segal, this volume), possibly sprinkled onto the fabric as part of the burial ritual (Schick, this volume). Red ochre symbolized life-blood, and has often been part of funerary rites, such as painting of skull, bones and other parts of the deceased, in ancient cultures (Brunello 1973:6–8).

**Experimental**

Varied beige, brown, and dark thread samples from the large and small textiles were analyzed for the presence of trivalent iron by chemical tests. High-performance liquid chromatography (HPLC) was also used to detect the possible presence of organic colorants. Longitudinal and cross-sectional microscopic tests were performed on each of the samples.

The chemical tests performed to determine the presence of iron in each of the differently colored samples were conducted according to the thiocyanate and ferrocyanide methods (Garner 1966:93, 94). A colored thread was treated to 1M hydrochloric acid (HCl) solution for 10 minutes at the boil so as to extract any ferric iron. The resulting mixture was centrifuged and the yellow-brown supernatant liquid was removed and divided into two portions. One portion was analyzed with potassium
thiocyanate (KSCN) and the other with potassium ferrocyanide, K₄[Fe(CN)₆]. In the first test, a few drops of the test solution was spotted onto a filter paper to produce a brown spot. The dried spot was then treated to a few drops of 20% potassium thiocyanate reagent to produce a red ring. The red complex indicates the presence of ferrithiocyanate, Fe(SCN)₃+, resulting from the extraction of the Fe³⁺ ion away from the center of the spot by the reacting SCN⁻ ion. According to the second test, the test solution was treated to potassium ferrocyanide. The product of this reaction was the Prussian blue pigment, Fe₄[Fe(CN)₆]₃, indicating the presence of Fe³⁺ in the original test solution. These tests indicate that an iron compound was present in all the samples examined. This same test was also performed by Taylor (1997), who treated each of the two colored samples with 10% aqueous sulfuric acid and then added a few crystals of potassium ferrocyanide.

Two sample preparation methods were used prior to the HPLC analyses for the detection of a dye that might be present in the textiles. In the method of extracting direct or mordant dyes, each fabric sample was treated with HCl and methanol (Koren 1995a). The resulting yellow solution was then evaporated and the brown residue was redissolved in methanol to yield a yellow-brown solution. In the other method, a textile sample was treated to warm methanol, in order to directly extract any organic matter. The resulting yellow solution was filtered prior to analysis. In both methods, the final color of the fabric was not visually different from the sample prior to extraction of the colorants. All the HPLC results, using both colorant extraction methods on both colored samples, were similar and are described below.

RESULTS AND DISCUSSION

The results regarding the microscopic analyses, the iron tests, and the HPLC analyses are here presented.

A. Microscopic Analyses
The microscopic analyses showed that each of the beige, brown, and dark threads analyzed consisted of two individual yarns that were plied together in an S-twist.

Longitudinal microscopic examinations revealed that the fibers within each dark yarn were 'glued' together by a binding agent, which will be discussed below, while each pair of the plied yarns in the dark thread showed only slight adhesion to each other. The fibers within the brown yarns were also somewhat glued to each other, but less so than the fibers in the dark yarns.

The dark threads from the decoration and near the corners of the large textile were similar in appearance and, to the naked eye, they appear black in color. However, microscopic investigations of these threads show that the dark colors are due to a very dark brown (nearly black) coloration on the surface of the thread, whereas the inner fibers are dark brown. This inhomogeneous color may be due to air-oxidation of the brown colorant on the exposed outer fibers, which yielded darker colors on the yarn surface, a process that may have been a deliberate part of the overall dyeing stage for the dark thread used in the decoration. The dark surface color, as presently seen, was not uniform along each yarn, with noticeable ordered gaps present at the points of inflection where the twisted yarns change direction. These gaps in dark color are situated at interior unexposed regions of each thread. Hence, these observations indicate that prior to weaving a dark thread into the decoration, dyeing was performed on an already plied thread and not on the individual yarns before plying.

Observations of the cross sections of the dark-brown fibers indicate that a brownish colorant was also visible in the interior of the fiber. These microscopic examinations clearly indicate that each dark thread in the decoration was dyed with a colorant that has some good affinity for linen. True dyeing is obtained by the immersion of the textile into a dye solution and generally yields relatively strong physical and chemical bonds between the textile fibers and the dye. It also produces good penetration of the dye into the fibers and not just on their surface. Various textiles from the third millennium contain colors that were produced not by dyeing, but rather by painting part or all of the surface of the textile (Koren 1993).

B. Iron Tests
Both of the two tests for iron were positive indications that the dark and brown threads in the decoration contained trivalent iron, with relatively more iron in the dark yarn. Taylor (1997) obtained the following results:

- Brown warp: some Fe detected
- Brown weft: no Fe detected
- Dark weft: Fe detected.

A beige-brown thread from the background of the large cloth was also examined. A microscopic analysis showed the presence of reddish areas on the fibers and an iron test showed the presence of a relatively large amount of iron.
The presence of iron in the samples analyzed may be due to (a) soil particles (rich in iron) adhering to the textile and/or to the soluble iron compounds that leached into the textile that was in contact with the ground, (b) surface-coloration by means of an insoluble ochreous compound, and/or (c) a solubilized iron compound that was deliberately introduced into the textile during the pre-dyeing stage (mordanting) or post-dyeing step (fixing). These chemical analyses indicate that iron may have been deliberately introduced into the dark yarns as part of the overall dyeing process. However, due to the presence of iron in the various colored samples analyzed, it is difficult to determine whether a soluble iron salt was, in fact, deliberately used in the overall dyeing process.

The dark-brown colorant that was present in the individual fibers themselves could not have been produced by means of an insoluble ochre, which is an oxide of iron. A major source of iron that was used by primitive man was an ochreous mineral (Robinson 1969:20–21), such as red-brown hematite (α-Fe₂O₃) and/or yellow-beige goethite, FeO(OH)·H₂O. Brunello cites a number of examples of clay ‘dyeing’ in various cultures, although the term ‘dyeing’ in this case should be ‘coloring’, as good penetration of the iron into the interior of the fibers is not possible with the dispersed undissolved clay in water. In one case, he cites Emil Ernest Ploss (Brunello 1973:8): I still remember how the old grandmother of our neighbor rubbed linen ... with greasy clay in a ditch in the ground. Then she would wet it and leave it in the colored water. A week later, as a result of the iron oxides it absorbed, it acquired a pleasing natural brownish color that remained until the apron made of this linen was finally in tatters. In another example (Brunello 1973: 19), Russell is cited as reporting that the Pima Indians of north Mexico obtain coloration when they apply a mixture of ochre in water to cloth made from the bark of a tree. The fastness, according to Brunello, is attributable to the reaction between the pigment’s iron salts and the tannic substances naturally contained in the fibers. Certain auxiliary agents, such as glues or other adhesive substances added to pigments can favorably modify the fastness of the coloration, as in the case of the Hopi Indians who add resins of coniferous trees to various pigments (Brunello 1973:19).

In order to produce uniform colors with an iron compound, the material must be dissolved to produce a dye bath so that the solubilised iron will penetrate into the textile fibers. However, the iron oxide minerals in clay are insoluble in water, and are only soluble in a strong acid, which was not available in antiquity. Thus, ochre cannot be used in a true dyeing process. Though ochre alone has been reported as being used to produce brown or red colors (Eastwood 1984; Brunello 1973:19–20; Wouters 1990), its use was limited to staining or painting a textile, i.e., surface-coloration. One of the oldest (c. 1900 BCE) of red-ochre colored textiles discovered so far (Wouters 1990), was surface-colored and not dyed, as microscopic analyses showed the presence of pigment particles on the surface of the fibers (Wouters, personal communication). In the current study on the Warrior textiles, the penetration of the color into the fibers indicates that ochre pigments suspended in water could not have been used for producing the dark colors.

C. Other Chemical Tests
The dark-brown colorant was extracted with hot methanol to yield a yellow solution; this is indicative of an organic colorant. However, the dark color was still visible on the thread without any visible reduction in its depth, which indicates that the colorant is only slightly soluble in methanol. Treatment of the fibers remaining from the previous methanolic extraction with dilute hydrochloric acid produced a yellow solution that showed the presence of an iron compound according to the Prussian-blue test described previously. However, once again, the fibers themselves showed no visible change in color. After washing the fibers with water, the dark colorant was finally stripped from the fibers by means of dilute sodium hydroxide, which produced a yellow-brown solution. This indicates that the dark colorant contains acidic groups.

A dark area from the large cloth was also examined and produced similar chemical results.

D. HPLC Analyses
The chromatographic analyses were performed to determine the identity or type of organic colorant present. In Roman times, brown and dark colors were produced by means of tannins from gall nuts, sumac, etc., combined with dissolved iron (Abrahams and Edelstein 1963). Though the warrior textile is about four millennia earlier than the Roman period, the possibility that the colorant was a tannin was nevertheless investigated.

The HPLC method used for the detection of yellow and brown organic dyes (Koren, unpublished) was performed on the methanol-only and the acid-methanol extractions described previously, and the results were similar for both extractions.
The presence of a constantly eluting yellow solution was detected, as seen from the chromatogram (Fig. 18.1). It shows the absorption of light by the eluting components at the time of their exit from the separating column. The chromatogram of the yellow solution extracted from the Warrior textile shows a broad band between about 5 and 28 minutes at a spectrometric detector wavelength of 380 nanometers, a wavelength indicative of the presence of a yellow substance. This band is not due to the dissolved iron, which was tested separately and produced negligible absorption. The broad band indicates that this colorant was smeared within the separating column and could not be easily separated with the chromatographic system used for typical monomeric dye molecules. These latter relatively small molecules yield the familiar sharp chromatographic peaks (Koren 1995a) that indicate that these dye molecules exit the column within a short time frame. The chromatographic results indicate that this brown colorant is macromolecular or polymeric and does not belong to any of the usual chemical groups of colorants normally encountered in dye analysis investigations (Koren 1996). Thus, this colorant is not a flavonoid—a yellow dye found in many plant leaves, nor a naphthoquinone from, e.g., green outer walnut peels or henna leaves. The possibility that this colorant is a tannin is discussed below.

Two of the more characteristic identifiable hydrolysis products of tannins that are obtained as a result of modern-day dye analysis schemes are gallic acid (GA) and ellagic acid (EA), which originate from vegetal matter containing much larger so-called gallotannin and ellagitannin molecules, respectively. No EA was found in the HPLC analysis and only a trace of GA or similar
molecule is present. Thus, the colorant is not a hydrolysable tannin from, e.g., sumac, galls, etc. A source of this dark brown colorant may be from a condensed (non-hydrolysable) tannin, which cannot be ordinarily decomposed to smaller molecules. The macromolecular nature of this type of tannin is consistent with the smeared band in the chromatogram obtained for the Warrior colorant. In addition, the chromatographic profile obtained in the current study is similar to the ones published for condensed tannins extracted from leather (Wouters 1993). However, it is plausible that the plant source providing the condensed tannin should also contain a detectable, though small, quantity of hydrolysable tannins from which GA and/or EA are produced. The fact that these characteristic acids have not been found in the Warrior textiles would indicate that the source of the colorant is probably not from a condensed tannin.

E. Brittleness

The dark fibers from the decoration and from the dark areas of the large cloth disintegrate into powder when handled. It was at first believed that this decomposition is due to the iron that is present in these fibers. However, this cannot be the explanation for the brittle nature of these dark-colored threads as the beige-brown fibers from the large cloth contained a rather large amount of iron, as discussed above, and yet these fibers were quite flexible and mechanically relatively strong. In addition, the red mummy linen fibers from about 4,000 years ago that were discussed above (Wouters 1990) have still survived without undergoing unusual decomposition. Hence, insoluble ochre pigments on textile fibers do not cause deterioration of the fibers. It has been found (Neevel 1995) that soluble divalent iron salts catalyze the oxidation, and consequently the degradation, of cellulose material. Thus, it can be surmised that the decomposition of the dark fibers in the Warrior textile is due to the rigidity of these fibers as a result of the gluey substance that was used on them. The slight movement of these brittle inflexible fibers will cause them to crack and this is the nature of the disintegration of the fibers.

Conclusions

Dark-brown (or nearly black) colors have been produced in classical and Roman periods by the combination of soluble iron salts and hydrolysable tannins, some particulars of which were described by Theophrastus and Pliny (Forbes 1964:126). However this is not the case in the present textile, as no such hydrolysable tannins were observed with the chromatographic technique that can detect these compounds. No other dyes that are usually present in ancient textiles found in Israel were discovered in this textile (Koren 1994).

What then is the basis of the brown and dark colors? The chemical, chromatographic, and microscopic results indicate that the dark colorant is a sticky organic acidic macromolecule to which a soluble iron salt may have been added. This material could have been a vegetal resin or oil, gum, bitumen liquid asphalt from the Dead Sea, or a proteinic material such as collagen. These possibilities are discussed below.

Forbes (1964:109) mentions the use of a dark red resin called dragon’s blood obtained from the fruit of Calamus draco Willd. (the climbing or rattan palm) and cites Pliny’s reference to it as cinnabanis, which was used as a lake-pigment in painting, but he did not believe that it was used in dyeing textiles. However, Brunello (1973:21) describes the use of this plant by the Dyak tribes of Borneo for affixing soot onto the fiber. The preliminary stage of this process includes treating the textile with dense fumes of highly resinous substances. Other red and yellow resins were also used, though typically in paintings (Mills and White 1987:124,126). It should also be noted that the famed madder dying of cotton in the last few centuries was conducted by mordanting the cotton textile fibers with a resin known as Turkey red oil (Rawson et al. 1926:335–339; Merck 1989:1545; Travis 1993:164–165; Brunello 1973:232–234). Additionally, Robinson (1969:21) describes an ancient textile coloring process that involves the fixing of pigments into the textile by means of either a resin from trees, glues, wax, or other binders. This latter process would not, however, lead to a true uniform dyeing and would produce a surface coloration of the pigment.

Gum, specifically gum arabic, and other resins are available from various acacia trees native to the Judean Desert (N. Lifschitz, personal communication), the site of the Cave of the Warrior. This would have been a readily available source for a glue-like brown colorant.

Asphalt, floating on the Dead Sea in antiquity (S. Zolotov, personal communication), may have been heated and the liquid of that substance used for dyeing the threads.

Collagen from bones had been used in the production of 8,000-year old vessels from Nahal Hemar in the Judean Desert (Nissenbaum 1997). This dark proteinic substance or related material may have also been used for the dyeing of the yarns that were woven into the
Warrior textiles. If this material were used, then the bones would have necessity been first dissolved in an alkaline medium, such as one or more of the following (Koren 1995b): stale urine, aqueous solutions of potash or soda ash from wood and plant ashes, lime, and combinations of the above. Air-oxidation or heat may have caused the 'blackening' of the colorant on the surface of the exposed fibers.

The darker brown color may have also been obtained by the addition of soluble iron, not from insoluble ochreous clay itself, but from local springs (or muddy waters) that contained iron salts in solution (Leggett 1944:92). A soluble iron salt, iron sulfate (FeSO₄), was already known in classical times (Singer 1948:14) and was also known later as the mineral 'copperas' and 'green vitriol' (Orna and Goodstein 1993:296). It can also be found mixed with alum near volcanic regions (Singer 1948:21).

The current overall physical state and coloration of the large textile may be explained in the following way. The missing parts of the large textile are due to the mechanical breakdown of the textile fibers. The textile was folded twice, producing four relatively equal sections, and enveloped the body of the deceased Warrior. Not only were the dark threads that were used in the decoration dyed with the glue-like colorant before weaving, but this same or a similar sticky liquid was poured over the body. Thus, all four sections of the textile that were below or on top of the body absorbed this material and the body weight lead to the cracking of these brittle fibers in the middle of the textile, which produced the symmetric spacing that can be seen in Color Pl. 3.3. This same liquid may have also been poured at or near the four corners of the twice-folded textile, as very dark areas are visible in these regions. The less dark, brown, areas on the large textile may be due to the oozing of the sticky liquid from the neighboring regions onto which the liquid was poured. The diffusion of this liquid colorant to a wider area produced less dark colors in these regions and, consequently, these less dark, brown, fibers were not as rigid or brittle as the darker ones and have thus survived within the textile matrix to this day.

The above scientific conjectures as to the nature of the colorant point to the difficulty in positively identifying this dark brown dye, as can also be seen from Taylor's dye analysis report, which stated that no identifiable colorant was found (Taylor 1997). Future research will be conducted to determine the nature of this brown dye.

This current study on the Warrior textile represents the oldest dyeing that has been chemically analyzed. Prior to this investigation, the earliest dyeing that had been chemically analyzed, according to Vogler (1982), is from about 2500 BCE, and was performed by Hübner, who identified mummy bindings as containing safflower and iron. However, the detection of the fugitive safflower colorant in such an ancient sample is questionable, and these bindings were also analyzed more recently by Wouters et al. (1990) via HPLC and the safflower dye was not detected. Thus, the reported use of that plant dye on these textiles should be disregarded. In other accounts on ancient dyeings, Barber (1991:224) cites the reported identifications of kermes red and blue dyes on late Neolithic textiles found in southern France, and according to Brunello (1973:12), W. von Stokar has reported the presence of blue, red, lilac, and yellow colors on Neolithic textiles after treatments with nitric acid. Colored scraps of woollen cloth found in the Judean Desert Cave of the Treasure, which were reported as being from the early fourth millennium BCE (Bar-Adon 1980:153), are most probably from the much later Roman era. Various artifacts from that archaeological site, which also includes items from the second century CE Bar Kokhba period, were undoubtedly mixed with those from the earlier (T. Schick, personal communication).

The relative uniformity of the dark brown color along the length of the inner dark fibers that comprise the decorations in the Warrior textiles is remarkable, given the fact that this textile is nearly six millennia old! In light of the above discussion, it can be stated that these dark brown threads are examples of the earliest dyeing of threads yet discovered.

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