THE DETECTION OF MORDANTS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY

N. Indictor, R.J. Koestler, & R. Sheryll

ABSTRACT—Twelve mordanted and cochineal dyed modern wool samples were subjected to scanning electron microscopy and energy dispersive X-ray spectrometry (SEM-EDS) analysis. The analyses for metallic elements matched in all cases those actually used in the preparation. The mordants detected contained the metallic elements: aluminum, chromium, copper, iron, and tin. SEM photomicrographs were also examined for the effects of mordanting on fiber surfaces. Atomic absorption (AA) analysis of the samples is also reported.

1 INTRODUCTION

IN A PREVIOUS STUDY A GROUP of modern mordanted textile samples was subjected to SEM-EDS analyses to determine the feasibility of identifying mordants on museum textiles. Successful qualitative identification was achieved on silk, cotton, and wool for samples containing the elements aluminum, iron, copper, tin and chromium. Some problems that appeared in that study were the following: significant elements are present very nearly at the limits of detectability of our analytical system; iron sometimes appeared as a trace element even when not used as a mordant; and some analyses of samples mordanted with chromium gave no indication of chromium; the same was true for tin but less frequently. Aside from the difficulties in obtaining unambiguous analyses for some samples, anticipated difficulties for museum and archaeological samples are foreseeable owing to loss of mordant during dyeing, washing, wear and aging that is certain to attend all historical samples. The presence of metallic elements from dust, dirt, soil, stains, treatment, etc., may also constitute a source of metallic elements that is not associated with the mordanting process requiring a cleaning or washing of the samples prior to analysis. Finally, not all mordants contain metallic elements and the mordants free of metallic elements or elements lighter than sodium would not be detected by EDS.

In the series of analyses described in this study, wool samples were mordanted and dyed with cochineal and submitted without identification for SEM-EDS analysis. For each sample analyzed, metallic elements of the mordants actually used were identified unambiguously. The quantity of metallic element present in the mordanted samples, as determined by atomic absorption (AA), was also obtained. SEM photomicrographs of the samples were taken and examined for indications of the effects that mordants and/or additives had on the surface structure.
2 EXPERIMENTAL

MATERIALS AND METHODS. Cochineal dyed wool samples were obtained from the Textile Conservation Dept., Metropolitan Museum of Art, New York. These samples were produced in a collaborative exercise during a 5-day workshop conducted by Fred Gerber in September 1978. The samples were stored on ragboard sheets in a bound sample book.

Although details are ambiguous, mordants were applied before dyeing. The following quantities of mordant were used per pound of wool yarn:
- K$_2$SO$_4$AI$_2$(SO$_4$)$_3$ ·24H$_2$O, 4.0 oz;
- CuSO$_4$ ·5H$_2$O, 1.0 oz;
- FeSO$_4$ ·7H$_2$O, 1.0 oz;
- SnCl$_2$ ·2H$_2$O, 0.5 oz;
- K$_2$Cr$_2$O$_7$, 0.5 oz.

Mordants were dissolved in sufficient quantities of water to insure solution of mordants, heated, and the wool yarn was then added to the mordant solution. The yarn was left in the solution for some time depending on the mordants. Dried cochineal insect grains from the Canary Islands were mashed and added to warm water. After the dye was extracted into the water larger dye baths were prepared and the mordanted yarn was added and simmered (90–100°C) ca. 1 h. Different dye baths were used for each mordant. The dyed yarns were then rinsed in cold tap water and dried. Some of the mordant/dye solutions contained unspecified amounts of additives other than metallic mordants: cream of tartar, oxalic acid, sumac. The cochineal and the sumac were not purified or refined products but used as received. The sumac was field collected on the morning of use.

ANALYSES. The samples were prepared for scanning electron microscopy and examined in an AMRay 1600T with attached Kevex X-ray spectrometer system. Details of the treatment for analysis and the equipment used has been described previously. In addition, elemental dot mapping and photomicrography were performed on the samples. For atomic absorption analysis (AA), samples were submitted to Schwartzkopf Microanalytical Lab, Woodside, NY 11377.

3 RESULTS AND DISCUSSION

WIDE COLOR VARIATIONS WERE ACHIEVED by the use of different mordants and additives. The same dye, cochineal, was used for each batch but with a different mordant and/or additive. In the absence of mordant or additive (sample 13) the wool fibers are nearly free of color. Each of the numbered samples was visually distinct. Visual examination of the fibers of each sample other than sample number 13 showed color well dispersed over the fibers. Table I shows the approximate sample size used for the SEM-EDS analyses and the elements observed in EDS scans of the carbon coated samples. At least three scans were performed for each sample. The table is divided into two parts: elements observed during each scan and elements observed in some
scans. The frequency with which the elements were observed is also given. As expected for wool samples sulfur is prominently present in each scan. Elements other than those from the mordant may be picked up by the wool from the wash water or the non-uniform wool-mordant-dye-additive system.

Table I WOOL. Results of EDS Scans

Table II summarizes the mordants identified by EDS analysis. Samples 13 and 15 gave such small weight percentages (approx. 1%) of aluminum and iron in some EDS scans that they were reported as probably absent. Samples 20, 24, 25, 27 and 28A gave trace analyses for aluminum or iron (about 1–2%) in all EDS scans and are reported as possibly present. Samples 23A and 26 had aluminum (4–6%); samples 14 and 24 had copper (16–70%); samples 16 and 27 had iron (9–19%); samples 17 and 28A had tin (about 70%); samples 25 and 26 had chromium (17–32%). The decision to report the presence or absence of elements was based on the peak heights of these elements relative to that of sulfur, the element persistently present in all of the scans. “Yes” values were reported when EDS scans showed the mordant element to be always present in amounts greater than 2% relative to sulfur. Variation in weight percent relative to sulfur was often greater than 100% from scan to scan emphasising the already noted difficulty in using EDS analysis for quantitative assay. 1 The percentages indicated above represent only the weight percents of elements above the atomic weight of fluorine detected in an individual scan and not the weight percent present in the sample.

Table II Detection of Metal Elements on Cochineal Dyed Wool Samples by EDS

The reporting of absolute weight percents for the elements under discussion would require: preparation of known samples with controlled quantities of additives uniformly distributed on the sample; or an independent elemental microanalysis of the samples of levels greater than the 10% obtained by AA (see below). It would also be necessary to perform replicate scans to account for non-uniformity of the surface and non-uniform attachment of the additives.

Table III shows the mordants and additives used in the preparation of the samples of Table I. It is seen that all the mordants actually used were unambiguously detected (cf. Table II). The presence of traces of aluminum and iron in some of the EDS scans suggests a small problem. Continued experience and information concerning the context of samples will help the analyst to know when to disregard trace element values. In this connection the assistance of the curator or conservator cannot be overestimated. It should be noted that sample 26 had a double mordant (aluminum and chromium) and each was detected unambiguously. No difficulty at all was encountered in the detection of Sn or Cr (cf. ref. 1).

Table III Mordants and Additives Used for Cochineal Dyed Wool Samples

Table IV provides data obtained independently by AA analyses for the elements present in the mordant and detected by EDS scans. The data of column 3 is calculated from the recipes and assumes that all mordant used was
incorporated into the yarn. As expected from our previous study, the quantity of mordant found in the dyed fabric is substantially less than the amount actually used except for the tin mordanted samples. The AA results suggest that a larger amount of tin compound was used than was reported in the experimental section. The data of Table IV also suggests that the process of dying after mordanting may produce a greater retention of mordant in the fiber than simply applying mordant. Previous studies showed retention of mordants to be approximately 10%. The entries under % Element by AA are replicates (since each mordant is applied according to the same recipe each time it is applied). It is seen that the values are excellent replicates in some cases but in other cases differences considerably exceed the experimental error of the analysis. One reason for the differences may be non-uniform sample preparation. The procedures for mordanting and dying maintained constant proportions among the ingredients but quantities of water were not measured in the mordant or dye baths or for the washing. The additives and impurities, furthermore, may have contributed differently to the partitioning of mordant between the textile and the aqueous phase. Another reason for the differences may be non-uniformity of the samples. Wool structure may vary considerably microscopically and macroscopically. Animal breed, treatment, processing, aging, differences in exposure to the environment, etc., all contribute to structural, mechanical and chemical variations in wool and its ability to interact with mordants, other additives, and impurities. Dot mapping scans of our samples indicated that the individual samples were quite uniform with respect to the metallic elements in the fiber surfaces.

Table IV Comparison of Mordant Quantities Applied to Cochineal Dyed Wool Samples with Quantities Analysed by AA

Each of the samples was examined by SEM photomicrography and the samples retained. Although not prepared with this investigation in mind, the samples examined in this study represent a good standard series since the same wool and dye were used throughout; the only difference in the samples should arise from the use of different mordants and/or additives. No clear-cut distinctions in surface appearance could be made among the various mordanted and dyed wool fibers. It is possible that surface characteristics of aged fibers provide a better indication of treatment.

The distribution of the mordant on fibers is an excellent subject for the elemental dot-mapping capabilities of SEM. Preliminary results indicate complete delocalization of elements without discernible pattern in the surfaces of the mordanted wool fibers. This result suggests that representative EDS results ought to be obtainable even with sample sizes as small as a single fiber.

4 CONCLUSIONS

1. The use of different mordants and additives in the cochineal dyeing of wool produced a wide variety of color.
2. The elements aluminum, iron, copper, tin and chromium were unambiguously matched respectively with wool samples which were
mordanted with K2O4Al2(SO4)3 ·24H2O, FeSO4 ·7H2O, CuSO4 ·5H2O, SnCl2 ·2H2O and K2Cr2O7, and dyed with cochineal.

3. Some samples gave trace analyses in EDS scans for iron and aluminum (although not actually used in the mordanting procedure) but far less than when these elements were actually used in the mordanting procedure. The ratio of the weight percent, metallic element/sulfur, appears to provide a useful criterion for deciding whether or not a mordant has been applied to wool. The criterion may also be extended to the analysis of silk samples (see Part II).

4. Atomic absorption analyses confirm the presence of metallic elements in greater than trace quantities as detected by EDS scans. EDS scans indicating trace quantities of elements (Al and Fe) are also confirmed.

5. The presence or absence of mordants or additives could not be inferred from differences in the appearance of fibers examined in this study by SEM photomicrographs.

BIBIOGRAPHY


Nobuko Kajitani, Textile Conservation Department, Metropolitan Museum of Art, New York, provided the samples of dyed wool and described sample preparation.


THE DETECTION OF METALLIC MORDANTS BY ENERGY DISPERSIVE X-RAY SPECTROMETRY

R.J. Koestler, N. Indictor, & R. Sheryll

ABSTRACT—Thirteen silk fibers from seven different historical silk textiles were subjected to EDS analysis. The major metallic elements detected were aluminum, iron, calcium, silicon and potassium. No evidence for copper, chromium, tin or zinc was found. These results were compared to analyses of known mordanted silk samples.

1 INTRODUCTION

THE SCIENTIFIC AUTHENTICATION OF HISTORICAL material is a difficult and controversial process. It is impossible strictly speaking to prove the authenticity of any object based on technical information, although it is sometimes possible to find the chronological age of the material employed. The manufacture of the object can rarely be dated with absolute certainty or precision based solely on scientific observations, and the dating of both the material and the manufacture can never be proved since it is possible to imagine modern craftsmen with a knowledge of ancient technology. The darker side of this pursuit may have much clearer and straight-forward results: it is sometimes possible to prove that an object or material is other than it purports to be by the objective dating of the material or by discovery of a manufacturing procedure inconsistent with the purported age of the object. Sometimes documentation can date an object and place it unambiguously in its historical context. Most frequently it is necessary to come to a conclusion concerning authenticity by means of considerations from more than one discipline—stylistic analysis, historical documentation, elemental analysis, visual and microscopic examination—which, taken together, present a picture consistent with a particular time, place, workshop or worker. Reading all these cues to form a coherent and consistent picture is gradually becoming more and more difficult owing to the high level of specialization needed to master the several disciplines involved. The collaboration of scientists and art historians becomes especially necessary in problem areas where contradictory evidence and opinions give an ambiguous assessment.

Such a problem area is found in a group of silk textiles usually referred to as “Buyid Silks” (see Figs. 1–4). These silks are said to have been found in 1925, during excavations in Bibi Shahr Banu, near Rayy, Persia. Some of these silks received extensive technical scrutiny with respect to pattern, calligraphy, use, weaving techniques and dye analysis in 1973–74.1,2 The absence of decisive pronouncements concerning the chemical analyses of the textiles was most unfortunate; analytical methods employed and uncertainties reduced the value of objective statements concerning authenticity. Dyes were analysed by thin layer chromatography and were matched with chromatograms of known dyes.
The present day state of the art which would utilize high performance liquid chromatography (HPLC) or gas chromatography-mass spectrometry (GC-MS) combinations should give identifications of the dyes (permitting smaller samples than earlier studies) with the likelihood of a more complete structure identification.\footnote{3} Carbon-14 dating gave results for the textiles sampled which proved to be uninterpretable, corresponding to neither the 20th century A.D. nor to the 11/12th century A.D. The present day state of the art for C-14 analysis permits analysis of much smaller samples with no larger uncertainty.\footnote{4} A large sampling of different textiles should be submitted to several laboratories. Finally, metallic mordants were not determined in these studies.

Fig. 1. (upper left). Fragment with equestrian King Falconer. Iran or Iraq, Abbasid Period, 9th C.A.D. The Cleveland Museum of Art, Purchase from the J.H. Wade Fund.

Fig. 2. (upper right). Fragment. Iran, Buyid Period, 10th C.A.D. The Cleveland Museum of Art, Purchase from the J.H. Wade Fund.
In recent studies in our laboratory the feasibility of detecting mordants on textiles has been explored by exposure of small samples to the high energy electron beam of a scanning electron electron microscope (SEM) with subsequent detection by energy dispersive x-ray spectrometry (EDS). Modern mordanted samples of silk, cotton, and wool were analysed successfully for aluminum, iron, copper, tin, and chromium. In Part I of this study cochineal dyed wool samples mordanted with the same mordants were also successfully analyzed for these elements. In this part, results are reported for a small number of “Buyid Silks” now in the Cleveland Museum of Art. Textiles sampled are pictured in Fig. 1. Each sample was taken from uniformly colored threads of the textiles and were analysed by EDS for the presence of metallic elements. The metallic elements found in the samples were calcium, iron, aluminum, silicon and potassium. No evidence of chromium, copper, tin, or zinc was found. These results are compared to results obtained for modern textiles.
2 EXPERIMENTAL

SAMPLES WERE TAKEN FROM SEVEN textile fragments. Individual fibers were separated according to color. A single fiber of each color was carbon coated with approximately 15 nm of spectroscopically pure carbon in an Edwards vacuum evaporator and viewed in an Amray 1600T scanning electron microscope with a Kevex EDS spectrometry system. The collection conditions were: 20 kV; 200 seconds; area scanned was full fiber width at about 1–2000 magnifications. The samples were analysed as received, without washing or cleaning. Samples appeared to be clean and unsoiled.

3 RESULTS AND DISCUSSION

TABLE I lists the textiles and acquisition numbers of the silk textiles studied. The color of the fiber taken from each textile is also given and the elements found are shown in descending order of abundance. Each sample showed the presence of sulfur as would be expected from silk. The level of sulfur appears to be slightly lower than that found in modern undyed mordanted samples examined in earlier studies with the exception of B-5-a and B-5-b. It is possible that this is the effect of aging (loss of sulfur) or the effect of dyeing or mordanting. The observed weight percent of any element will obviously decline in the presence of added matter. The weight percent in all samples reflects only weight percent of elements above the atomic weight of fluorine and not the weight present in the sample. The brown and gray fibers appeared to have significantly less sulfur than the other colored fibers. Lowered sulfur content of proteinaceous fibers has often been associated with aging.

Table I also indicates the presence, at least in trace amounts, of aluminum and iron in all fibers except B-5-b, undyed.

Table I Historical Silks: Results of EDS Scans

The judgment as to whether the aluminum or iron has been used as a mordant or was present from some other source was tentatively based on the ratio of metallic element to sulfur rather than the absolute value of the element (Table II). A similar procedure was used successfully for mordanted, dyed modern wool samples on which sulfur was also used as an internal standard (see Part I). A “yes” entry was made for aluminum when the ratio of aluminum to sulfur was ca. 2:1; a “?” was entered, possibly present, when the ratio of aluminum to sulfur was ca. 1:1; “(-)”, probably absent was entered when the ratio of aluminum to sulfur was less than 1:1. For iron “yes” was entered when the ratio was much greater than 2:1; a “?” was entered when the ratio was ca. 2:1; “(-)”, probably absent, was entered when the iron to sulfur ratio was ca. 1:1; and “-“ was entered when the iron to sulfur ratio was less than 1:1. It may be observed that the brown colors were achieved in more than one way (cf. B-2-c, B-3-c iron mordant; and B-4 probably neither aluminum nor iron). Finally it may be observed that calcium was present in very substantial quantities in all samples. It was usually the most abundant element indicating the possible
presence of calcarious material associated with the surface of the textile. A group of mordanted (undyed) modern silks studied previously as standard also showed substantial calcium in EDS scans but approximately half the amount observed in the sample described here. The consistently high percentages of silicon in the scans indicates the presence of siliceous materials as well. The presence of iron and/or aluminum associated with the siliceous or calcarious material rather than as mordant cannot be excluded; nor the trace presence of aluminum and/or iron associated with some additive (e.g., sumac or tannin, as discussed at some length in ref. 1). It should also be added that sulfur as part of the proteinaceous backbone and sulfur as adventitious material (mordant, salt, soil, etc.) cannot be distinguished.

Table II Presence of Metallic Mordant on Historical Silks

The foregoing technical information illustrates some points made in the introduction. Authentication of the materials under discussion is not possible based on the data obtained. However none of the elements detected suggests a technology in the mordanting procedures at odds with analyses of other archaeological material. In order to demonstrate a late date for these textiles further analyses would be required. Since the technology is now available to do mordant analyses, dye analysis, and C-14 dating on micro-samples it would be a valuable contribution to the study of textile technology to continue this investigation.

We plan to enlarge our study of mordants on historical textiles; we are also planning a study of metallic yarns and weighted-silk fabrics.

4 CONCLUSIONS

1. Metallic elements detected on all colored silk fibers of the group of textiles studied were calcium, aluminum, iron, silicon, potassium.
2. Undyed silk showed the absence of aluminum and iron.
3. The metallic elements chromium, tin, copper, and zinc were absent from the silk fibers of the group of textiles studied.
4. Judgments as to the presence or absence of metallic elements as mordants were made by using sulfur as an internal standard.
5. This group of samples indicated a larger weight percent calcium than a group of modern undyed mordanted samples studied previously.
6. This group of samples indicated a lower weight percent sulfur than a group of modern undyed mordanted samples studied previously.
7. The data obtained do not permit the dating of the textiles; but the elements detected by EDS suggest mordanting materials consistent with those found on ancient textiles.
REFERENCES


ACKNOWLEDGEMENTS

We would like to thank the J.H. Wade Fund of The Cleveland Museum of Art for permission to publish the photographs.
IDENTIFICATION OF DYES ON OLD TEXTILES

Helmut Schweppe

ABSTRACT—A method for the differentiation of natural from synthetic dyes on textiles is discussed, and a simple method for the identification of natural dyes on old textiles is established. Identification is accomplished by the preparation of lakes of the dyes and their color comparison with lakes of known dyes. Thin-layer chromatography for the identification of certain red dyes and yellow dyes is also discussed, and several examples of identification of unknown dyes are described.

1 INTRODUCTION

ONLY A FEW EXPERTS are capable of identifying dyes on old textiles, because most of the methods currently used require expensive apparatus, are time-consuming, and can be evaluated only by people with much experience, or because the necessary collection of authentic samples is not available. I wish to introduce here a method of analysis that is simple, quick, and cheap and is suitable for identifying the most important natural dyes on textiles. However, even this method cannot be carried out without making color comparisons, and I have therefore included a list of suppliers of natural dyes and books on dyeing with natural dyes (Appendices 1 and 2).

In contrast to methods previously known, I identify the natural dyes on the fibres, without taking them up into solution. Many of the natural dyes are mordant dyes, present on the fibre as insoluble lakes, for example aluminum lakes. In such cases one can form different lakes by boiling with aqueous solutions of tin, aluminum, iron, copper, or uranium salts, and then one obtains a series of lakes of different shades. By making comparisons with known dyeings it is very often possible to make an unambiguous identification of particular natural mordant dyes. This method of analysis is really based on the method of dyeing whereby the color is first developed on the fibre. This method of dyeing with mordant dyes is used when a metal salt is not suitable for direct mordanting of the fibre. For instance, one can dye wool mordanted with alum and then treat it with an aqueous solution of, say, copper sulfate, forming the copper lake on the fibre.

I shall give a short sketch of the method of analysis and then enlarge on this with the aid of specific examples. However, I should first like to mention some preliminary tests, which in some cases can give important indications.
2 PRELIMINARY EXAMINATION

A SMALL SAMPLE of the colored fabric is first boiled in a 1% ammonia solution, in order to remove soil and finishes. Most natural dyes do not run when subjected to this treatment, since they are usually mordant dyes, that is to say they are present in the fabric as insoluble lakes. Indigo is also fast to dilute ammonia. Most of the earlier synthetic dyes made prior to the end of the 19th century run considerably. The same observation is made by textile restorers when they wash carpets with anionic surfactants in ammoniacal solution: if they see that no dye runs they draw conclusions about the presence of natural or synthetic dyes.

Prior to testing the fabric sample is washed with water and then with methanol, pressed between filter papers and set aside to dry.

A small piece of the cleaned dyeing is boiled successively with water, ethanol, glacial acetic acid, and a 20% ammonia solution. The material should be thoroughly rinsed in water before being transferred to the ammonia solution. The extents to which the various extracts are colored allow conclusions to be drawn about the types of dyes present. Synthetic acid and direct dyes are extracted by water and by ammonia solution. Synthetic basic dyes are extracted by ethanol and glacial acetic acid. Indigo (natural or synthetic) is extracted by glacial acetic acid.

Most of the natural dyes are extracted only slightly or not at all. There are a few exceptions however, one of which is provided by safflower, whose most important color constituent is carthamic acid. The red carthamic acid loses its color irreversibly when boiled with ammonia, while the safflower yellow that accompanies it goes into solution without change in color. Indigo extract is also extracted to a considerable extent by boiling ammonia. This dye, which has been made by treating indigo with sulfuric acid since 1740, consists principally of indigo-disulfonic acid.

When a synthetic dye is believed to be present because the color is extracted by water and ammonia, or ethanol and glacial acetic acid, simple dyeing tests can be used to indicate whether it is an acid, basic or direct dye. The most strongly colored extract is evaporated to dryness and the residue is taken up in a little water. The solution is divided in two portions; one is acidified with acetic acid, and to part of the other (5 ml) a 5% sodium sulfate solution (1 ml) is added. The solutions are tested on wool and tannin-mordanted cotton. If the wool is stained more strongly by the acid solution than the cotton, an acid dye is present. If the cotton is dyed more strongly, a basic dye is present. A direct dye can be recognized by the fact that it easily goes onto unmordanted cotton from the neutral solution containing sodium sulfate.

Two simple tests can be used to confirm the presence of synthetic dyes. If the
ammonia extract is strongly colored and the color disappears when the extract is shaken with a little zinc powder at room temperature, the dye is an azo dye. If a few drops of concentrated sulfuric acid are poured over a small portion of a dyed fabric and observed for a few minutes, the acid may develop an intense color (red-violet, blue, or green); and if it does so, this is a certain indication of synthetic dye.

3 COLOR REACTIONS FOR THE IDENTIFICATION OF NATURAL MORDANT DYES

THE PRINCIPLE of the reactions described here is that natural mordant dyes form lakes of various colors with tin, aluminum, iron, copper, and uranium. In addition, treatment of the tin lakes with 20% ammonia solution sometimes results in very striking color changes that can lead to the identification of certain dyes, such as orchil or sandalwood. The complete set of six colors is usually unique and provides a rapid and simple means for identifying many natural mordant dyes, provided of course that comparison sets obtained from authentic samples are available.

It is usual to form the tin lake first, since treatment with a strong solution of stannous chloride destroys the color of most acid and direct azo dyes and of acid metal-complex dyes, thus providing an additional indication that a synthetic dye is present.

The stannous chloride reagent is prepared by dissolving stannous chloride dihydrate (1 g) in concentrated hydrochloric acid (1 ml) and diluting with water (4 ml). The procedure is to take a small portion of the fabric that has been cleaned with dilute ammonia solution, boil it in the stannous chloride reagent, allow it to stand in the reagent for 10 minutes, wash it thoroughly with water (until the washings are neutral) and divide it into halves. Drying the treated material for this and the following tests can be assisted by washing it with methanol and then pressing it between filter papers. One half is dried and set aside for comparison purposes. The other half is treated with 20% ammonia solution.

The other lakes are formed similarly by treating four separated portions of the clean sample with 2% aqueous solutions of alum, ferrous sulfate, copper sulfate, and uranyl acetate. As in the formation of the tin lake, the solutions are boiled and then allowed to stand for 10 minutes before the material is washed with water.

The following figures illustrate the various lakes formed by natural dyes of more than local importance that are, or were, used for dyeing textiles. The dyes are grouped by color, since this is the most obvious classification for the analyst.
4 YELLOW

FIGURE 1 shows the lakes formed by the yellow natural dyes that are most frequently encountered: weld extract, quercitron, Persian berries, old fustic, turmeric, and kalama. Shown are the colors of the aluminum, iron, copper, and uranium lakes of the dyes just mentioned, and also the colors of the tin lakes both before and after treatment with ammonia. In practice the dyes are usually in the form of the aluminum lake in the fabric, so that boiling with alum solution seldom changes the yellow shade, except perhaps to brighten it through soil removal. The lakes whose colors differ distinctly from the others are marked with a cross.

Looking at Figure 1 one can see that only the tin lakes of quercitron and turmeric are orange. When the tin lake of turmeric is treated with ammonia it turns brown at first and then becomes yellow when washed with water. That of quercitron turns deep orange when heated with ammonia. These observations are sufficient to distinguish the two dyes from the other four. Old fustic and kalama both have orange-yellow tin lakes, but can be distinguished by the behavior of these lakes when treated with ammonia and also by the colors of their iron and copper lakes. Weld extract and Persian berries both have yellow tin lakes, but can be distinguished particularly by the behavior of these lakes when treated with ammonia and by the different colors of their copper lakes.

5 ORANGE AND BROWN

FIGURE 2 shows the lakes of the commonest orange/brown natural dyes. These
include young fustic (the most commonly-encountered orange natural dye), henna, annatto, walnut-shell, and cutch. Here too you can see that the colors of the individual lakes can be very different. Henna dyeings can be distinguished by the color of the iron lake, and annatto dyeings by the color of the uranium lake.

An important point to note about brown fabrics is that they are sometimes made from brown wool, and scarcely change color when treated with the various metal salts.

6 RED

FIGURE 3 shows the lakes of the most important red natural dyes: madder (the most commonly-encountered natural red dye), orchil, cochineal, kermes, lac dye, redwood, sandalwood, and safflower. Madder can be recognized by its orange tin lake. Orchil can be identified with certainty by its failure to form colored lakes with tin and the intense violet formed on subsequent treatment with ammonia. Redwood can be recognized by the intense red solution formed when the material is treated with stannous chloride reagent. Sandalwood can be recognized by the change from red to almost black when the tin lake is treated with ammonia and the reversion to red when the ammonia is washed out by water. Safflower dyeings are bleached by treatment with stannous chloride, and remain colorless when subsequently treated with ammonia. Cochineal, kermes, and lac dye cannot be distinguished by means of their lakes; here it is necessary to make use of thin-layer chromatography.
THE COLORS OF THE LAKES formed by the two natural black dyes logwood and tannin are shown in Figure 4. The two types of black can be distinguished unambiguously by treatment with stannous chloride. Logwood blacks change to violet, and the solution is colored an intense magenta. Tannin blacks lose their color when boiled with stannous chloride; the color is not restored on treatment with ammonia. They also lose their color when treated with 10% sulfuric acid.

8 MIXTURES OF NATURAL DYES AND INDIGO

IF THE FABRIC has a green or violet shade obtained by the use of natural dyes, and in the preliminary test a blue color is extracted by boiling glacial acetic acid, one should test for indigo by the method described by Hofenk-De Graaff (“A Simple Method for the Identification of Indigo,” *Studies in Conservation*, v. 19, [1974]: 54–5). If the result of the test is positive the indigo should be removed from the fibre by repeated boiling with dimethylformamide until the solvent remains colorless. Once the indigo has been removed the yellow component (in green dyeings) or the red component (in violet dyings) is left behind and can be identified by forming the various colored lakes as described above.

An interesting example of the method just described was the examination of a fragment of Coptic fabric dating from the 6th century that had been dyed with indigo and madder, a mixture that has been called Egyptian purple. The color of the original sample was dark violet. Treatment with ammonia did not change the
color but extraction with dimethylformamide took out the indigo, leaving the red on the fibre. The colored lakes formed by the red dye matched those of the red obtained from wild madder (*Rubia peregrina*). It was confirmed by thin-layer chromatography that ordinary madder from *Rubia tinctorum* was not present, since only purpurin (1, 2, 4-trihydroxy-anthraquinone) was found: alizarin (1, 2-dihydroxyanthraquinone) was absent.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Sn–Lake</th>
<th>NH₄OH</th>
<th>Al–Lake</th>
<th>Fe–Lake</th>
<th>Cu–Lake</th>
<th>U–Lake</th>
</tr>
</thead>
<tbody>
<tr>
<td>Logwood</td>
<td><img src="image" alt="Logwood Solution: magenta" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tannin</td>
<td><img src="image" alt="Tannin Solution: orange" /></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 4. Lakes of black natural dyes.](image)

**9 RAPID TEST FOR DISTINGUISHING AMONG MADDER, COCHINEAL, AND KERMES**

ONE TAKES A SMALL PORTION of the red dyeing, adds a few drops of concentrated sulfuric acid, and waits for a few minutes until the dye has colored the acid. Madder gives a dull red solution that fluoresces orange in ultraviolet light; cochineal (and lac dye) gives a magenta solution; kermes gives a dull red-violet solution. If a few milligrams of boric acid are then added to the sulfuric acid, color changes may be observed. If cochineal (or lac dye) is present the color changes to blue; if kermes is present the color changes to brownish-violet; if madder is present there is no change in color. If the solution is diluted with about ten times its volume of water and shaken with a little ether, madder and kermes go into the ether phase, coloring it orange; cochineal (and lac dye) remains in the aqueous phase but can be extracted with pentanol.

The ether and pentanol extracts can be washed throughly with water to remove acid and used for identification of the dyes by means of thin-layer
chromatography. The latter is the only simple way by which one can distinguish between cochineal and lac dye.

10 THIN-LAYER CHROMATOGRAPHY

THIN-LAYER CHROMATOGRAPHY can be carried out with minute samples, needs little apparatus, and is quick. If a natural dye contains several red-colored substances, thin-layer chromatography should be the method of choice. This is particularly true of identifying hydroxyflavone and hydroxyanthraquinone dyes.

My experience has been that for the separation of natural dyes the best material for the stationary phase is polyamide powder. Figure 5 shows the chromatograms of various yellow natural dyes of the hydroxyflavone class. Polyamide was used for the stationary phase, and the mobile phase consisted of a mixture of chloroform, methanol, butanone, and formic acid in the proportions by volume of 6:2:1:1. To show up the spots the chromatogram was sprayed with a solution of uranyl acetate. The chromatograms shown include those of old fustic, young fustic, weld, quercitron, Persian berries, and dyers' broom. the two natural dyes weld (no. 3) and dyers' broom (no. 6) contain luteolin as the principal coloring material, and are included in the Color Index as Natural Yellow 2.

Fig. 5. Thin-layer chromatography of yellow natural dyes.
Figure 6 shows the chromatogram of natural red dyes containing hydroxyanthraquinones. The stationary phase was polyamide but two different mobile phases were used. The chromatograms on the left were developed with a mixture of methanol and formic acid in the ratio 95:5, while those on the right were developed with a mixture of butanone, methanol, and formic acid in the proportions 65:30:5. Both sets of chromatograms include madder, wild madder, soranji (a type of Indian madder), cochineal, kermes, and lac dye. You can see that the first mobile phase madder and wild madder, and cochineal and lac dye can be differentiated.

Fig. 6. Thin-layer chromatography of red natural dyes.

An example of the use of this method was the investigation of a piece of satin
that the dye used was Polish kermes, since this is the only dye containing both these acids.

Another example was the study of a piece of an old Ushak carpet said to have been made about 1600. The various dyes were identified by means of their colored lakes. The red was madder, the brownish-yellow weld, and the green was also shown to be weld after the material had been extracted with dimethylformamide.

The results obtained by forming the colored lakes were confirmed by thin-layer chromatography. Chromatograms of the dyes from the red, yellow, and green knots showed clearly that the chromatogram of the red is identical with that of madder and that the yellow and the yellow component of the green agree with the chromatogram of weld.

A further case was furnished by the examination of a piece of a 19th century Kazak carpet with two shades of red, which we will call red 1 and red 2.

Red 1 was identified as a madder dye, while red 2 was an acid red azo dye. Boiling with dilute ammonia had almost no effect on red 1, only traces of red going into solution. Red 2 however could be almost quantitatively removed from the fibre with ammonia. Red 1 could be identified as madder by means of comparison of the colored lakes. Red 2 was found to be Crystal Ponceau 6R by color reactions and paper chromatography. This dye is listed in the Color Index as Acid Red 44, whose synthesis was discovered by Hoffmann in 1883. In this case the date of discovery of the synthetic dye showed clearly that the carpet was not made before 1883. The synthetic red was used all over the carpet for various ornaments, indicating that it was not just used for restoration work.

This last example in particular demonstrates that very useful results can be obtained without employing very elaborate equipment or methods.

APPENDIX

1 APPENDIX 1: SUPPLIERS OF NATURAL DYES/DRUGS

Paul Müggenburg, Drogen and Vegetabilien, Einfuhr- und Ausfuhrhandel, Wandalenweg 24, 2 Hamburg 1, West Germany
Hellmuth Carroux, Import-Export, Drogen-Talkum-Schwefel-Gummiharze-Schellack-Kernmehle, Neuer Wall 37, 2 Hamburg 36, West Germany
C. E. Roeper, Fach-Importeur, Drogen-Harze-Quellstoffe, Klosterallee 74, 2 Hamburg 13, West Germany
Etablissements A. Longeval S.A., Herboristerie en gros-Drogues-Produits chimiques-Essences-Gommes, Grand'Rue, 48, B-7870 Deux-Acren, Belgium
APPENDIX 2: BOOKS ON COLORING WITH NATURAL DYESTUFFS


NOTES

1. The 20% ammonia solution can be replaced by 25% ammonia solution (d = 0.91), which is the solution usually supplied commercially.

2. Dissolve tannic acid (0.6 g) in water (100 ml), heat the solution to 60–70°C, and immerse cotton yarn (10 g) in the hot solution. Set aside the whole for 2 hours until it is cool, then remove the cotton, squeeze it free of liquid, immerse it in a cold solution of tarter emetic (prepared by dissolving 0.3 g antimony potassium tartrate in 100 ml water) for 20–30 minutes, and finally rinse it thoroughly with water. After the yarn has dried in air small portions of it can be used for dying tests.
FIBER IDENTIFICATION IN PRACTICE

Martha Goodway

ABSTRACT—Brief case studies of the problems in identification of a wide variety of ethnographic and archaeological fibers are given. The strategy of identification varied with the purpose (choice of treatment, assessment of damage or identification of its cause, or authentication) but most of all with the condition of the fibers. Fibers from ethnographic or archaeological sources tend to be aged, and are sometimes fragmentary or decayed, fossilized or charred. With fibers in such condition, the simpler methods of preparation for microscopic observation were found more successful than the classical biological methods of soaking, clearing and staining. Not all fibers could be identified. Fur fibers from characteristic areas of the pelt were usually diagnostic as to species as well as to genus. Vegetable fibers were often not morphologically specific to species. Unless "guide elements" were present, or special limitations on species distribution were known, the identification of the genus of a vegetable fiber was often the best that could be done. Instructions for an optical test for flax, and a report form for the observation of fur and wool fibers, are included. The identification of fibers in archaeological and ethnographic objects in practice is a great deal more difficult than the texts on fiber identification lead one to believe. For example, the solubility tests which are a mainstay of synthetic fiber identification are of no use since archaeological and ethnographic fibers are natural ones. The various chloroiodine stains, Herzberg's and others which stain cellulose red, violet or blue and ligno-cellulose yellow, seldom act on old and dessicated fiber unless at nodes or points of fracture. These and many other methods recommended for use with textile fiber identification often give equivocal results when applied to archaeological or ethnographic material. Experience has shown that complicated and lengthy preparation procedures do not repay the time and effort they require and, more importantly, often fail altogether. Perhaps the single most useful generalization that can be made about archaeological and ethnographic fiber identification is that not all fibers can be identified on the basis of the information we now have. Nevertheless, a surprising number of these fibers can be identified, or at least classified, by microscopical observation and a few simple tests. The following examples may suggest useful approaches in dealing with material of this sort.

IN PRACTICE, THE FIRST STEP in identification of natural fiber was to classify it by material, whether of animal or vegetable origin. To differentiate between cellulose and protein fiber where this was not obvious, an ash test detected protein by the characteristically nitrogenous odor of burnt hair. If it was not protein then the twist test quickly differentiated right-hand vegetable fibers such as flax and ramie, from the left-hand fibers such as hemp, jute, and most ethnographic fibers. Right-hand fibers were also distinguished from left-hand fibers microscopically, by a method described in the Appendix.

In the twist test, care was taken that only a single fiber was wetted so that the
direction it rotated upon drying could be clearly observed. Flax, a right-hand fiber, was used as a comparison standard in these tests so as to establish the direction of rotation. Flax rotated swiftly on drying, but the left-hand fibers were often more subtle. If not repeated several times, the test could be misleading. An example of this occurred in examination of a pulley rope from the sunken warship Tecumseh, in which a red marking thread was found. The naturally colored fibers of the rope consistently gave a slow but distinct left rotation on drying, confirming their microscopical identification as manila hemp. The red-colored fibers, repeatedly wetted and dried, gave contradictory results. When this fiber was also examined microscopically (Figure 1) it was obviously cotton. Cotton, a seed hair, has the form of a collapsed hollow tube. It collapses randomly, with a right-hand twist in one short section followed by a left-hand twist in another; this randomness of twist was faithfully reflected in the contradictory results of the twist test.

![Figure 1](image1.png)

Fig. 1. Collapsed-tube morphology and random twist characteristic of cotton fiber. 500x, 70° cross polars.

With natural fibers, microscopy was the method of choice for identification because the morphology of these fibers can be distinctive. Unfortunately, the differences in morphology among some species are not always sufficiently distinctive to allow precise identification since nature tends to use the same repertoire of cells in constructing the fibers of different plants.

In mounting a fiber for microscopical observation, care was taken that adventitious material—such as cotton from clothing, or processed wood fibers from tissue—were not embedded with the sample in the preparation. Most fibers from objects already bore a large amount of extraneous material, which was distracting and could be misleading. It was also possible for an entire sample to consist of adventitious material. For example, a long, black animal fiber which had come from a cave being excavated proved to be a bristle from a brush used as a tool in excavation.

It has become customary to use a mounting medium such as Monsanto's Aroclor 5442, which is permanent and has an index of refraction about a tenth higher than that of natural fibers, whose indices in general are about 1.54 or 1.55, as a
convenient method of enhancing contrast at the surface of the fiber. Some degree of contrast is essential so that surface detail becomes visible. These high-index media contain nasal irritants and when heated the vapours should not be inhaled, in addition to observing the rules for the use of PCBs imposed by the Environmental Protection Agency.

The most usual stem or bast fiber encountered was flax. Since linen was in common use before the spread of cotton, its identity is sometimes useful in problems of dating. In one such case a conservator was interested in the date of a repair to the joint of an 18th-century harpsichord stand, where a piece of cloth had been used as a filler. Flax fiber was identified, and the use of linen indicated to him, along with other observations, that he was dealing with an early repair. In another case, the presence of flax was useful in establishing the late date of a Plains Indian ceremonial object.

When fresh, stem fibers were generally more flexible than the fiber from leaves (hard fiber). Most vegetable fiber samples examined were left-handed. Of the commercial stem fibers, only flax and ramie are right-hand fibers. An optical method for determining the direction of the cellulose, whether it is right or left handed, mentioned by Luniak1 proved to be particularly useful, in addition to the observation of a fine lumen visible at the center and the cross hatchings called nodes, in identifying flax. See Plates 1–3 and the Appendix on the red plate test for details of this method.

Fig. . Flax fibers in crossed polarized light. Note vertical fiber which is nearly totally extinguished (dark). 165x, 90° crossed polars.
Silk from very early objects was usually in excellent condition. It was more recent silk, especially weighted silk of the 19th century, that showed signs of splitting in characteristic green-stick fracture (Figure 2). Silk that appeared in this condition was already recognized by the conservator as brittle, but cracks at the cross-over
over indentations in silk fibers also gave a characteristic silhouette to silk (Figure 4) in addition to its triangular cross section.

Fig. 2. Partial fractures in silk fiber, indicating brittleness. Green-stick fracture is characteristic of silk. Crossover indentation in lower fiber. 500x, 73° crossed polars.

Fig. 3. Partial fractures at a crossover indentation, an early indication of brittleness in silk. 500x, 71° crossed polars.
Fig. 4. A pair of crossover indentations characteristic of silk. 500x.

It is from such characteristic silhouettes that it was possible to classify fibers, if not always to identify them precisely, when they were charred or fossilized. Once charred, a fiber transmits no light, so only silhouette and size remained to be observed. It became routine to measure the width of every fiber as a check on tentative identifications. This dimension was included in all reports of microscopical observations, however brief.

If the material was a bast or leaf fiber, but not flax, there was a more difficult problem of identification and not one that could be solved in every case. These fibers could be particularly featureless. In such a case what in English are called “guide elements,” from the German “Leitelemente,” were searched for. These associated structures, such as parenchymatous cells or so-called baggy cells in tula ixtle, spiral vessels in sisal and some other agaves (Figure 5), stem hairs in esparto (Figure 6), and also crystals, such as oxalate crystals in hemp, were often diagnostic.
Fig. 5. Spiral vessels characteristic of sisal and other agaves. These occurred in *Tula ixtle*. An example of a “guide element.” 200x.

Fig. 6. Stem hairs characteristic of exparto, shown here in cross section. Another example of a “guide element.” 325x.

Cross-sections adequate for identification were prepared quite successfully without a microtome using equipment no more elaborate than cork, a C-clamp, and a razor blade. In practice a smooth, featureless area of the cork was chosen and the fibers were clamped between two pieces. Thin slices containing the fibers were then carefully shaved off. Sometimes this procedure was made easier if the fibers were glued to the cork first. The mounting medium itself was used as the glue. Hand-sectioning succeeded even with a single fiber of less than 15 μm diameter (Figure 7a and b). In most cases cross sections were not required because the cross section could be inferred by slowly focusing up and down upon the fiber at fairly high powers. This “optical sectioning” was a quicker and much less tedious procedure than cutting cross sections.

In the preparation of vegetable fibers the usual biological methods, such as soaking in order to separate individual cells, were either unnecessarily complicated or actually misleading. The cells from different comparison vegetable fibers tended to look very nearly alike. For example, cells of known specimens of agave resembled
those of coir or of cotton. When applied to these separated cells, the red plate test also was not particularly informative. So-called “clearing” of thick vegetable fibers in methyl salicylate did render them more nearly transparent for microscopical observation, and was compatible with the Aroclors, for which methyl salicylate is a solvent.

Ethnographic samples were particularly difficult to identify because the necessary references in fiber atlases were wanting. Comparison material from herbarium samples in the National Herbarium, housed at the Smithsonian, were equally dessicated and as difficult to prepare as ethnographic material. The identification of the species of all but a few of the non-commercial vegetable fibers was not possible from their morphology. Matthews proved to be the single best source of the possibilities to explore. The situation as far as the scaled fibers—wool and furs—were concerned was, however, somewhat better.

The scales on wool or fur fibers were themselves an insufficient basis for identification, but the pattern could be used as confirmation. The scale pattern was best observed directly, using a high-index medium rather than taking a cast of the scales by pressing the hair into a film of dried but still plastic clear nail polish (Figure 8) or some other casting medium, then removing the fiber. The result of attempting a cast of a fiber which was not fresh was usually to pull the scales off the fiber, if not to break it altogether.

Fig. 7. Cross section made by hand using a razor blade, with fiber clamped in cork. This example is vicuna, and is only 20 μm thick. 283x. a: end view; b: side view.
Keys for the identification of the fur of animals of specific geographical areas are listed in the Appendix on fur and wool fibers. The keys were useful outside their geographical limits for the larger species, which have fewer members but wider ranges. The use of a key suggested that the fur from a single pelt large enough to be used as a saddle pad was from a particularly large marten found in the West, the *Mustela caurina* (Figure 9). This is a marten so uncharacteristically large for its genus that at first an expert on mammals failed to name it as a possibility. The keys correctly directed attention to the mustelidae, which was confirmed by the expert once he saw the entire pelt. The keys had several limitations. They were usually based upon the longest guard hair, occurring only at the midline of the back. Another limitation was that the underfur of most animals is closely similar. Color was sometimes a clue, but burial tended to stain fibers various shades of brown.

Sometimes when attempting fiber identification it is possible to identify the dye as well. For example, in an early Spanish writing box from Peru pieces of dark blue...
wool was very fine. The scales were ashed, using a red-hot dissecting needle on a short length of the blue wool fiber while it was resting on a microscope slide. The scales were separated by this procedure, and quite unexpectedly a blue haze condensed on the cold glass slide (Figure 10). This condensate suggested that the blue dye might be indigo, since indigo sublimes at temperatures above 300°C. As confirmation, another blue fiber was bleached in nitric acid and the resulting orange crystals were identified as isatin by their optical characteristics. The fiber itself (Figure 11) was differentiated from sheep wool by its even pigmentation, faintness of scale pattern, scarcity of medulla, and a round rather than oval cross section, all characteristic of camel hair. It is easy to be misled by current-day criteria of value and utility in projecting the possible identities of a fiber sample. This wool sample came from one of the South American camels, the vicuna, and a material one would not expect to find used in so offhand a way. Also possible are mixtures of fibers, and of later mending materials.

Fig. 10. Condensed indigo, sublimed from ashed fiber of dyed vicuna. 433x.

Fig. 11. South American camel wool (vicuna), bleached of indigo dye in nitric acid. 283x.

Sometimes microscopical examination revealed insect damage (Figure 12). In other
fiber was not from the seal but from the caribou (Figure 13). Though perishable, because its very thin cortex results in a brittle fiber, it was an excellent choice for a parka because caribou fur is in fact warmer than seal.

Fig. 12. Damage to horsehair by carpet beetles, typical of insect damage. 17x.

Fig. 13. A very thin cortex is typical of the fur of the deer family. This example is caribou. 500x.

Several quite different categories of fiber are barbed. For example, the dandelion is barbed with the barbs alternating on each side of the fiber (Figure 14). It differs from feather fibers, where the barbs are opposite each other. Thus opposing barbs on fibers in a thread described as “mammal yarn” from a tapestry from Spiro Mound, Oklahoma (Figure 15) indicated the use of feathers. Until this sample was examined microscopically, feathers spun into thread had not been identified in Indian textiles east of the Pacific Northwest.3
Fig. 14. Dandelion fiber, with alternating barbs. 500x.

Fig. 15. Feather fibers, with opposing barbs. From thread of tapestry, Spiro Mound, Oklahoma. 500x.
description were excavated in Labrador from a level just above the permafrost. No matter what the magnification, their microstructure could not be brought into focus, and it seemed that the microscope would require a major realignment. When a preparation containing fresh comparison material was observed, however, the fresh material came into sharp focus. Apparently the excavated fibers had decayed to the point where the microstructure had lost its definition so that in effect it was no longer there. Excavated cotton fiber has also been observed whose surface was so distressed that it had an appearance very similar to the surface scales found on wool or fur fibers, except that those of wool or fur would have been more regular in pattern.

These examples demonstrated some of the problems encountered when attempting the identification of fibers from archeological or ethnographic materials. Even where these fibers eluded precise identification, it was possible to make a general classification and an assessment of their condition which made the effort to identify them worth while.

REFERENCES


APPENDIX

1 APPENDIX

1.1 THE RED PLATE TEST

LUNIAK, FOLLOWING HERZOG, suggested the possibility that the direction (right- or left-hand) of cellulose could be determined optically using a polarizing microscope. Specifically, he states:

For the differentiation of flax and hemp fibres their opposite behaviour in polarized light between crossed Nicol prisms after insertion of a selenite plate Red I in the 45° position may be noted. Flax fibres display addition colours when parallel to the plane of the polarizer, and subtraction colours when at right angles; hemp fibres vice versa. A part of the fibres may be neutral; in general the differences are not so pronounced with hemp fibres. Comparison with known samples is advisable.
In order to put this suggestion into practice it is necessary to have a polarizing microscope with a compensator slot and a first-order, so-called red plate. Actually, the color of the field of view when the polars are crossed and the red plate is inserted in the compensator slot may be more accurately described as magenta. It is more convenient if the microscope, as do most polarizing microscopes, has a rotating stage.

Since bast and leaf fibers are polycrystalline they do not behave optically as neatly and unequivocally as a single crystal, and complete extinction under crossed polars does not occur in these fibers. For this test an individual fiber is more likely to give a definite response than a bundle of fibers, but not all individual fibers are good subjects. Colors under the red plate often cannot be observed when the fiber is in the 45° position which gives maximum brightness under crossed polars alone. To yield diagnostic colors when the red plate is inserted, the fiber should be observed first under crossed polars in a “nearest-to-extinction position” (since they do not extinguish completely) of 0° or 90° that is, the fiber should be parallel to the optical direction of either the polarizer or analyser. Rather than as an extinction position, this might be described better as the position in which the fiber appears most gray, or darkest.

The fiber to be identified must be observed first without the red plate in order to locate exactly an area of the fiber most nearly totally extinguished by crossed polars (Plate 1). When the red plate is inserted, areas that were black under crossed polars become either yellow or blue (Plate 2). If the stage, with the slide, is then rotated 90° the other color should appear, blue where it was yellow or yellow where it was blue (Plate 3). The colors depend on the orientation of the polarizer, the analyzer, and the red plate. Therefore each time this test is used, the orientation of the optical elements should be determined by using a comparison standard known to be flax. A left-hand fiber will give the same colors but each in a direction 907deg; from that or flax or ramie. In some cases the color shift will not be very distinct. That is why locating those areas of the fiber which are darkest under cross polars before the red plate is put in, and using only those areas for identification is so important.
1.2 IDENTIFICATION FROM

ABSTRACT—Infrared spectroscopy has been used successfully in the characterization of several types of painting materials. Although most often employed with organic materials, the technique can also yield valuable structural information on many inorganic compounds. Several applications of infrared spectroscopy to inorganic pigments are reviewed, the theoretical bases for the spectra of these materials considered, and characteristic spectra presented. The materials discussed include chrome greens, green earths, and chromium oxide and viridian. Synthetic organic pigments can also be readily identified by infrared spectroscopy and one example (phthalocyanine blue) is discussed. All spectra were obtained from minute samples comparable in size to those often available from art objects, and were recorded using a Fourier transform IR spectrometer.

1 INTRODUCTION

ANALYTICAL TECHNIQUES used in the characterization of the materials of painting are many. Those used in a particular case are dependent upon available instrumentation, time or financial considerations, amount of sample available (if sampling can be done), and so forth. If possible, a variety of techniques is often used to characterize the material, the particular combination being determined by the general type of material in question.

Infrared spectroscopy is most widely used with organic materials, since carbon-hydrogen, carbon-oxygen, and other types of bonds which are found in compounds of this category have fundamental vibration frequencies in the infrared region, particularly in the “mid-infrared” which extends from about 2.5 to 25 microns (4000 to 400 cm\(^{-1}\)).* Among the difficulties often encountered when this instrumental technique is employed for pigment analyses are the presence of binding media which may mask or distort the characteristic absorptions of pigments (particularly if the latter are organic compounds), the presence of several pigments which may also mask absorptions or generally make assignments difficult, and sample sizes. Although beam condensors and sample preparation techniques for very small samples are widely available, the quality of spectra obtained from microsamples may often be poor, and weaker absorptions tend to become lost in the instrumental noise. It is often possible to make definite or fairly definite identifications of many painting materials on the basis of the general shapes and intensities of only a few major absorption bands, but in other cases an overall pattern of a large number of peaks is sought, and in these situations the difficulty in separating weaker absorptions from instrumental noise may be a serious problem. These are all factors which limit the use of the infrared technique in studying paint samples.
The spectra in this paper are presented as a function of wavenumber (cm$^{-1}$). In other publications, spectra and positions of absorption bands may be given in wavelengths (\(\lambda\)) rather than wavenumbers. The relationship between these two numbers is: \(cm^{-1} = (104/\lambda)\). The units for \(\lambda\) in this formula are microns (10$^{-6}$ m).

However, infrared spectroscopy has been used successfully for a number of special problems involving painting materials, such as the identification of “copper resinates”\(^1, 2\) and organic lake pigments\(^3, 4, 5\) and the characterization of binding media, including varnishes\(^6, 7, 8\) Special note should be made of the pioneering studies by M.J.D. Low with N.S. Baer on the application of the Fourier transform infrared technique in conservation science\(^9, 10, 11\) Publications thus far by these authors in this field have been concerned with “fingerprinting” natural resins and distinguishing between red lakes prepared on different substrates.

Applications to inorganic pigments have been fewer, perhaps because of the widespread availability of other techniques for these types of materials which in general require smaller sample sizes, including X-ray diffraction, and various elemental analytical techniques (emission spectrography, electron beam microprobe, etc.) But the potential of infrared spectroscopy for the study of certain materials in this class has been shown by C. Grissom in her study of green earths\(^12\) and work has also been published on iron oxide-containing earth pigments\(^13, 14\) There is no lack of reference spectra for materials in this class. High-quality spectra of modern inorganic pigments have been published by the paint industry\(^15, 16\) The literature on the infrared study of minerals is voluminous\(^17\) and much of value to the study of pigments is to be found in that literature since many pigments are minerals or synthetic versions thereof.

The purpose of this paper is to review several applications of infrared spectroscopy, particularly in the realm of inorganic pigments\(^18\) The materials chosen for this study were ones for whose characterization infrared spectroscopy may be particularly valuable. Many of the materials studied were taken from reference collections in the Center for Conservation and Technical Studies; Fogg Art Museum\(^19\) Although very large quantities of most of these were available, all samples were purposely kept small, generally on the order of the size of sample that would often be available from an art object, in order that the quality of spectra that may be expected from such samples is more readily evident. Of the infrared spectrometers available to the author, a Fourier transform instrument was found to give the highest quality spectra with the sample sizes here used. The theory of the operation of this type of spectrometer and details of the instrumentation have been well described elsewhere\(^9, 20\)

2 APPLICATIONS

2.1 Sample Preparation and Instrumentation

ALL SAMPLES were crushed and mixed with spectrographic grade KBr and
pressed into 1.5 mm diameter pellets using a vacuum pump and Perkin-Elmer microdie. The samples were run with the aid of a Perkin-Elmer 3X beam condensor. According to Perkin-Elmer, sample concentrations as small as 10 μg in 1.5 mm KBr pellets will provide good spectra, although in preparing the spectra presented in this paper, sample sizes were usually several times greater than this (up to approximately 50–60 μg in a few cases). The spectra were collected on a Nicolet 7199 FT-IR spectrometer (Nicolet Instrument Corp., Madison, Wisconsin) equipped with a Zeta digital plotter. The spectra were obtained in the 4000–400 cm\(^{-1}\) range using a liquid nitrogen-cooled HgCdTe detector. The resolution in all cases was 4 cm\(^{-1}\), and the number of scans either 128 or 256. All of the spectra were automatically ratioed by computer against a blank KBr pellet. N2 was continuously flowed through the sample chamber in order to eliminate interference from atmospheric H2O and CO2. Residual water not ratioed out is the cause of the sharp band(s) appearing in several spectra at 670–690 cm\(^{-1}\).

Plotting of the spectra was done under the control of the computer. For more convenient comparison of separate spectra or portions thereof various manipulations of the ordinate and abscissa were carried out with the aid of the computer on many of the full spectra.

Particularly with inorganic compounds of high refractive indices relative to the matrix material (for KBr, \(n = 1.56\)), the quality of the spectra may be very poor due to scattering and reflection losses if the particle size is much greater than the wavelength of the incident radiation. This scattering and reflection causes anomalies in the relative intensities of absorption bands, anomalies which are not entirely eliminated until the particle size is considerably smaller than is normally practically obtainable. In an attempt to reduce these effects, the samples studied here were crushed as finely as possible before mixing with the salt, but some lack in the reproducibility of relative intensities of bands from sample to sample of a given material would be expected since particle sizes are probably still rather variable. There are certain other anomalies that may on occasion occur in the spectra of materials prepared in KBr matrices, but these are probably not of much significance in the spectra here recorded.

Theoretically, the pigment samples may be largely recovered from the pressed pellets by dissolving away the KBr salt with water. This is a very tedious operation, but it could be undertaken if the amount of sample available were very limited and other types of examination were necessary.

### 2.2 Modern Synthetic Organic Pigments: Phthalocyanine Blues

IN THIS CENTURY, literally hundreds of synthetic organic pigments and dyestuffs have been created, a few of which are currently routinely used by artists. One of the more widely used class of these pigments are the phthalocyanine blues and greens which were first introduced commercially in the 1930's.
polymorphic forms, the two most common of which are designated α and β. Although the polymorphs may be prepared in well-crystallized forms, amorphous forms are actually preferred by color manufacturers because of their more suitable properties, and consequently X-ray diffraction data may be unobtainable.

In the mid-infrared region, the phthalocyanines give very distinctive spectra which (particularly below about 1700 cm\(^{-1}\)) contain many sharp bands due to stretching deformations of the aromatic ring system carbon-carbon bonds, and in-plane and out-of-plane bends of the carbon-hydrogen bonds in the ring system. Fig. 1A shows the full spectrum of a dry copper phthalocyanine pigment and an expanded portion of its spectrum. Fig. 1B reproduces the spectrum of a copper phthalocyanine oil paint film. The oil medium produces bands at 1715–1732 cm\(^{-1}\) and probably contributes to a general increase in absorbance between 1200–1000 cm\(^{-1}\). This paint is also extended with BaSO\(_4\), which is often the case with the strongly tinting phthalocyanines; the bands at 1186, 1120, 1082, 983, 638, and 610 cm\(^{-1}\) are due to this sulfate compound (see Section 2.C). In spite of these interferences, the pigment is readily identifiable, and the polymorph may be definitely established as α on the basis of the sharp band at 723 cm\(^{-1}\), due to out-of-plane bending of C-H bonds. This band is located at 730 cm\(^{-1}\) in the β modification. The dry pigment is also the α polymorph.

Infrared spectroscopy is a technique widely employed in the analysis of modern synthetic colorants and reference spectra of many of the important pigments and dyestuffs have been published.

2.3 Inorganics Containing Polyatomic Ions

2.3.1 Theoretical Basis for the Infrared Spectra of Polyatomic Ions

MANY TRADITIONAL and modern inorganic pigments, both mineral and synthetic, contain polyatomic ions. Those ions most frequently encountered include carbonate (malachite; azurite; blue verditer; calcite; cerussite; hydrocerussite); sulfate (gypsum; anhydrite; barite or ‘blanc fixe’); and chromate (chrome yellows; chrome orange; chrome greens).

In compounds of these types, the binding forces between atoms within the polyatomic ions are appreciably stronger than those between these ions and the metallic cations in the crystal lattice. As a consequence of this fact, different compounds containing a specific polyatomic ion will exhibit spectra which display general similarities in the mid-infrared frequency range.

The fundamental vibrations of polyatomic ions may be divided into two classes: (1) internal vibrations of the atoms comprising the ion which cause stretching of the bonds between these atoms or deformations of the bond angles (bending); and (2) external vibrations, which are either restricted translations of the entire ion or rotations (usually referred to as librations) of the ion about a certain axis and do not cause distortions of the equilibrium bond distances and angles within the ion.
Fig. 1. Structural formula and spectra of phthalocyanine blue pigments: A. Phthalocyanine blue dry pigment, Krebs Pigment Corp. (Wilmington, Del.), 1935 (Forbes Pigment Collection no. 11). B. Phthalocyanine blue oil paint. Winsor & Newton; scraped from a film prepared on aluminum, 5/1936 (Gettens pigment and resin test panels, Fogg Art Museum).
The external or lattice vibrations, combined with similar displacements of the metallic ions, usually occur at relatively low frequencies (below 300 cm$^{-1}$) in the far-infrared region. The internal vibrations involving the covalently-bonded atoms of the polyatomic ion occur at higher frequencies in the mid-infrared region (but usually below 1500 cm$^{-1}$).

A non-linear polyatomic ion possesses 3N−6 fundamental vibrational modes, where N is the number of atoms in the ion. Ideally, each type of ion has a certain degree of symmetry, and considerations of this symmetry cause some of the fundamental modes to be degenerate, that is, to occur at identical frequencies. In addition, not all of these modes may be active in the infrared region, since a change in the ground-state dipole moment of the configuration is necessary if absorption in the infrared is to occur. On the basis of studies of polyatomic ions in isolation, in which their ideal symmetries are preserved, these fundamental frequencies have been determined for many ions. By convention, the fundamental vibrational frequencies are designated by the usual symbol for frequency, $v$, with numerical subscripts which are assigned according to symmetry considerations and, for vibrations possessing the same symmetries, in order of decreasing frequency.

If the polyatomic ion becomes part of a crystal structure, to a first approximation lattice vibrations may be ignored in considering the internal vibrations. However, if this approximation were correct, then the internal vibrational absorption bands would be very sharp and display little breadth; in reality, these bands are always observed to be rather broad. The broadening is caused by various couplings of internal vibrations and lattice vibrations.

The equilibrium potential energy field of the crystal may be distorted by a lattice vibration, one result of which is the splitting of degenerate internal vibrational modes and the appearance of normally infrared-inactive modes.

The symmetry of a polyatomic ion in the crystal lattice is usually lower than its ideal symmetry due to anisotropic interactions with surrounding cations or neighboring anions, and these interactions also serve to remove the ‘equivalency’ of some of the bonds within the ion, thus causing splitting of degenerate modes.

The potential energy field of the crystal lattice ultimately determines the exact positions of the fundamental vibrations of a given polyatomic ion. Certain regular shifts in these bands have been observed for some polyatomic ions. For example, in carbonates and sulfates, there is a regular relationship between the cationic radius (for cations of similar electronic structures) and the position of the fundamental frequencies, an effect which is probably due to increasing compression of the atoms in the polyatomic ion as the cation increases in size; this compression changes bond strengths.

Thus, as a consequence of several factors, the fundamental vibrational frequencies
of polyatomic ions in a crystalline environment cannot be expected to be identical from one compound to another. Furthermore, the same number of fundamental vibrations would not always necessarily be visible, since degeneracies may be removed to various extents depending upon the precise structure and even the conditions under which the compound crystallized. For identification purposes, a general pattern of intensities and frequencies is sought. In Fig. 2, the vibrational bands of 5 carbonates, 3 sulfates, and 3 chromates are shown. The general spectral appearance of these different ions will be evident from these spectra, but the often small but significant variations in the exact frequencies at which the bands will be found according to the particular compound should also be noted.

2.3.2 Specific Applications

CHROME AND ‘Brunswick’ green pigments, which contain two or more different polyatomic ions, may be at least partly characterized by infrared spectroscopy. These mixed pigments, consisting of Prussian blue, chrome yellow, and often BaSO4 and/or China clay (kaolinite) as extenders, were widely used in the 19th and early 20th centuries. Two samples of ‘Brunswick’ greens with high BaSO4 contents were studied. X-ray diffraction patterns of the two pigments showed only BaSO4 unambiguously. Emission spectrographic analysis indicated that both contained minor amounts of Pb, Cr, and Fe. Fig. 3B is the spectrum of a green pigment found during the excavation of the site of a 19th-century paint factory. Fig. 3C is the spectrum of a green pigment taken from a panel painting probably of 19th century origin. Chrome green pigments of very low BaSO4 content have also been produced, and the spectrum of one of these is given in Fig. 3A.

Prussian blue may be identified in all three by the band at 2070–2080 cm$^{-1}$, which is due to vibration of C≡N in the ferrocyanide ion, Fe(CN)$_6^{4-}$ This is a strong sharp absorption which is particularly suited to the identification of Prussian blue, since it occurs in a region where virtually no other commonly-encountered organic or inorganic group absorbs. Prussian blues are often difficult to analyze by X-ray diffraction when Cu Kα radiation is used because of high absorption of this radiation by Fe. But the ferrocyanide radical is readily identifiable by infrared spectroscopy even when the blue pigment is a minor component in a given sample, as is the case with the green pigment in Fig. 3C, in which it is probably present to an extent of less than 5% by weight (estimated by emission spectrographic analysis).

Fig. 3A and 3B are spectra of dry pigments, whereas the pigment in Fig. 3C contains a carbohydrate binding medium. This accounts for the broad hydroxyl band centered at about 3400 cm$^{-1}$, the C-H absorptions between 2800–2900 cm$^{-1}$, and the carboxylate group absorptions at 1622 and 1419 cm$^{-1}$. 

45
Precipitated PbCrO₄ (chrome yellow) contains isolated CrO₄²⁻ ions. This tetrahedral ion possesses nine fundamental vibrations, several of which are degenerate in the free ion. The absorptions of the chromate ion in the chrome
O stretching deformations; the shoulders which occur on both the low and high frequency sides of this pair may be due to splitting of the degenerate modes by the crystal field. Cr-O bending deformations occur at lower frequencies, usually below 400 cm$^{-1}$, and consequently are not visible here. Fig. 4D and 4E represent two chrome yellow pigments; the principal bands in 4D occur at 854 and 832 cm$^{-1}$, and those in 4E at 860 and 835 cm$^{-1}$. In both cases, several shoulders bands are more or less evident.

Unfortunately, in the presence of major accounts of SO$_4^{2−}$, the CrO$_4^{2−}$ ion does not appear to be readily identifiable. For example, there is no evidence of the stretching absorptions in the green pigments whose spectra are given in Fig. 4B and 4C. This is not surprising as these absorptions were barely discernible in a simple physical mixture made in the laboratory of 20% by weight of PbCrO$_4$ and 80% BaSO$_4$ (spectrum not shown). The PbCrO$_4$ content of the pigment in Fig. 4C was estimated by emission spectrography to be approximately 10–15% by weight.

The sulfate ion, SO$_4^{2−}$, possesses the same symmetry in its free state as the chromate ion, and also gives rise to four fundamental frequencies and nine total fundamental vibrations.

In crystal environments, at least some of these degeneracies are always observed to be removed and the inactive 983 cm$^{-1}$ mode usually becomes visible. The absorptions of the SO$_4^{2−}$ ion in the BaSO$_4$ found in the pigments whose spectra are given in Fig. 4A–E, with the corresponding absorptions found by other authors for mineral BaSO$_4$ (barite) and the laboratory precipitated compound, are given in Table I. It can be seen that the majority of the barium sulfates give virtually identical spectra. The single exception among the few here examined is one of the chrome yellows (Fig. 4D); the difference perhaps reflects a different order of symmetry in this particular BaSO$_4$.

Both of the ‘Brunswick’ greens (Fig. 4B and 4C) also appear to contain α-quartz, two of whose transverse lattice vibrations produce the pair of absorptions at 794–797 and 780 cm$^{-1}$ in the samples. The 1033 and 1008 cm$^{-1}$ bands in the green pigment in Fig. 4C occur in positions in which certain silicate minerals (particularly clays) absorb and may be due to such a component. As noted above, ‘Brunswick’ greens were also extended with China clay, and this may be the case with this This small group of spectra indicates the unambiguous possibilities of identifying certain polyatomic ions in pigment samples. In favorable cases, it may also be possible to distinguish between different compounds of the same anion on the basis of exact frequencies of the absorption maxima. The spectra shown here also indicate that a particular anion, present as a minor constituent, may be undetectable because of interferences from absorption bands of another, major constituent; this was the case with CrO$_4^{2−}$ in the presence of SO$_4^{2−}$.

TABLE I VIBRATION FREQUENCIES OF MINERAL AND PRECIPITATED BaSO$_4$ (IN WAVENUMBERS)
Fig. 3. Spectra of Chrome Green Pigments

A. Chrome green dry pigment, F. Weber (Philadelphia), 1925 (Forbes Pigment Collection no. 60).
B. Green dry pigment from 19th century paint factory (H. Wood's Mineral Paint Manufactory, presently on the grounds of Wellesley College).
C. Green watercolor pigment from painting of an Angel (Fogg Art Museum, 1975.41.41).
Fig. 4. Portions of Spectra of Barium White, Chrome Yellow, and Pigments Containing Both of These Compounds A. A. Barium white dry pigment (Forbes Pigment Collection no. 34). B. Green dry pigment from 19th century paint factory (see Fig. 3B). C. Green watercolor pigment from painting of an Angel (see Fig. 3C). D. Yellow watercolor pigment from painting of an Angel (see Fig. 3C). E. Yellow dry pigment from 19th century paint factory (see Fig. 3B). F. Chrome green dry pigment (see Fig. 3A).
2.4 Green Earths

2.4.1 Composition of the Silicate Minerals in ‘Green Earth’

THE PIGMENT ‘green earth’ has been available since ancient times, and in the medieval and Renaissance periods was probably most widely used in the underpainting of flesh tones by tempera painters. C. Grissom has previously discussed the use of infrared spectroscopy in the study of green earths and has presented spectra of green earth pigments collected from several sources. The colorant in this pigment is one of two layer silicate minerals, glauconite or celadonite. Although very similar in chemical composition, these two minerals are formed under different geological conditions and would not normally occur together: glauconite is found in marine sediments, whereas celadonite is a secondary mineral found in certain basalts. Both minerals belong to the mica group. The composition of this group of silicate minerals consists of a layer of octahedrally-coordinated ions (Al³⁺, Mg²⁺, Fe²⁺, Fe³⁺) sandwiched between two sheets of SiO₄ tetrahedra whose unshared apical oxygen atoms are directed inward. The tetrahedral silicon in these layers may be partially replaced by aluminum. Hydroxyl groups are located in the centers of the hexagonal rings formed by the apical oxygen atoms in the SiO₄ sheets. Successive groups of these three-layer sandwiches are held together by K⁺ ions, which may be partially replaced by water or metallic ions.

Minerals of the type to which celadonite and glauconite belong are referred to as diotahedral 2:1 layer silicates (“diotahedral” since the total number of octahedrally-coordinated ions per formula unit is 2). From the point of view of their chemical compositions, both celadonite and glauconite may be regarded as derivatives of muscovite, KAl₂(AlSi₃)O₁₀(OH)₂. The most important differences are that in both of the green earth minerals the two octahedrally-coordinated Al³⁺ ions of muscovite are partially or totally replaced by Mg²⁺ or Fe³⁺, and the tetrahedral Al is at least partially replaced by Si.

Neither glauconite nor celadonite is a mineral of one specific composition, and some members of the two may very closely approach each other in composition. X-ray diffraction patterns of both are generally indistinguishable and are of a type (designated 1M) widely occurrent in the minerals of sedimentary and low-grade metamorphic rocks.

2.4.2 Infrared Spectra of the Green Earth Minerals

THE SPECTRA of two dry green earths (both celadonite) and of mineral
The other absorption bands of interest in identifying these minerals occur below 500 cm$^{-1}$ and are known to be very sensitive to variations in the octahedrally-coordinated ions in these structures, and particularly to Fe$^{3+}$. The triplet of bands found by Farmer and Russell at 494, 457, and 442 cm$^{-1}$ occurs in virtually the same position in the two dry green earth pigments (celadonite) and in the glauconite sample, which indicates a similarity in octahedral ion compositions. This is further confirmed by the nearly identical positions of the high-frequency R-OH stretching bands (at about 3560 and 3535 cm$^{-1}$).56

Fig. 6D is the spectrum of a green pigment from a 2nd-century (?) Coptic carved limestone figurine. The stone and pigment had been consolidated with an unidentified binding medium which was leached several times with CCl4 before the sample was prepared for infrared spectroscopic analysis. The spectrum shows calcite bands (probably from the stone), and bands probably due to the binding medium, but the distinctive pattern of celadonite is nevertheless readily evident. Table II summarizes the absorptions of the celadonites discussed here (see also Fig. 6).
Fig. 5. Spectra of Green Earth Pigments, A. Terre verte dry pigment, Winsor & Newton (Forbes Pigment Collection). B. Green earth dry pigment, Fezandie & Sperrle (New York) (Forbes Pigment Collection no. 4). C. Glauconite, mineral from Birmingham, New Jersey (Geology Department, Harvard University, Sample no. 112823).
Fig. 6. Portions of Spectra of Green Earth Pigments, A. Terre verte dry pigment (see Fig. 5A). B. Green earth dry pigment (see Fig. 5B). C. Terre verte, Paciosi (Rome), 1928, unground, unwashed earth pigment (Forbes Pigment Collection). D. Green pigment from Coptic 2nd-century (?) “Follower of Isis” limestone figurine (Memorial Art Gallery, Rochester).
TABLE II VIBRATION FREQUENCIES OF SEVERAL CELADONITES (IN WAVENUMBERS)

A complex spectrum (Fig. 7) is also included here to indicate the difficulties encountered with paint samples containing many materials. This sample was taken from the underpainting of the flesh in a 16th-century Italian egg tempera painting. Relatively little green pigment was present in the sample, and the principal bands of the recorded spectrum indicate CO$_3^{2-}$ and SO$_4^{2-}$ ions, probably to be ascribed respectively to lead white (apparently hydrocerussite in this case) and anhydrite (from the underlying ground layer); α-quartz may also be present in the sample. The broad band centered at 994 cm$^{-1}$ and the triplet of bands at 495, 468, and 440 cm$^{-1}$ may be due to the suspected green earth pigment. The band at 1655 cm$^{-1}$ may be assigned to C = O stretching in amide bonds (e.g. the protein-containing paint medium). The following list summarizes these assignments:

\[
\begin{align*}
\text{CO}_3^{2-}: & \nu_3 = 1419, 1403, 1373 \text{ cm}^{-1} \\
\nu_2 & = 838 \text{ cm}^{-1} \\
\nu_4 & = 682 \text{ cm}^{-1} \\
\text{SO}_4^{2-}: & \nu_3 = 1153, 1115 \text{ cm}^{-1}
\end{align*}
\]

- α-SiO$_2$ stretching and bending lattice vibrations: 1173, 797, 780 cm$^{-1}$
- ‘Green earth’ Si-O lattice vibrations: 994 cm$^{-1}$
- Si—O—R$^3+$ and R$^3+$—OH: 495, 468, 440 cm$^{-1}$

In view of the complicated nature of this mixture, these absorptions may be used as pieces of evidence in fully characterizing the constituents of the sample, but should realistically be corroborated by microscopy or other analytical procedures since by themselves they could be subject to misinterpretation.
Fig. 7. Partial Spectrum of a Paint Sample, Below: Expanded portion of spectrum of light green underpaint, from face of Mary, in “The Holy Family,” by Jacopo di Domenica Foschi, 16th century (Fogg Art Museum, 1957.61). Above: Four representative spectra of materials suspected to be contained in the Foschi paint sample.
2.5 Amorphous Inorganics: Cr2O3 and Viridian

THE ELEMENT CHROMIUM was discovered by Vauquelin in 1797. The opaque oxide, Cr2O3, was known at that time and in 1809 was suggested as a ceramic glaze colorant. The transparent hydrated oxide, Cr2O3·3H2O (viridian), may first have been introduced as an artists' color in 1838; however, both pigments were apparently not widely available until after about 1862.57

Both of these oxides have a low order of crystallinity and consequently do not give X-ray diffraction patterns,58 but both give characteristic infrared spectra below 800 cm\(^{-1}\) which may be used for identification purposes (Fig. 8). The broad band centered at approximately 3400 cm\(^{-1}\) and the sharp peak(s) around 1600 cm\(^{-1}\) in viridian are due to the water of hydration in its structure.

As noted earlier, the infrared spectra of oxides, sulfides, and other compounds of high refractive indices are often poor due to scattering losses, and in addition the number of absorption peaks as well as their positions may be profoundly affected by particle dimensions and shape and the refractive index of the matrix material.59 The Cr2O3 dry pigment whose spectrum is given here was not further ground, but its spectrum does compare favorably with spectra published elsewhere in which sample preparation included careful grinding.60, 61

In Cr2O3, each O2\(^{-}\) is coordinated by four Cr3+ in a distorted tetrahedron.62 The strongest bands, at 632 and 566 cm\(^{-1}\) in Cr2O3, do not correspond to specific O2\(^{-}\) displacements and are probably due to various combinations of O2\(^{-}\) and Cr3+ displacements in the lattice. The pair of sharp bands at 443 and 416 cm\(^{-1}\) corresponds to two specific O2\(^{-}\) displacements in the lattice. The hydrated oxide (viridian) has not been studied, but the absorptions are probably due to similar types of displacements, whose frequencies have been shifted due to the presence of water in the structure.
Fig. 8. Spectra of Chromium Oxide Pigments, A. Chromium oxide green, opaque, dry pigment, Imperial Paper & color Corp. (New York), 1941 (Forbes Pigment Collection no. 39). B. Viridian dry pigment, Geo. Rowney & Co. (London) (Forbes Pigment Collection no. 43).
3 CONCLUSION

THIS PAPER has been intended as an introductory review of a few of the possible applications of the infrared spectroscopic technique in the realm of ‘routine’ characterization of painting materials. The materials chosen for this study were ones for whose characterization the structural information provided by infrared spectroscopy may be of great value. Mixtures of pigments produce complex spectra which can be difficult to interpret, and absorptions of certain functional groups may obscure those due to other groups, even if the latter constitute a significant part of the given sample. These difficulties, in addition to the somewhat large sample size required in order to obtain a useful spectrum, limit the applications of infrared spectroscopy to the study of painting samples. Nevertheless, numerous publications attest to its value, and the technique continues to be an important means of characterizing the materials of painting.

REFERENCES

Flieder, F. “Mise au point des techniques d'identification des pigments et des liants inclus dans la couche picturale des enluminures de manuscrits.” St. in Cons. 13 (1968): 49–86
Low, M.J.D.; Baer, N.S. “Dammar and Mastic Infrared Analysis.” Preprints, ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978: 78/16/5
Low, M.J.D.; Baer, N.S. “Advances in the Infrared Spectroscopic Examination of Pigments.” Preprints, ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978: 78/20/3
Grissom, C.A. “A Literature Search for a Pigment Study.” Preprints, ICOM Committee for Conservation, 4th Triennial Meeting, Venice, 1975:75/21/5


Afremow, L.C.; Vandeberg, J.T. “High Resolution Spectra of Inorganic Pigments and Extenders in the Mid-Infrared Region from 1500 to 200 cm⁻¹.” J. Paint Tech. 38 (1966): 169–202. Spectra of most of the types of pigments discussed in this paper are included in this article.


Some applications in this area have also been recently reviewed in: Laver, M.E.; Williams, R.S., “The Use of a Diamond Cell Microsampling Device for Infrared Spectrophotometric Analysis of Art and Archaeological Materials,” J. IIC-Canadian Group 3 (1978): 34–39

The catalog numbers given in the captions of the Figures for the “Forbes Collection” pigments refer to bottles in the wall case displays in the Center of Conservation and Technical Studies, Fogg Art Museum. Several Museums, including the Fogg, own samples from a second and not identical “Forbes Collection,” which is catalogued in a different manner.


Perkin-Elmer Corp., Norwalk, Conn.: Instructions, Combination Accessory for Perkin Elmer Infrared Spectrophotometers 186–0373 (1972)

Located in the Chemistry Department, Harvard University, Cambridge, Massachusetts


Miller, R.K. “Infrared Spectroscopy,” in Ref. 26, pp. 197–216


Ref. 17(b), pp. 54 ff.


The absorption bands reproduced in the Figures are those in the mid-infrared range which are caused by the polyatomic ions contained in the compounds, but are not necessarily the only ones which would occur in the full spectra. For example, the water of hydration in gypsum causes bands at 3554, 3408, and 1690 cm⁻¹. The hydroxyl groups in the basic carbonates also cause absorptions: in azurite, at 3425, 1035, and 952 cm⁻¹; in malachite, at 3400, 3320, 1045, and 875 cm⁻¹; and in hydrocerussite, at 3535, 1047, and 1040 cm⁻¹. See Ref. 17(b) for a discussion of these.


Ref. 25, pp. 105–106


Ref. 37
R-OH stretching and librational bands, where R = octahedrally-coordinated ions, are discussed in Ref. 46 and: Russell, J.D., Farmer, V.C., Velde, B. “Replacement of OH by OD in layer silicates, and identification of the vibrations of these groups in infra-red spectra,” Min. Mag. 37 (1970): 869–879.

Ref. 25, p. 107 and pp. 173–174

Ref. 27

Ref. 17(b), Ch. 3 & 10

Ref. 15, 16


Ref. 17(b), pp. 188–189

ACKNOWLEDGEMENTS

THE AUTHOR would like to thank Eugene Farrell (conservation scientist, Center for Conservation and Technical Studies, Fogg Art Museum) who prepared some of the samples and helped the author with acquiring the spectra. This study would not have been possible without the use of the Nicolet 7199 FT-IR spectrometer, and for allowing us to use this instrument and training us in its operation, I gratefully acknowledge Dr. Gregory Exarhos and particularly Barry Nelson (both Chemistry Department, Harvard University).
PARTICLE CHARACTERISTICS OF PRUSSIAN BLUE IN
AN HISTORICAL OIL PAINT

Frank S. Welsh

ABSTRACT—This paper outlines current research to identify the pigments, specifically the blue pigment, used to make the original 18th-century finish paints in the Long Gallery and in the Tower Stair Hall at Independence Hall in Philadelphia. The restoration of these rooms' blue and blue-green painted finishes was carried out from the mid-1950s to the early 1970s under the guidance of the National Park Service Historical Architect, Penelope Hartshorne Batcheler. The recent analyses confirmed that a blue pigment in these paints was one very commonly used in the 18th-century, Prussian blue. This study and confirmation not only establishes one of the very earliest uses of the pigment in this country in that century, but it brings to light the obvious differences in physical appearance between 18th-century Prussian blue agglomerates (large and angular) and the small, amorphous 20th-century Prussian blue agglomerates. The research also establishes light microscopy as the method of choice for analyzing architectural paint pigments.

1 INTRODUCTION

THE ANALYSIS OF HISTORIC ARCHITECTURAL PAINTS involves not only the identification of layers and colors of paint, but also it requires the accurate analysis and identification of the component pigments in the paint films. This is either out of historical, empirical interest or else out of an interest to more accurately understand a paint film's original color. Most often, though, the identification of pigments is undertaken to help prove the age of the paint film, since many pigments are commercially prepared and were not, therefore, necessarily available before a certain time.

Thirty years ago, an attempt was made to identify an original paint's component pigments at Independence Hall; however, the findings from the analyses were inconclusive. The equipment and information available for the analysis at that time was not much different than that used for this recent study, which was undertaken in an attempt to answer the lingering questions. What has changed in the intervening years is our increased knowledge of the materials to make architectural paints 200 years ago and, consequently, what we might expect to find in them. With our enhanced knowledge and expectations, the full capabilities of the variety of scientific instruments available to us can be best put to use.

2 LONG GALLERY

THE LONG GALLERY (Fig. 1), a second-floor room running the width of Independence Hall, was Colonial Pennsylvania's version of Versailles Palace's
Hall of Mirrors. The site of 18th-century banquets and concerts, the room also served on a day-to-day basis as a reception and waiting room. The office of Pennsylvania's governor adjoined it—Independence Hall was Pennsylvania's State House—and legislators probably caucused there. In Charles Wilson Peale's self portrait owned by the Pennsylvania Academy of Fine Arts, one can get a sense of the room's scale and note its unfinished floors of random width, face nailed, tongue-and-groove yellow pine, and nine large, hung-sash windows.

Fig. 1. Long Gallery Independence Hall, Philadelphia, PA

During the 1950s and 1960s, the National Park Service (NPS) restoration architects found on the window sash what appeared to be the room's original blue color remaining in the grain of wood. Subsequent microscopical paint analysis on other pieces of original trim established that this medium blue-tinted oil paint was the first finish on all wood. (There are three exceptions: The baseboards and the top surfaces of the chair rails and window sills were all originally dark brown.) In the opinion of all who looked at it, the blue pigment used in this original trim color was Prussian blue. However, it was never microchemically analyzed until 1985, when Mrs. Penelope Batcheler, NPS Historical Architect, pursued further analysis of the pigment with the author.

Stereo microscopical examination of a small piece of a 1730s window splayed jamb board from the Long Gallery (cat. #8428-A) confirmed Mrs. Batcheler's original finding that the first finish is ca. 1730s medium blue oil paint applied over a thin red iron oxide prime coat. Within this blue finish paint, there were large blue-black pigment agglomerates averaging 250 micrometers in diameter. Several of them were removed with a tungsten needle for further examination. One sample was mounted on a glass slide in a permanent mounting medium (Aroclor® 5442), and inspected with a polarized light
particles.

A comparison of the unknown sample was made to known samples of natural ultramarine blue and Prussian blue. The unknown blue pigment has optical characteristics similar to both.

Standard microchemical tests on the blue pigment agglomerates were carried out.\footnote{1} These established that the unknown blue pigment was Prussian blue rather than natural ultramarine.

Also known as Berlin blue, Paris blue, Antwerp blue, and Chinese blue, Prussian blue is the earliest modern synthetic color. It is a complex chemical compound, ferric ferrocyanide (Fe₄(Fe(CN)₆)₃), first mentioned in 1710, but its preparation was kept secret until 1724. A London manufacturer named Wilkenson began production, and gradually more and more color firms followed suit. By 1750, Prussian blue must have been well known all over Europe.\footnote{3} Long before that, however, Prussian blue was in use in this country. In 1732, for example John Gibbs used it to paint irons for hanging the brass chandeliers in Boston's Old North Church.\footnote{4}

To verify the identification of Prussian blue in the Long Gallery paint, Dr. Walter C. McCrone at the McCrone Research Institute in Chicago was consulted. The paint sampled was the same first (original) 1730s finish above a red oxide primer. Stereo microscopical inspection at 70x again revealed within the film large blackish-blue pigment agglomerates. These were removed with a tungsten needle along with some of the surrounding blue paint for examination by polarized light microscopy, microchemical testing, and electron microprobe analysis.

Mounted on a glass slide in Aroclor® 5442, the first Long Gallery sample revealed two pigments, a pseudo-opaque white and a blue (Fig. 2).\footnote{5} The sizes of the individual anisotropic white particles generally ranged from 0.9–3.8 micrometers. Their optical properties, e.g. refractive index of \(\approx 2.00\), showed they were white lead, \(2\text{PbCo}_3\text{Pb(OH)}_2\).\footnote{6} The whole paint film itself contains close to 75%–85% of this pigment.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{pigment_particles}
\caption{Pigment Particles identified as Prussian blue (associated with white lead), from windows jamb, Long Gallery.}
\end{figure}
The blues were large isotropic glassy flakes with well-defined edges and corners and a refractive index of 1.56–1.57 as determined by dispersion staining. Their purple-blue color was slightly mottled, not consistently uniform. Their size generally varied from 4.0 micrometers all the way up to an incredibly large agglomerate of 46.8 micrometers.

Comparison was made of the above blue particles with those of other blue pigment samples, natural ultramarine (ground lapis lazuli) and modern Prussian blue. In color and shape the Long Gallery blue pigment sample was more like the ultramarine. Like the sample, ultramarine particles are glassy, have well-defined edges and corners, and are isotropic.

There, however, the similarity ended. While the Long Gallery blue color was mottled, natural ultramarine’s is consistently uniform. Their respective refractive indices also are different, that of ultramarine being 1.50.

In a comparison of the shape of the Long Gallery 18th-century blue pigment sample to the shape of the 20th century Prussian blue sample (Fig. 3), a distinct difference is apparent. The 18th-century pigment has sharp, well-defined edges, and the 20th-century Prussian blue has rounded edges—almost amorphous in agglomerate shape. The color of the 18th-century blue is mottled, but the 20th-century Prussian blue is very dark and more uniformly blue. Both have an identical refractive index of 1.56.

When viewed at 400x magnification, the shape of the Long Gallery 18th-century blue pigment resembled natural ultramarine but could be distinguished from ultramarine by the unknown pigment's color and refractive index which strongly suggested Prussian blue. This was confirmed by standard microchemical tests. Electron microprobe analysis verified this identification of the blue and of the white as white lead.
3 TOWER STAIR HALL

FEW, IF ANY, have postulated that Prussian blue was also the pigment used in the original finish paint found in Independence Hall's grand stair area, the Tower Stair Hall (Fig.4). A broad stair in a room some 36 feet high, it was designed by Edmund Woolley and dates from the 1750s. For more than 20 years in this century, the Liberty Bell stood encased on the hall's brick floor. Growing crowds of visitors speeded deterioration of the Stair Hall's woodwork, and so the Bell was relocated to its own building in time for the nation's 1976 Bicentennial.

Fig. 4. Tower Stair Hall, Independence Hall, Philadelphia, PA.

Over the past three decades, a number of laboratories have analyzed the Stair Hall's pigments. Samples of the original paints were submitted by Mrs. Batcheler to the National Lead Company Research Laboratory (December, 1956), to the Freer Gallery, whose laboratory was then headed by Rutherford P. Gettens (November, 1957), and to The Glidden Paint Company of Reading, Pennsylvania (May, 1958). The conclusions of all analyses were contradictory and never resolved. National Lead concluded the blue pigment in question was natural ultramarine. Glidden Labs concurred, even after conducting X-ray diffraction and spectrographic analyses. Dr. Gettens disagreed. He found no blue in his microscopical analysis-only iron oxides and charcoal black. 14
The conflicting analysis left the identity of the Stair Hall's original paint's pigments a mystery. In 1985, the files were reopened to attempt to find an answer. From the NPS architectural storage collection was retrieved a carved wooden rosette (cat. #1271) that was part of the main cornice of the Tower Stair Hall. Although the cornice was installed in the 1750s, the first finish paints may or may not have been applied at that time.

Stereo microscopical inspection indicated the first finish to be a light grayish-greenish blue oil paint over a very light oil primer. Through the stereoscope we saw large black pigment agglomerates. Agglomerates of the pigments in the paint were too small to see easily at 20–80x. The absence of large blue pigment agglomerates, similar to those found in the 1730's Long Gallery paint, suggests this Tower Stair Hall paint layer, potentially from the 1750s, may have been made with a different blue pigment or else the same one but more finely ground before dispersal into the liquid paint. A tiny sample (0.5mm) of the entire paint layer was removed with a tungsten needle and mounted on a glass slide in Aroclor® for inspection with the polarized light microscope. Easily seen were white, black, yellow and red pigment particles. The blue pigment particles were difficult to find—they were remarkably small.

The characteristics of the black pigment were those of charcoal black. The pieces were large and very angular, very unlike lamp black, which is very tiny and rounded.

The yellow and red pigments looked like yellow and red iron earths. The white had characteristics of white lead. The blue had identical optical and shape characteristic of the blue sample from the Long Gallery's window jamb board, with one exception. This sample's agglomerates size was generally much smaller, ranging from 3–11 micrometers with 75% closer to 4 micrometers—a factor contributing to the potential for its misidentification.

These particles were examined one by one with the polarized light microscope and with microchemical testing and found to be the following: black, charcoal black; red, red iron earth and haematite; yellow, yellow ocher; white, white lead, and the blue, Prussian blue.

4 DISCUSSION

4.1 Appearance: 18th-century vs. 20th-century Prussian blue

THESE RESULTS raise the important question: Why does Prussian blue from the 18th-century samples differ so much in size and shape from that of the 20th century sample? Has a change in ingredients or preparation changed the aggregate appearance of this compound?

A quick glance at a mid 18th-century recipe for Prussian blue is helpful here. In his book, *The Handmaid to the Arts*, London, 1758, Robert Dossie describes the pigment's preparation, “as practiced on the continent and in this country.”
The first method employed to obtain Prussian blue was first to calcine dried bullock's blood with potash, in a crucible at red heat. The mixture was now poured into a quantity of water. During the heat, the animal substance afforded the prussic acid, which was caused by the potash forming the prussiat of potash. This compound dissolved in the water, constituted what was then called the Prussian lixivium. To this was added a mixture of sulphate of iron and sulphate of alumine, in a state of solution. The prussic acid takes the iron, while the potash combines with the sulfuric acid. The excess of alkali precipitates the alumine from the alum, which becomes mixed with the prussiat of iron, and forms the substance which when separated from the liquid, washed and dried, forms a blue concrete mass, called Prussian blue…

In contrast, note the preparation of Prussian blue in Gettens and Stout's *Painting Materials*:

[Prussian blue] is now commonly made by the action of an oxidizing agent, such as potassium bichromate and sulfuric acid upon a mixture of copperas (ferrous sulphate), sodium ferrocyanide, and ammonium sulphate, giving a blue with the approximate formula Fe(NH4)fe(CN)6. The pigment which is precipitated from dilute solutions of those salts is a deep blue, finely divided compound which, after it has settled and after the mother liquor is drawn off, is washed, filtered, and dried. The product is amorphous in colloidal aggregates and so finely divided that it has almost the characteristics of a dye. By control of conditions of precipitation and oxidation, variations in shades and physical characteristics of the blue may be had….blue-black, but with some varieties, especially those prepared with bleaching powder as the oxidizing agent, have a reddish, coppery lustre. It is a transparent color but has very high tinting strength.

Clearly, the preparation methods are different, but are these differences dramatically sufficient to alter Prussian blue particles' size and shape? Dr. Robert L. Feller, Director of the Center on the Materials of the Artist and Conservator, Mellon Institute, Pittsburgh, agrees that the difference in aggregate shape between 18th-century vs. 20th-century Prussian blues may well lie in the old method's choice of material, namely blood (protein), and possibly in the mixing and accidental meeting of ions.\textsuperscript{17} Today, by contrast, precipitation methods are much more clean and direct. Dr. McCrone concurs.\textsuperscript{18} Dr. Feller has kindly sent a sample of Prussian blue made by Bernard Keisch, a former research fellow at the Mellon Institute, following the old method using bullock's blood (Fig. 6). The pigment agglomerates of this sample are also large and angular.
Fig. 5. Pigments identified as charcoal black, Prussian blue, white lead, and calcium carbonate, from the resette, Tower Stair Hall, reproduced at the same magnification as Figure 2.

Fig. 6. Prussian Blue made by Barnard Keisch, Mellon Institute, following an 18th century recipe, reproduced at the same magnification as Figure 2.

5 CONCLUSION

CARE MUST BE USED in identifying blue pigments in early paint films. In particular, the present paper has shown that 18th-century Prussian blue particle agglomerates, which can be very large or small and angular, may be mistaken for natural ultramarine which they more closely resemble morphologically than they do particles of modern Prussian blue, which is very amorphous in shape. Careful use of analytical techniques, especially polarized light microscopy, can help prevent misidentifications. Blue paint films containing Prussian blue in the form of larger angular particle agglomerates may have been prepared from the pigment made by the earliest described process for its preparation. Such paint films therefore, may be relatively early.
ACKNOWLEDGEMENTS

THE AUTHOR wishes to thank and acknowledge the many hours of expert assistance of Dr. Walter C. McCrone and Mrs. Penelope H. Batcheler, and for the critical insight of Dr. Robert L. Feller and others, for without their support, this project could not have been completed.

NOTES
. 1 Joyce Plesters, “Cross-sections and Chemical Analysis of Paint Samples,” in Studies in Conservation 2, No.3, April, 1956, pp. 110–157, Microchemical tests used included hydrochloric acid which bleaches ultramarine blue, and sodium hydroxide which discolors Prussian blue to a dark orange yellow.

NOTES

NOTES
. 3 Gettens and Stout, p. 151.

NOTES

NOTES
. 5 Walter C. McCrone, Lucy B. McCrone, and John Gustav Delly, Polarized light Microscopy (Ann Arbor: Ann Arbor Science Publishers Inc., 1979). p. 35. A pseudo-opaque white appears to be opaque because the light that is transmitted though the thicker agglomerated particles is bent and does not enter the objective lens.

NOTES
. 6 Gettens and Stout, p. 147.

NOTES
. 7 McCrone, McCrone and Delly, p. 169. The refractive index determination using dispersion staining was carried out by Dr. Walter C. McCone in the conservation lab at N.Y.U.

NOTES
. 8 Natural Ultramarine, Forbes collection, 7.01.13.

NOTES
. 9 Prussian Blue, Forbes Collection, Azzuri de Prerlino and Bibbiena.

NOTES
. 10 Gettens and Stout, p. 148b.
. 11 Prussian blue, Slide reference set of 1982 from The McCrone Research Institute.

NOTES
. 12 Plesters. HC1 and NaOH microchemical tests, p. 137.

NOTES

NOTES

NOTES
. 15 The size of the particle agglomerates visible in the paint film do not necessarily indicate an early or late date of manufacture. I have seen very large Prussian blue agglomerates in early 19th century blue paint films from buildings in Tennessee and in Texas.

NOTES
. 16 Charcoal Black (Forbes: 2.01.7) and Lamp Black, McCrone Research Institute.

NOTES
. 17 Private communication with Dr. Robert Feller. 1986.

NOTES
. 18 Walter C. McCrone, written correspondence to the author: “Even with the same process, there can be differences in the product, especially particle size. This would be due to variations in temperature and time.” 1987.
A STUDY OF THE MATERIALS USED BY MEDIEVAL PERSIAN PAINTERS

NANCY PURINTON, & MARK WATTERS

ABSTRACT—The paper includes a comparison of information about pigments in the literature on Persian painting to an analysis of the pigments in a group of Persian paintings at the Los Angeles County Museum of Art. A description of the classical medieval Persian painting technique is given as it is described in the literature.

1 INTRODUCTION

THE AIM of this paper is to compare information obtained through a technical analysis, using modern scientific equipment, of some Persian paintings with the information available in the literature on Persian painting technique. The sources of information ranged from a translation of a 16th-century manuscript written by Sadiqi Bek to current technical analyses of the materials used in the manufacture of Persian paintings. The technical information given in this paper was obtained from a study of 19 Persian paintings dating from the 15th to the 17th centuries in the Los Angeles County Museum of Art (LACMA) collection. The miniatures were executed in Persian art centers such as Herat, Shiraz, Tabriz, Bukhara, Qazvin, Isfahan, and Gilan. They were chosen because of known provenance and secure dating.

The LACMA paintings were examined using a binocular microscope, ultraviolet fluorescence, and infrared reflectography. Pigment identification was based primarily on energy-dispersive x-ray fluorescence analysis. This nondestructive technique provides an elemental analysis of selected color areas of each painting but is reliable only for those pigments containing elements with atomic numbers above that of potassium. The presence of particular elements is indicative of certain pigments and thus aids in their identification. Pigment identification can be confirmed by x-ray diffraction and/or polarizing light microscopy in conjunction with x-ray fluorescence.

Many pigments were also analyzed using a polarizing light microscope. This combination of analytical techniques allows the researcher to identify pigments that would not be detected by the x-ray fluorescence spectrometer. Every pigment in every painting was not analyzed, but every color in a painting (e.g., red, orange, yellow, green, blue, violet, white, black) that could be analyzed was. Further differentiation among the green pigments was done by x-ray diffraction. This analysis enabled the identification of a variety of copper-containing green pigments.

This paper is a preliminary comparison of scientific data with the texts about Persian painting technique. Keeping in mind the incomplete state of
scholarship concerning the materials of Persian manuscript painting, the reader should remember that the following exposition is only a preliminary investigation of the pigments employed, their sources, and their manufacture or preparation.

2 TREATISES ON PERSIAN PAINTING

ONLY TWO translations into English of technical treatises on Persian painting exist. One is *Qanun us-Suvar* (Canons of Painting) by Sadiqi Bek, a royal painter in the 16th-century Safavid Iran. Sadiqi Bek wrote the Qanun sometime between 1576 and 1602 (Dickson and Welch 1981). The second work, *Gulistan-i Hunan* (Rose Garden of Art), was an appendix to a text written by Qadi Ahmad circa 1608 (Minorsky 1959).

In his treatise, Sadiqi Bek discussed theoretical aspects of painting such as the basic categories of decorative art and its different idioms, including animal and decorative drawing. He also gave practical information on the techniques of manufacturing artists' supplies and the application of colors. In Sadiqi Bek's opinion, two types of drawing require different types of observation. For instance, for human figures only careful study from nature would do, while for animal figure studies one must study the past masters as models. A popular type of drawing featured animals locked in battle, and Sadiqi Bek advised that the animals be drawn with tense bodies in a clawed grip (Dickson and Welch 1981). A toned drawing of animals locked in battle included in this study (M.73.5.12, fig. 1) does follow these rules.

![Fig. 1. A Lion Attacking a Dragon That Has Wrapped Itself a Ram](image-url)

*Fig. 1. A Lion Attacking a Dragon That Has Wrapped Itself a Ram*, Iran Safavid period, Isfahan, 1691, Ink and color washes on paper, 12.75 × 20.25 cm. Los Angeles County Museum of Art, The Nasli M. Heeramanek Collection, Gift of Joan Palevsky. M. 73.5.12.
Sadiqi Bek stated that a painting would have a two-layer ground. The bottom layer would be a mixture of glue, plaster, and grape treacle; on top of that would be a layer of white lead and oil-varnish. The term for oil-varnish in Persian, *rang-i rowghan*, is difficult to translate, but Dickson and Welch (1981) determined it probably meant a cooked oil and resin varnish. This study is concerned only with paintings on paper, and we found no such ground on any of the paintings. This type of ground was probably intended for book bindings or paintings on stiff layered paper (like cardboard) surfaces (Dickson and Welch 1981).

Sadiqi Bek also described the manufacture of some of the colors used in a painting (Dickson and Welch 1981). The only white pigment he mentioned was white lead produced by melting lead in a closed vessel and then, after it had cooled, alternately washing it with a saline solution and pounding it with sal-am-moniac and vinegar. To make red lead, the white lead was roasted. The green pigment, verdigris, was made by burying copper plates, immersed in vinegar, in a pit two meters deep for one month. Sadiqi Bek also described a red lake that was made from boiling lac in a soda solution to which possibly lime was added. He instructed the artist to make vermilion by pounding mercury and sulfur in a mortar and then heating it for several hours.

The *Gulistan-i Hunan* was written around 1608 A.D., but probably not by Qadi Ahmad himself (Minorsky 1959). While less thorough than Sadiqi Bek's treatise, this appendix, nonetheless, covers some different topics. For instance, it includes instructions for ruling framework, or drawing decorative margin lines around calligraphy. As far as one can discern, given that the original is written in medieval Persian and that there are inherent pitfalls in translating ancient languages, those margins would be (from the interior line to the outside line) black, ultramarine, black, gold, ultramarine, black, and pale green. Other margin suggestions are arrangements of black, gold, and ultramarine.

The author then explained how to grind and dilute the pigments made of lapis lazuli and gold. Gum arabic was the only medium mentioned, and artists were advised to add it to colors. The pigments included in this section of the treatise are cinnabar, lapis lazuli (ultramarine), orpiment, and white lead. All these colors would be washed as a final preparation step by adding water to the pigment in a vessel, allowing it to settle; and then decanting the liquid. Gum arabic was added to the colors before they were ground. The passage describing this process is difficult to understand. At one point the artisan is advised to add vinegar to lapis lazuli (a blue stone) and grind it until it turned green. In another the artisan is instructed to mix verdigris (a green) with white lead to make pink. Such instructions suggest that at least some information in this treatise is inaccurate. This appendix also described four methods of preparing a black ink: one from lampblack, another from baked wheat starch paste, another with gallnuts and lampblack, and the last with tin and mercury.
A 17th-century version of contemporary liquid correction fluid is also given: mistakes could be covered with white lead and then the surface burnished to make writing disappear (Minorsky 1959).

Both treatises give directions for making pigments. Sadiqi Bek described the production of white lead, red lead, verdigris, vermilion, and a red lake (Dickson and Welch 1981). The appendix to Qadi Ahmad's text included instructions for preparing ultramarine, gold, cinnabar, and so-called red orpiment, but it is devoted mostly to the preparation of black inks (Minorsky 1959). Although the authors of these treatises use different names for a red pigment—vermilion and cinnabar—the pigment is the same chemically. Vermilion is manufactured by grinding mercury and sulfur together, while cinnabar is the naturally occurring form that is simply ground (Gettens and Stout 1966).

Much of the information on materials used in Persian paintings offered in 20th-century art historical literature has been based on speculation rather than factual evidence. One author incorrectly stated that *peori* (Indian yellow, an organic yellow pigment) is a yellow earth (Martin 1912, 108–9). Another refers to verdigris (a copper acetate) as an arsenical green (Gray 1961). Even those authors dealing specifically with the technical aspects of Persian painting disagree on such basic matters as the primary constituents of the vehicle (or binder) for the pigments. Laurie (1935), who seems to have been particularly interested in the materials used in Persian paintings and made many astute pigment notations, speculated on the possible use of several materials including gums, waxes, and oils. Behzad (1939) stated that albumin was the earliest medium, followed by glue and gum arabic, but he gave no documentation. Martin (1912, 109) suggested a variety of materials, including gum arabic water, glue water, and linseed water as well as sugar. It is hoped that this study and others like it, will help to determine what Persian artists actually used by examining the art works with scientific analytical equipment.

### 3 PIGMENT ANALYSIS

#### 3.1 REVIEW OF PREVIOUS WORK

VERY LITTLE substantive chemical or physical analysis of the materials of Persian-manuscript painting has been published. Other individuals have carried out pigment analyses of Islamic manuscript paintings previous to this study. Four unpublished papers discussed here were written by students at Harvard University. A fifth is an article by Gordus (1968), who was mainly interested in demonstrating the advantages of neutron activation analysis. With that analysis, he identified cinnabar, orpiment, and verdigris in an unidentified Persian painting. The sixth paper, by FitzHugh (1988), published in a catalog of the Vever collection at the Arthur M. Sackler Gallery in Washington, D.C., was a study of the pigments in some of the paintings of that collection.
Holmberg's paper (1978), one of the student papers, described the identification of pigments on pages from the Demotte Shahnama, so named because an early 20th-century dealer, Demotte, sold 58 individual pages from an early 14th-century copy of Firdawsi's epic poem, the Shahnama (Book of Kings), to different patrons. Holmberg examined 11 paintings to determine whether they had been retouched. The analytical methods used were microscopic examination, microchemical testing, energy-dispersive x-ray analysis, semiquantitative laser spectrographic analysis, and x-ray diffraction. Miniatures in three separate collections were examined: three in the Freer Gallery of Art, Washington, D.C.; two in the Museum of Fine Arts, Boston; and six in the Fogg Art Museum, now in the Arthur M. Sackler Museum, Harvard University. Holmberg concluded that all the miniatures had been retouched and sometimes she found evidence of more than one layer of retouching.

St. Laurent-Lockwood (1981) sampled blue, white, and yellow from four Persian paintings in the Sackler Museum, Harvard University. She found that the only blue pigment used was ultramarine, the only white was white lead, and the only yellow was orpiment.

The other two student papers were studies of royal Persian paintings and compared royal workshop paintings to provincial ones. One, by Khoury (1985), was an analysis of four royal Persian miniatures from the 16th and 17th centuries. Khoury found that the technique used in the execution of the miniatures was the “classical technique,” except in one case in which the artist was particularly innovative. She found no Indian yellow in the Persian paintings. The fourth student paper by Bailey (1985) compared four paintings, two royal and two provincial, and found that the traditions for both were the same but the provincial works demonstrated the need to economize by using, for example, carbon black to imitate tarnished silver.

3.2 REPORT OF THIS PIGMENT ANALYSIS

According to our observations, pigments were rarely used as pure color; the artists apparently preferred mixing their pigments for more subtle coloristic effects. The pigments used in a medieval Iranian kitabkhana, or workshop, were probably manufactured there. Some of the pigments used by the Persian artists were produced from mineral ores and, in some cases, semiprecious stones. The purity of the color in those pigments would depend on the quality of the natural mineral and the care of the preparation.

The pigments of medieval Persian manuscript painting can be conveniently divided into two chemical groups, inorganic and organic. Apparently, the artists relied much more heavily on inorganic pigments, and some scholars insist that only inorganic pigments were employed in Persian painting (Behzad 1939). The artists must have valued inorganic pigments for their superior covering power and their relative physical and chemical stability in addition to
their resistance to fading. Many of the inorganic pigments were prepared from mineral ores, while others were chemically manufactured. In the finest examples of Persian painting, the purity of the colors as well as the precision displayed in the finish attest to the careful preparation of the pigments. Ore that is relatively unadulterated is necessary for the production of a good natural mineral pigment. Generally, the raw material must be fractured and coarsely ground. To purify and reduce the mineral to a powder suitable for use as a pigment, washing in water and levigation—a procedure of grinding and washing in which fine particles float while coarse ones sink—should follow. In most cases, the finest grades of pigment are removed in the first washings and levigations. Alkaline washings can be employed to facilitate the separation of the finest grades as well (Minorsky 1959).

Some earth pigments derived from clays are simply mixed in water. While the desired portion of the clay remains in suspension, sand and heavy impurities sink to the bottom and humus floats to the top. Chemically manufactured pigments often require grinding. When a pigment is produced by altering another finely ground pigment, further grinding may not be necessary. The procedures outlined here are essential to the manual preparation of fine pigments in all parts of the world.

Organic materials constituted the second major group of pigments. They must have gained acceptance as painters came to value an enhanced variety of color harmonies. Many of these pigments were derived from extractions of vegetable matter or from insects. In some cases, the raw organic material, when properly powdered, could serve directly as a pigment.

A tendency to fade and a lack of covering power characterize organic pigments, and most were likely relegated to a subordinate role in painting.

Although pigments known as lakes have been used in Western artworks, the use of lakes in Persian painting has not been studied. To produce a lake, the raw material, usually an intensely colored dye or stain, was precipitated on a finely powdered, colorless or white inert substrate such as calcium carbonate (chalk or limestone) in order to function as a pigment. The final pigment color could vary depending on the substrate. The gradually expanding range of colors found in Persian paintings from the 15th and 16th century and the ready availability of organic lake pigments used at that time in the textile industry strongly support the hypothesis that these pigments were employed in manuscript paintings (Wulff 1966, 189–92).

3.2.1 Blue Pigments

Most scholars of Persian painting have acknowledged natural ultramarine as the most important blue pigment in the Persian painter's palette (Welch 1972; Laurie 1935; Martin 1912, 108). The use of ultramarine was mentioned by Sadiqi Bek and in the appendix to Qadi Ahmad's treatise. Gettens and Stout
(1966) reported early occurrences of ultramarine as a pigment in the 6th and 7th centuries in the Iranian plateau. Lapis lazuli, the mineral from which natural ultramarine is prepared, was readily available from the mines of Badakhshan along the shores of the upper Oxus (in modern northern Afghanistan), a source known since antiquity (Laufer 1919, 520). The brilliant blue of ultramarine was extracted in an alkaline solution (lye) from a kneaded wax resin ball containing powdered lapis lazuli. The blue was then thoroughly washed to remove any residual alkalinity. Laurie (1939) suggested that the improved method of preparation for ultramarine was first developed in Europe and later transmitted to Iran in the 15th century. However, he provided no conclusive evidence as a basis for his suggestion.

In this investigation ultramarine blue was found to be one of the two most commonly used pigments, white lead being the other (see table 1). The ultramarine was very finely ground for Rustam Approaching Tents from a 16th-century copy of the Shahnama at LACMA (M.73.5.592). It was also found in a more coarsely ground form in a chapter heading from a Khamsa of Nizami (M.73.5.606). Both were executed in the 16th century, so it appears that different types of preparation methods could have existed in different workshops or for different purposes.

TABLE 1 Pigments Identified in 19 Medieval Persian Paintings in the Los Angeles County Museum of Art

Another blue pigment used in Persian painting was azurite. Holmberg (1978) found azurite in the Demotte Shahnama, made in the 14th century. The paintings analyzed in her study date from the 15th through the 17th centuries, and azurite was found in six of them. It may have been more widely used in earlier times according to Laurie (1935), who described a blue in a 14th-century Persian manuscript as azurite but without any analytical evidence. Farooqi (1977) did not even list it as part of the Persian or Indian palette. Vajifdar (1981) did, however, include azurite in his list of Persian pigments.

The Chinese, who employed azurite more than any other blue pigment, may have exported it to Iran (Schafer 1963). Wulff (1966, 3) has mentioned that northern Iran is rich in copper carbonate ores. Since azurite is a basic carbonate of copper, the raw material for the pigment may have been obtained there. Ground comparatively coarsely, azurite provides a deep blue pigment; it loses its color when ground too finely.

Another blue pigment, indigo, is a vegetable extraction from Indigofera tinctoria and other plants and was introduced into Iran from India in the middle of the 6th century according to Laufer (1919, 370). It had long supplied textile dyers with a deep blue stain. As a blue pigment, it is relatively stable and has good covering power. The use of indigo as a pigment was documented for neighboring regions by Gettens and Stout (1966), suggesting its importance in the Persian palette.
Laurie (1935) also listed two organic blues he felt may have been employed in Persian painting. One was indigo, and the other was more of a purple, the Tyrian purple made from shellfish. Vajifdar (1981) and Farooqi (1977) mentioned indigo. It cannot be certain that the organic blue found in this study is indigo, but the 16th-century scene of a Prince and Princess in a Garden (M.73.5.16) does contain an organic blue pigment. This evidence is contrary to Behzad's (1939) contention that only mineral colors were used in Persian paintings.

3.2.2 Red Pigments

Another organic pigment found during this analysis was a red used in a Youth Pouring Wine M.73.5.570. This painting is unusual among the paintings in this study because it was produced as an independent work of art in 1681 and not as an illustration in a narrative manuscript. We cannot determine what type of red organic pigment this is, but there are several possibilities.

Wulff (1966, 189–90) has commented on the presence of the kermes (Kermes vemilio) and the cochineal (Coccus cacti) insects in parts of Persia. The red colorant carmine was extracted from the bodies of the dead female insects and precipitated on a white or colorless inert substance to produce kermes (grain or crimson) lake and cochineal lake. The kermes lake is one of the most ancient of the natural dyestuffs, and cochineal lakes were imported to Europe from the New World in the 16th century (Gettens and Stout 1966). The root of the madder plant (Rubia tinctorum), which was cultivated in Persia, provided the deep red color of madder lake (Wulff 1966, 190). Another red lake, imported from India, derived its color from the exudation of the lac insect (Coccus laccae) (Schwepppe and Roosen-Runge 1986). As already noted, whether Persian painters made use of organic colorants as lakes or in pure form has not been investigated.

The other red pigments found in our study were all inorganic and are also mentioned in the literature. Cinnabar or vermilion (red mercuric sulfide, HgS) can be produced by grinding the mineral cinnabar (referred to as cinnabar) or it can be manufactured from mercury and sulfur (to make vermillion) (Gettens et al. 1972). These were the most widely used red pigments found in this study, but they have been combined in table 1 because the process used to indicate the mercury-containing pigment (x-ray fluorescence) did not allow for differentiation. Rich in sulfide ores, Iran may well have supplied the demand for vermilion within its own borders (Wulff 1966, 3). It has been found in many works of art, even in antiquity (Filippakis et al. 1979).

The appendix to Qadi Ahmad's treatise offered instructions for making the red from cinnabar, and Sadiqi Bek described the manufacture of vermilion by pounding mercury and sulfur together before heating (Minorsky 1959; Dickson and Welch 1981). From earlier times, the pigment had also been manufactured from mercury and sulfur (Kopp 1843–47; Cennini 1960, 24).
This red has long been valued for its stability and excellent hiding power. Many other authors have referred to the pigment, so this information reconfirms the general opinion regarding the importance of vermilion (or the natural form in the mineral cinnabar) for Persian artists.

Several iron oxide reds (earths or ochres) may have been employed by Persian artists, including a brick red, sometimes called Venetian red, and a deep purple-red rich in the mineral hematite, also known as Indian red. This is an ochre, one of the earth pigments which include clays, ochres, siennas, and umbers. Ochres consist of silica and clay, and red ochre is colored primarily by anhydrous iron oxide (the mineral hematite). Extensive deposits of iron oxide exist all over the world, one particularly good-quality source is the island of Hormuz in the Persian Gulf (Gettens and Stout 1966). Iron oxide has been used extensively as a pigment throughout history and prehistory, and it is no surprise that it is found in these paintings. It is mixed with white lead and vermilion in two paintings (M.73.5.412 and M.73.5.437) to give a richer, cooler red. Of the red pigments, iron oxide red was the second most frequently occurring red pigment in this study.

Red lead is the only other red pigment identified in these paintings. Laurie (1935) considered it to be a particularly fine orange type of red lead and observed it in Persian paintings as early as the 13th century. Red lead is produced by roasting white lead. The result is red tetroxide of lead (Pb3O4) that is, as Laurie correctly identified it, a very finely textured orange-red pigment. Red lead is less stable than the other reds found in these paintings, a characteristic that might explain why it is used less often. It was identified in only five of the paintings studied here, and in none of those was it the only red pigment used.

Another red pigment mentioned in the literature is realgar (Vajifdar 1981). This is an orange-red sulfide of arsenic that is closely related chemically to and associated in nature with orpiment. Qadi Ahmad’s appendix mentioned a “red orpiment” that resulted when yellow orpiment is ground exceptionally fine. He claimed that the more it was ground, the redder it became (Minorsky 1959). The pigment described is more likely to be realgar, the natural sulfide of arsenic. This is a separate pigment and does not result from grinding orpiment. It is not as plentiful in nature as orpiment, and it seems reasonable to expect that it would be found less often as a pigment. It was not found in this study.

### 3.2.3 Yellow Pigments

A variety of yellow pigments were mentioned in the literature. Some, like orpiment and yellow ochre, were from mineral sources. Others, like gamboge and Indian yellow, were organic pigments (Minorsky 1959; Laurie 1935, 1939; Vajifdar 1981). Other inorganic yellow pigments, like massicot, could be manufactured. Not all the yellows mentioned in the literature were detected.
in this research.

The most popular yellow pigment was orpiment, affirming Gettens and Stout's (1966) opinion that orpiment as a yellow was widely used, especially in the East. Wulff's (1966, 3) comment on Iran's wealth of sulfide ores suggests that orpiment, the yellow sulfide of arsenic, was available from local sources. The mention of orpiment in the appendix of Qadi Ahmad's treatise provides additional evidence of its importance in the Persian palette (Minorsky 1959). This pigment is no longer used because it is poisonous (Gettens and Stout 1966). Orpiment may have fallen out of favor because of a technical problem as well, for it can cause white lead to discolor and turn gray (White 1984). The two pigments do not need to be mixed together or applied on top of each other for this discoloration to occur; it can occur even if the orpiment is only adjacent to the area of white lead. An example of the discoloration of adjacent paint is seen in the faces of the Flaying Scene (M.73.5.437). In the painting Laila and Majnun at School (M.73.5.417, fig. 2) orpiment and white lead were mixed together before application, and the yellow robe worn by a figure on the right side of the schoolroom shows discoloration. This problem of discoloration did not deter artists from using orpiment, however. It was used throughout the three centuries investigated.

The other yellow pigment mentioned in the literature was yellow ochre, and it was found in only three paintings. All three were earlier paintings from the 15th and 16th centuries, depicting The Appearance of Sakyamuni (M.73.5.412), Laila and Majnun at School (M.73.5.417), and Lady with a Fan (M.73.5.587). We cannot be sure if there is any significance to the fact that yellow ochre was found only in earlier paintings. Further study may disclose any possible trends. According to this research, Persian artists preferred inorganic yellow pigments, possibly due to their availability and color stability. The problems mentioned with orpiment notwithstanding, its color is stable.

Organic yellow pigments were not found in this analysis, but they may have been used. Indian yellow, a brilliant, stable, yellow pigment prepared in Bengal from the urine of cows fed on mango leaves, may have been used by Persian painters. Saffron, a rich golden yellow powder from the flower of the plant, Crocus sativa, that was cultivated from Sassanian times in Iran, probably could have served directly as a pigment (Laufer 1919, 320). The Persian painters may have found this powder particularly useful in combination with gold pigment. Because saffron has always been dear, less expensive colors such as the orange from safflower (Carthamus tinctorius) or the yellow from shoots and roots of tumeric (Curcuma domestica and Curcuma longa) were often combined with saffron as adulterants (Laufer 1919, 309–10; Wulff 1966, 191). Wulff (1961) has indicated that both colors were employed in Persian textile production as well. Iranian textile dyers employed yet another yellow prepared from Persian berries (Rhamnus infectorius) as a lake; it might have been used as a pigment, too.
3.2.4 Green Pigments

The most common green pigment mentioned in the literature on Persian
painting techniques is verdigris (Dickson and Welch 1981; Laurie 1935; Vajifdar 1981). Historically, verdigris is a general term for green corrosion products that form on copper, brass, or bronze. Sadiqi Bek gave the most complete instructions for the making of verdigris. One must dig a pit two meters deep and in it bury copper plates immersed in wine vinegar for a month (Dickson and Welch 1981). Other recipes include vinegar and copper but can include salt and sugar (Farooqi 1977). The various recipes produce verdigris with different chemical compositions. Kühn (1970) found that verdigris could contain one copper acetate or a mixture of different copper acetates. Depending upon its chemical composition, verdigris can have a basic or neutral pH. The neutral verdigris (Cu(CH3COO)2H2O) is produced by grinding basic verdigris in strong acetic acid; this could be accomplished by recipes that include vinegar. Banik et al. (1981) investigated the deterioration of green copper pigments and the destructive effect on paper supports. In several of the paintings examined, copper greens have turned the paper below it brown and finally made it so weak that it cracked and broke apart.

Malachite is found in nature as a mineral. It is a basic copper carbonate, chemically similar to azurite and occurring with it but with different proportions of carbonate to hydroxide. The synthetic product is known as green verditer (Banik et al. 1981). Malachite, although a natural mineral, can cause degradation in a paper substrate at elevated temperatures (Banik et al. 1981). There was only one questionable occurrence of this pigment in the LACMA paintings. Holmberg (1978) did not find malachite in the Demotte Shahnama.

Green earth pigment may have been employed by Persian painters as well. Its simple preparation and its availability in the form of green clays (or earth) have contributed to its early and continuing widespread use in all parts of the world (Gettens and Stout 1966). Green earth was not found in this study or by FitzHugh (1988) in the Vever paintings.

We did identify some other copper greens in the paintings from the LACMA collection. One of the unusual greens, a basic copper sulfate identified by means of x-ray diffraction, was brochantite. Our observations are preliminary and tentative, but the brochantite seems to have caused less damage to the paper substrate than the basic copper chlorides, atacamite and/or paratacamite. The painting that contains brochantite (M.83.27.2) has been mounted so the reverse of the painting cannot be examined. Plesters has also identified brochantite by x-ray diffraction in a sample of powdered artificial green supplied from old stock given to her by an English colorman (Gettens and FitzHugh 1974).

Farooqi (1977) gave the ingredients for an “artificial verdigris” as orpiment and indigo. Such a pigment, a green that was a mixture of orpiment and an organic blue pigment, was found in the trees of the image Prince and Princess in a Garden (M.73.5.16). In that same painting, however, a copper green was
found in the rug used by the royal couple. The paper beneath the copper green pigment has turned brown while the paper under the “artificial verdigris” has not. A similar situation with regard to degraded paper substrate in conjunction with two green paints was observed in *Laila and Majnun at School* (M.73.5.417). The chemistry of copper green pigments, and their effect on paper, require further research.

### 3.2.5 White and Black Pigments

The two most essential pigments in any painter's palette are black and white. The unanimous choice for white in these paintings was white lead. This finding is consistent with treatises, which mentioned white lead as the only white used (Minorsky 1959; Dickson and Welch 1981). Other writers, however, listed other possibilities: whiting, chalk, and zinc white (Laurie 1935, 1939; Vajifdar 1981; Farooqi 1977). Whiting and chalk, are two natural forms of calcium carbonate (Gettens and Stout 1966). Zinc was detected in one of the LACMA paintings (M.73.5.417) with x-ray fluorescence spectrometry, but only in a tiny and insignificant amount. We found titanium only in inpainted areas of one painting (M.83.27.2). Zinc and titanium whites were not commercially available until the 19th and 20th centuries respectively (Gettens and Stout 1966) and so would be found in inpainted areas. St. Laurent-Lockwood (1981) also found white lead to be the only choice of Persian painters.

*Chandra (1949, 19–20)* suggested that zinc white might have been available in Iran long before its initial mass production in Europe at the beginning of the 19th century. He used the term *safeda*, however, which could refer to zinc white or to white lead, so it is impossible to determine which pigment he meant (FitzHugh 1988).

Black pigments are mentioned by Laurie (1939) in his discussion of the Persian painters' palette. He thought the material of the black pigment was lampblack, an understandable conclusion since lampblack is the only black mentioned in some treatises. Bukhari (1963) and Vajifdar (1981) mention lampblack as a black pigment. In the appendix to Qadi Ahmad's treatise, however, are four recipes for black inks (Minorsky 1959). Two require lampblack, or soot, combined with a gum in addition to other ingredients. The lampblack was produced by collecting the soot deposited on an inverted earthenware bowl from a lamp burning hemp oil. Baking the collected soot in the center of a dough ball extracted oil residues and resulted in a pigment consisting largely of amorphous carbon, a deep black powder. The other two recipes require charred wheat starch or tin combined with quicksilver (mercury) to provide a black substance (Minorsky 1959).

In all the black paint samples in this study only one black pigment, charcoal, was identified by polarizing light microscopy. Charcoal is not mentioned as a pigment in the literature on Persian painting techniques; it is mentioned only
as a material used in underdrawings. Charcoal was used in the form of a charred tamarind twig as a drawing tool or powdered and then pounced (by means of a cloth bag) through pricked stencils used to transfer drawings (Titley 1983, 216). With powdered charcoal already available to them, it makes sense that Persian painters would use it as a pigment.

In her analysis of the pigments in the Demotte Shahnama Holmberg (1978) also suggested that the black pigment was charcoal rather than lampblack. Perhaps lampblack was not used as a black paint in paintings or in illuminations, but the recipes mentioned are only for black ink. Was it used as an ink? We could not explore the question extensively, but the ink sample examined was lampblack. Therefore, there may well have been separate types of black color used in separate workshops. Perhaps the finer texture of the lampblack made a superior ink for writing, while the coarser-grained (and more easily produced) charcoal made a better color for the painter. The particles that result from lampblack, made by collecting the soot of burned oil, are tiny and round, while the particles from ground charcoal are larger and more fractured in appearance under the microscope (Gettens and Stout 1966). Using a polarized light microscope to view particle morphology, we concluded that the paintings examined for this study did not contain lampblack as a pigment.

3.2.6 Metals

Metallic powders crowned the precious palette of Persian miniature painting. Iran was rich in alluvial gold and copper ore (Wulff 1966, 2, 13–14; Laufer 1919, 510–12). The mines of Badakhshan supplied Iran with silver. Two forms of colors are recorded as being used: ground particles in a binding medium and metallic foil applied on a binding medium (Dickson and Welch 1981). The paintings examined did not contain gold leaf used as a color. Gold was used, but in the form of ground particles in a medium. This finding corroborates Laurie's (1935) observations that a gold paint was used on most Persian paintings.

The preparation of the gold paint was a laborious process. First, gold leaf was made by pounding gold between layers of deerskin until the gold was extremely thin. Then the gold leaf was pounded on iron or stone with glue until it formed paste. This paste was dissolved in water and allowed to settle. The water was poured off, and the sediment was mixed with dry glue and saffron. The gold paint was then ready for use. Another possible preparation of powdered gold included mixing the gold with honey or glue between one's fingers, which could take hours, and then dissolving the resulting paste in water. After the gold was applied with a brush, it was “cooked,” meaning burnished, until it was a bright glossy gold surface (Behzad 1939). St. Laurent-Lockwood (1981) describes the mixing of gold with copper to make the gold a warmer color and with silver to make it cooler. In Youth Pouring Wine (M.73.5.570), gold was mixed with silver for the vessel the youth holds,
which is a noticeably cooler gold than the gold of his boots. This metal combination was compared with other gold areas in other paintings by x-ray fluorescence and confirmed.

Laurie (1935) mentioned a “heavy dull grey gold” used in Persian paintings of the 13th century. Although he observed it in later works, it was rare in subsequent centuries. An example of this gray-gold may be present in a Battle Scene from the Big Head Shahnama (M.75.24). In this painting a charcoal gray was applied over the gold helmets of the warriors.

Silver was also used, but is now only seen as black in the paintings because it is tarnished. The water in the image of King and Sage in Landscape (M.73.5.29) is silver, as are the gray steps in Zahhak Enthroned with Two Sisters (M.83.27.2). Holmberg (1978) also found tarnished silver during her study. When the silver is as tarnished as the examples in these paintings, the techniques used for this analysis cannot determine whether the silver was applied as particles in a medium or as silver leaf. The Persians must have known that silver tarnished because Bailey (1985) found carbon black where silver would have been expected in a composition from Shiraz. This Shiraz painting could have been copied from an older, tarnished model.

Any identification of pigments employed in Persian painting by simple visual examination is highly unreliable. Differences in the source and manufacture of each pigment, which produce variations in the finished color, complicate the problem of identification. The large body of technical information on painting techniques, tools, and pigments used in Western paintings has proved valuable in dating, authenticating, and distinguishing between original painting and restoration. Persian painting techniques and tools are so different from Western painting traditions that a new body of information needs to be assembled before it can be applied to the study of Persian paintings.

4 OTHER MATERIALS USED BY MEDIEVAL PERSIAN PAINTERS

4.1 VEHICLES, SIZES, AND ADHESIVES

IT IS important to note that the information in this section is a compilation of the literary evidence only. No analytical work was done on the media. Materials with adhesive properties like vehicles and paper sizing can be most conveniently divided into four groups: proteinaceous materials including gelatin, glue, egg yolks, and egg whites; starches from rice or wheat; vegetable gums; and waxes and oils.

Schulz (1914, 22) has suggested that gelatin, a highly purified form of glue, was employed as sizing for some paper in Persia. Without providing convincing evidence, other scholars have postulated the use of glue as a binder for many pigments in Persian painting (e.g., Behzad 1939). The writer of Qadi
Ahmad's appendix mentioned glue as a binder for gold pigment. He also indicated that egg yolk was employed as a vehicle for some pigments (Minorsky 1959). Schulz (1914, 23) has speculated that egg white might have been employed to prepare the surface of writing paper.

Hunter (1978, 194) claimed that starches were the most commonly used sizes in Persian papermaking. Wheat starch cooked in water to make paste was required for laminating papers and for inlaying miniature paintings as well (Grohmann 1967, 126).

The appendix to Qadi Ahmad's treatise discusses the addition of gum (arabic) as a vehicle for many pigments (Minorsky 1959). Grohmann (1967, 128–29) has carefully documented the use of gum arabic as a vehicle for black and colored inks. Such convincing evidence supports the notion that gum arabic (From Acacia senegal) constituted the essential component of the medium employed in most miniature paintings of the 15th and 16th centuries. Gum tragacanth, which swells considerably in water, could have provided an alternative adhesive to starch pastes, according to Grohmann.

A number of scholars have suggested that, in addition to the aqueous base of gum arabic, the vehicle used in Persian painting must have included one or more materials to impart greater flexibility and durability to the paint films. One such combination, wax and gum arabic, postulated by Laurie (1939) as the binder in Persian painting, has handling characteristics and a finish that probably would not have met the requirements of the Persian painter. Grohmann (1967, 128) commented on the addition of linseed oil. One can still find the addition of oil to gum mentioned in modern literature on artists' techniques as a method of strengthening the medium (Mayer 1970). Another combination suggested by Martin (1912, 108) includes glue. Persian miniaturists could have added a variety of other materials to particular pigments in combination with the vehicle. Honey and sugar, due to their hygroscopic qualities, when combined with gum arabic solution, might provide flexibility (Mayer 1970). Grohmann (1967, 129) has mentioned the addition of pomegranate juice to cinnabar. No doubt throughout the period under consideration Persian artists employed several variations of the basic medium, depending on availability of materials and changes in technique.

4.2 DRAWING AND PAINTING IMPLEMENTS

According to the literature, the Persian artist used a charred twig, possibly of tamarind, for drawing. Powder from the charred twigs for pouncing and a finely pointed awl (minfād) for punching holes through the paper were both important to the Persian technique of copying (Martin 1912, 103; Grohmann 1967, 126).

According to Grohmann (1967, 126), calligraphers (and possibly painters), filtered the dust and other unwanted particles from their inks (or paints), by
saturating a lump of cotton wool with color (*liqa*) from one palette and transferring it to another by squeezing the color from the wool with a conoid, ebony rod (*milwag*). During the painting of a manuscript illumination or an individual painting, the paper was secured to a portable, smooth wooden panel with a clamp (*Welch 1972*, 26). The painting technique depended on extensive burnishing. Polished agate, rock crystal, or carnelian could have served as the burnisher (*Martin 1912*, 108; *Behzad 1939*). The bristles of the painter's finely pointed brushes probably consisted of either the hairs from the throat of a Persian kitten or the hairs from the tail of a squirrel (*Behzad 1939*).

*Behzad (1939)* has described a method for making brushes that might have been followed in Iran. Hairs for brushes were collected and floated on water to separate them. They were then laid on a smooth, slick surface such as a faience slab. When dry, they were gathered with a silk thread, fitted directly into the quill opening, and secured. According to Behzad, the painters preferred the first three feathers of the pigeon's wing for the production of brush handles. Sadiqi Bek gave an elegant description of the making of a brush from squirrel's fur. The hairs from the squirrel's tail were combed, sorted according to length, and then tied together with three separate knots (*Dickson and Welch 1981*).

### 4.3 PAPER

Paper was manufactured in Iran perhaps as early as the 8th century. The Arabs learned the craft, so the story goes, from Chinese craftsmen (*Vajifdar 1981; Pedersen 1984*, 61). Rag papers, or papers made from linen fibers, were available as well as silk papers. Locales known for their paper production were Samarkand, Zasim Beg, and Tabriz as well as sites in India and China (*Vajifdar 1981*). Pedersen (1984, 64) also notes Baghdad and Egypt as places where paper was made as early as the 12th century. Paper made in Tabriz was characterized by a yellowish color, according to *Farooqi (1977)*. All paper was not necessarily from rags, however. An 11th-century description of papermaking from plant fibers mentions a quicklime process for softening raw fibers (*Bosch et al. 1981*, 28). *Snyder (1988)* found evidence in the papers that she examined of both rag and plant sources for the paper fibers. In Islamic paper, the mold left laid lines in the paper but not chain lines because the horsehair thread used to stitch the mold together did not leave impressions in the paper (*Snyder 1988*). Watermarks, common in European papers, are not found in Islamic papers (*Bosch et al. 1981*, 30).

All the paintings in this study were executed on burnished paper. *Snyder (1988)* found inclusions in the papers she studied that might have been introduced in the papermaker's vat or during the burnishing process.

The majority of paintings in this study were on thin, fine paper. In this context, “fine” denotes a paper with very few incompletely beaten fiber inclusions. One painting was on a thicker sheet of paper that was equally fine. Four
paintings were on sheets of coarser paper, implying that the paper contained small, uneven clumps of paper fibers. Not all the paintings were done on a single sheet; four were on layered paper. All the papers were a creamy white color, and only one had been decorated with flecks of gold prior to the application of paint. None of the paintings in this survey were on tinted paper, although tinted paper was used in Persia, (Bosch et al. 1981, 34).

In this discussion a concerted effort has been made to include all possibilities and to indicate which materials and implements were most probably employed. With additional technical research, such as the pigment analyses reported here and others mentioned in the pigment section of this paper, future discussions of Persian painting will benefit from a more substantial base of documented information.

5 THE CLASSICAL TECHNIQUE

The techniques described in this section are those employed during the golden age of Persian painting that began early in the 15th century. The Persian method of painting can be properly described as a watercolor technique since an aqueous gum solution probably most frequently served as the essential ingredient of the pigment binder (see section 4.1). Western terms such as “wash” (in which the color of the paper creates the lights through translucent or transparent layers of paint) or “gouache” (in which opaque, sometimes thick, often textured and chalky layers of paint include their own highlights through the addition of white or light pigments) are not applicable to Persian technique (Cohn 1977). Persian painters aimed to produce slightly glossy, smooth, opaque layers of paint. And while creating the illusions of three-dimensional space and a natural light source constituted primary goals for Western painters, Persian artists did not concern themselves with these illusions. The beauty of Persian technique derived both from a harmony of colors and from a poetic interplay of line and pattern with the solid colors. At the same time, the paintings depict animals or figures in landscapes or architectural settings, illustrating the poetry with which they often appear.

Before the preliminary drawings for the paintings could be made, the paper required preparation. The paper support received a thorough external sizing, possibly with wheat or rice starch, egg white, or gelatin. The starch was cooked in water, probably diluted in the same, and applied in a thin coat to the paper's surface. The papermaker must have performed this part of the preparation (Hunter 1978, 194–95). The paper was thoroughly burnished on both sides with a crystal egg, polished agate, or other polished stone (Hunter 1978, 196; Brown 1924). The paper was placed on a smooth hardwood plank and burnished until front and back surfaces achieved the proper gloss. The preparation resulted in a slick, somewhat impermeable surface.

In Western watercolor painting, the paper must be stretched to prevent excessive cockling (Cohn 1977). This practice precludes reversing the paper
during painting since all the edges must be attached firmly to a rigid support. In the Persian technique, in which reversals throughout the painting procedure were critical for burnishing, the paper was not stretched. The artist, seated on the floor, one knee raised to support the drawing board with paper clamped to it, began his work (Welch 1972, 26).

Preliminary drawings followed the preparation of the paper support. The great masters of the traditional technique may have made the initial sketch with a slightly wetted, finetipped brush or a charred twig of tamarind. The artist set basic geometric forms and lines with this sketch. He may have elaborated on the rough underdrawing with outlines made by a fine brush. Persian sources seem to refer to such an underdrawing as the *tarh*, which connotes diagram or program rather than sketch or study (Schroeder 1942, 10).

In the paintings examined for this study we found clear evidence of 12 underdrawings in a variety of colors. Two of those had brown underdrawings, two were partially red. The other colors (pink, purple-red) would likely have been combinations of pigments, possibly mixtures of leftover pigments in the painter's palette. The remaining underdrawings found were done in black. Only one of the underdrawings, a black one, had a white wash, or a translucent white layer of paint, over it. This type of preliminary wash over the entire drawing is common in Mughal paintings but not usually found in Persian works (Johnson 1972). An unusual example of underdrawing found in a painting of the *Appearance of Sakyamuni* (M.73.5.412) was executed partially in red and partially in black. Only one painting revealed a change from the original underdrawing in the final painting; instead of the boots shown in the underdrawing (revealed by ultraviolet examination), leggings were depicted in a painting of a *Youth Pouring Wine* (M.73.5.570). Although perhaps not an underdrawing, the drawing of a *Lion Attacking a Dragon* (M.73.5.12) is done in both brown and black.

Apparently even master painters employed tracings copied from other paintings or drawings as an aid in creating new compositions. In that way isolated elements could be repeated in the new compositions. In order to copy a partial or entire composition, a thin piece of paper (or translucent gazelle skin) was laid over a master drawing or painting. The design outlines were then traced; possibly with a piece of charred tamarind twig. The tracing was then carefully pierced along the traced lines. Charcoal powder held in a thin fabric (pounce) bag was then pounced through the piercings of the tracing onto a sheet of prepared paper (Martin 1912, 108; Chandra 1949, 39). Such pierced tracings could be used repeatedly for copying (Welch 1972, 26). Outlining concluded the copying technique. Lentz and Lowry (1989) discussed the repeated use of compositional elements, or even whole compositions, in 15th-century Timurid Persian art. They thought the repetition of images allowed Timurid artists to create a codified visual aesthetic.

Apprentices ground each pigment to its proper particle size (Brown 1924). The
artist then mixed his pigments with vehicle. The paint also required proper
dilution in water. For broad areas of color, the paint must have been diluted
just enough to flow easily, but not as much as a Western watercolor wash
would have been. For lines and details, the paint may have been somewhat
less diluted. The outlines of the preliminary drawing determined the basic
color areas of the painting. In each area, the artist applied one thin layer of the
appropriate color at a time with a medium- or large-tipped brush according to
the size and shape of the area. Layer was built upon layer, with each allowed
to dry completely and burnished frequently until a slight gloss, opacity, and
the desired intensity of hue were achieved.

Not all colors were burnished, however. Sadiqi Bek warned the reader about
ultramarine blue (Dickson and Welch 1981, 266). This color should be “laid
directly with the medium” and not polished to a lustrous sheen. Instead, the
artist was advised to apply medium (possibly with a rabbit's foot) over the
ultramarine and then gently smooth it with his hand. This step was taken to
smooth any cracked surfaces in the paint. We found evidence of this technique
in the illuminated colophon (M.73.5.518) dated 1564–65 from Bukhara.
Neither was the ultramarine in Flaying Scene (M.73.5.437) burnished. This
technique particular to ultramarine seems to have been used on both
illumination and miniature paintings because it occurs in two pieces from the
same manuscript produced in Shiraz in 1517, the Khamsa of Nizami: a chapter
heading page of calligraphy (M.73.5.606) and an illustration of Majnun at the
Kaaba (M.73.5.423). Another exception, gold pigment, was burnished directly
if the artist wished to create a glossy finish or through a thin piece of paper
when he wanted a more raw appearance (Behzad 1939).

The colors of the painting were applied over the underdrawings and often in
sequence. That is, one color would be applied wherever it was desired
throughout the painting and then the next color would be applied in the
appropriate areas. The painter seems to have begun with the background
colors and then moved to the animals and figures, applying the flesh tones first
and finishing with the clothing (Binyon et al. 1933).

The sophisticated Persian painter apparently cut, or mixed, his colors, sensing
that the interplay of pure hues would result in a garish effect rather than the
desired harmony. A good example of this toning of colors for the sake of
visual harmony is found in a 15th century painting from the Shahnama of
Firdaws, entitled Isfandiyar and the Simurgh (M.73.5.410). In this painting,
two different shades of yellow were used in the Simurgh's body. The primary
pigment in both these yellows is orpiment, but gold, vermilion, and white lead
have been added to the yellow in the body to make a warmer tone. The yellow
in the bird's wings, however, has ultramarine added to it to produce a cooler
tone. Colors were never cut to the extent of creating an atmospheric
perspective, however. Particular combinations of pigments for flesh tones,
water, landscapes, and the like may have been favored by the Persian artists
(Minorsky 1959).
Certain pigments may have required the addition of white to display their brilliance and to assist in developing opacity. In this study, white lead was found in many colors of the paintings. Even colors used for animals or clothing that appear to be black contained white lead. In the Flaying Scene (M.73.5.437) a horse, which appears black, contains white lead.

Adjustments or corrections were necessary. When two adjacent color areas required the same hue, the painter could render one slightly more brilliant or cut the other slightly. To brighten a color already applied, the artist simply moistened the area and, employing a brush loaded with a dilute solution of the same color, swept it in rapid strokes (Chandra 1949, 43). Besides cutting a shade by adding a little black or a complement, the miniaturist could also deepen a color by applying more layers of the same. To compensate for specks, unevenness, or other slight imperfections in a color, another layer could simply be added (Chandra 1949, 44). When removal of a color was desired, the area could be wetted and stroked with a dry brush, this procedure being repeated until all the color had been removed. If a color overlapped a previously fixed line, the final outline was adjusted to accommodate the change. The aesthetic demands of the overall color harmony determined the choice of colors for the details as much as representational or naturalistic considerations.

Two of the most important finishing procedures were final outlining and the shading and blending of colors. For these procedures, the miniaturist used the finest of his fine brushes, the tips of which culminated in no more than a few hairs. Employing a cut shade or an intense, closely related hue, he reinforced the outlines of the color areas. Black was often used for this purpose. The sweeping calligraphic strokes used to accomplish the final outlining demanded great finesse.

Persian painters also delighted in blending and shading colors for purely decorative effect and coloristic enhancement. A repertoire of essential techniques provided the artist with the means of achieve those ends. The techniques included stippling or dotting as well as parallel hatching. The effect of this hatching or stippling could be varied by altering the thickness and the spacing of the elements. Often, the elements were applied so that each remained distinct, but they could also be executed so that one blended into the next. Incredible precision and facility were absolutely necessary to execute the subtle variations in Persian technique successfully. In some cases, the work is so fine that it must be viewed with the aid of magnification to detect clearly the individual elements of shading or blending.

During our examination we observed some techniques not mentioned in the literature. One was delicate punchwork, or a pattern made of tiny impressions, that can be seen in the gold areas of some paintings. An example is Yusuf in Meadow (M.73.5.443) in which punchwork is seen in the gold of the flames and around the central figure's head. St. Laurent-Lockwood (1981) also
noticed punchwork during her examination of Persian miniatures.

In a painting from a *Khamsa* of Nizami, however, another technique was used to depict the floor tiles on the smooth burnished paint. The outlines of the floor tiles in *Laila and Majnun at School* (M.73.5.417) were gently incised into the paint to create the image of rectangular floor tiles. Paint is used for the vertical and diagonal lines in the floor, but the horizontal lines in the floor are incised. A linear design on the floor is also incised in another work examined for the study, the *Prince and Princess in a Garden* (M.73.5.16) dated 1580 from Qazvin.

Another technique not in the Persian painting literature was used on two paintings, both possibly from the same *Shahnama* dated to the late 15th century. In these works, a layer of saturating medium was applied to some colors to tint and enhance them. This application was made around the edge of the pit in *Army a in Pit* (M.73.5.23), where the stronger pink perimeter was produced by a layer of semitransparent medium rather than a direct application of more pigment. The medium layer, when analyzed under the polarizing light microscope, did contain a few grains of pigment, but the dominant visual effect was caused by the saturation of the underlying color. The rosy cheeks of the soldiers were produced using the same technique. In other painting (M.75.24) the horse's reins were made shinier and darker by an application of a layer of saturating medium.

When a painting was complete, it was given to a binder. Marginal decoration may have been added to the painting before it was bound. Alternatively, the decoration could have been done at the time the preliminary drawing was complete. Qadi Ahmad gave a detailed account of the rulings that should be applied in Persian manuscripts (Minorsky 1959). One set of rulings observed in this study was done in this manner, a page of calligraphy with a delicate illuminated panel at the top, and rulings of black, gold, blue, and pale green (M.73.5.518). The rulings cover the edges of applied borders, so further examination is necessary to determine the completeness of the piece.

6 CONCLUSION

THIS PAPER has presented an overview of the information available on Persian painting technique. The tools and paint application techniques used have been reported with evidence of those tools and techniques found in specific paintings. The pigments discussed in the literature about Persian paintings have also been reviewed and compared to a scientific analysis of pigments found in paintings at the Los Angeles County Museum of Art.

Simple visual identification of pigments has proven to be unreliable, as has been seen in the literature. The work reported here has provided more specific pigment identification. Ultramarine blue and white lead were the two most popular pigments used in the paintings examined in this study. Other blue
The pigments used were azurite, found in six paintings, and an organic blue. The evidence of an organic blue is contrary to Behzad's (1939) statement that only mineral ores were used by Persian painters.

Another organic pigment, a red pigment, was detected in a painting produced as an independent work of art and not as a manuscript illumination. The source of this red cannot be identified at this time. Vermilion (or cinnabar in the natural form) was the most used red pigment. As oxides were plentiful on the island of Hormuz, it is not surprising that iron oxide red was found in the paintings. Next to vermillion, iron oxide was the second most frequently occurring red pigment. Realgar was not found, although it has been found in previous studies.

The number of yellow pigments mentioned in the literature was not reflected in this research. Out of the five mentioned in the literature, orpiment was the most popular yellow pigment, despite its poisonous character and its graying effect on white lead. Yellow ochre was found in only three, earlier paintings, but no significance can be attached to that fact at this time.

The only green pigments found were copper greens. Brochantite is a basic copper sulfate, and atacamite and/or paratacamite are basic copper chlorides, but brochantite may have had a less damaging effect on the paper substrate. Further exploration of this effect is needed. Verdigris, a copper acetate, was found in several paintings. Greens resulting from the mixture of yellow and blue pigments were found in two paintings (M.73.5.16 and M.73.5.417). The mixtures were not the only green in the paintings, however, because both paintings also contained copper greens.

The unanimous choice for white in the paintings in this study was white lead. Although lampblack was the only black pigment mentioned in the literature, charcoal was the only black pigment found in the paintings examined in this study. Lampblack was found in an ink. Future research on carbon pigments is needed to make such identifications certain.

Gold was not applied to the paintings as gold leaf, but as ground particles in a medium. The “dull grey gold” mentioned by Laurie (1935) was found to be a layer of charcoal paint applied over the gold in a Battle Scene from the Big Head Shahnama (M.75.24).

Because the silver in all the paintings examined was tarnished, it was not possible to determine how it was applied. Bailey (1985) found carbon black used to imitate tarnished silver in a Shiraz painting.

The information found in this study is admittedly preliminary. Further study of the materials and techniques used in Persian paintings should be done. The simple visual identification of pigments is not accurate, as mixtures, method of manufacture, and natural source can all have an affect on the color in a
finished painting. We hope that additional studies will add to the body of information about Persian paintings and can be applied to advance the study of these beautiful works of art.

ACKNOWLEDGEMENTS

We would like to thank Victoria Blyth-Hill, John Twilley, and Thomas Lentz of the Los Angeles County Museum of Art for their help. We would also like to thank Elisabeth West FitzHugh for her encouragement and advice. Part of this research was supported by a grant from the National Endowment for the Arts.

REFERENCES


Filippakis, S. E., B. Perdikatsis, and K. Assimenos. 1979. X-ray analysis of


AUTHOR INFORMATION

NANCY PURINTION graduated from the University of Delaware/Winterthur Art Conservation Program. She has had internships at the Center for Conservation and Technical Studies, Fogg Art Museum, Harvard University, and at the Los Angeles County Museum of Art. At the Norton Simon Museum, Pasadena, she held the position of conservator for the collection. She is presently a conservator at the Conservation Center for Art and Historic Artifacts in Philadelphia. Address: Conservation Center for Art and Historic Artifacts, 264 S. 23d Street, Philadelphia, Pa. 19103.

MARK WATTERS took his bachelor's degree in art from Stanford University in 1975. He specialized in paper conservation at the Institute of Fine Arts, New York University, taking his master's degree there in 1980. He interned at the Intermuseum Conservation Center in Oberlin, Ohio. More recently his work in the paper conservation studio at the Los Angeles County Museum of Art was supported by a National Endowment for the Arts grant. Currently he works in private practice with colleague Robert Aitchison. Address: Aitchison and Watters Inc., Conservators of Art on Paper, 740 North La Brea Avenue, Los Angeles, Calif. 90038.
ULTRAVIOLET-FLUORESCENCE MICROSCOPY OF PAINT CROSS SECTIONS

JOHN M. MESSINGER

ABSTRACT—Cycloheptaamylose-dansyl chloride complex, a new fluorochrome specific for proteins, has been investigated as a stain to identify artists' paint media. Its selectivity and limitations are compared to those of the following commonly available fluorescent and nonfluorescent stains: lissamine rhodamine B sulfonyl chloride, 5-fluorescein isothiocyanate, amido black, Sudan black, rhodamine B, and 2’,7’-dichlorofluorescein. The methods used to examine the characteristics of these stains were reflected visible light microscopy and ultraviolet-fluorescence microscopy. The known samples of artists' media analyzed with the stains were linseed oil, casein, tempera, glair, gelatin, rabbit skin glue, and acrylic emulsions.

1 INTRODUCTION

This study was undertaken to investigate the viability of using cycloheptaamylose-dansyl chloride complex (DC-C7A) as a fluorochrome marker for detecting proteins in paint cross sections. Dansyl chloride is a common reagent used for the fluorescent labeling and microanalysis of proteins (Kinoshita et al. 1974, 1975). In water it is insoluble and hydrolyzed to the sulfonic acid. Dansyl chloride can be complexed with B-cyclodextrin to yield cycloheptaamylose-dansyl chloride complex, a reagent that is both soluble in aqueous urea solution, and very slow to hydrolyze. It was felt that this reagent might selectively stain proteins so that they could be examined by fluorescence microscopy.

To ascertain the strengths and limitations of DC-C7A, it was imperative to compare the selectivity to stain protein containing materials and the color and uniformity of staining of DC-C7A to the those properties of two other fluorochromes commonly used to detect proteins in paint cross sections: lissamine rhodamine B sulfonyl chloride (LISSA) (Wolbers and Landrey 1987) and fluorescein isothiocyanate (FITC) (Wolbers and Landrey 1987; Wolbers 1988). These stains were also compared to the commonly utilized non-fluorochrome protein stain amido black (AB2) (Martin 1977), and the stains for oil: Sudan black (SB) (Johnson and Packard 1971), and the fluorochromes rhodamine B (RB) (Wolbers and Landrey 1987) and 2’,7’ dichlorofluorescein (DCF) (Wolbers and Landrey 1987).

These stains were used to stain the following types of known media: linseed oil, casein, tempera, glair, gelatin, rabbit skin glue, and a few acrylic emulsions. Some of the media were also examined while loaded with such pigments as gypsum, whiting, titanium white, zinc white, turquoise, lamp black, and ultramarine. It was also noted whether the samples exhibited...
autofluorescence (fluorescence in the absence of any stain).

2 EXPERIMENTAL

The various media were purchased commercially and painted onto glass microscope slides or onto canvases that had been preprimed with acrylic gesso. The samples on canvas that contained linseed oil were allowed to dry and cure at room temperature for 11 months. The linseed oil samples on glass were cured in the dark at 60°C for 2–3 weeks. The acrylic samples were cured for several days at room temperature. The tempera and glair samples were taken from paintings that were 7–10 years old. The sample of casein paint was taken from a piece of furniture about 16 years old.

After the known samples had cured, large representative chunks were removed from the test paintings and encased in cubes of Bio-Plastic polyester resin. After curing, the cross sections were ground and polished with odorless thinner as the cutting fluid.

The samples were examined with a Zeiss Universal microscope with dark-field reflected light. The illumination was either in the visible light range with a 12 volt tungsten lamp or in the ultraviolet range with a high-pressure mercury vapor lamp. The filter set used with ultraviolet illumination was Zeiss catalog no 487702, which allows excitation of the sample with wavelengths up to 365nm and passes visible fluorescence above 420nm (fig. 1)

![Fig. 1. Transmittance versus wavelength for filter set used with ultraviolet illumination (Zeiss catalog no. 487702). Reprinted from Zeiss product literature](image)

Photomicrographs were recorded on Kodak Ektachrome 200 daylight film (ED 135). When ultraviolet illumination was used, exposure times were four seconds. No filtration was used for ultraviolet illumination. To obtain proper color rendition with tungsten illumination, a Wratten 80A filter was required.

DC-C7A is not commercially available, but its preparation from commercially available starting materials is easy. It was prepared, as outlined by Kinoshita.
et al. (1975), by the following procedure: a 125 ml flask containing a magnetic spin bar was charged with 2.0 g of beta-cyclodextrin and 100 ml water. Fifteen minutes of stirring was required for complete dissolution of the cyclodextrin. Then 0.40 g of dansyl chloride was taken up in 3 ml anhydrous acetone and added to the cyclodextrin solution via dropper over 5 minutes. A fine yellow precipitate of the DC-C7A complex is formed in the flask during the course of addition. The flask and its contents were cooled in an ice bath for 30 minutes, centrifuged for 10 minutes, and the supernatant liquid decanted and discarded. The resultant lemon yellow powder was dried overnight over anhydrous CaSO4 at reduced pressure. The DC-C7A complex can be stored several months over CaSO4 in the dark.

Just before use, about 10 mg of the DC-C7A complex is stirred into 5 ml of 8 M urea solution, and one drop of 10% triethanol amine in isopropanol (v/v) is added. The stain solution may be used immediately even though it takes 2–3 hours for all of the DC-C7A complex to dissolve. The solution remains effective as a stain for at least 4 hours. The stain was applied by soaking the sample cross sections in the solution for 8–10 minutes.

The other fluorochromes were applied to the cross sections in solutions more dilute than those recommended by Wolbers and Landrey(1987), but otherwise the procedures were the same. It was felt that more dilute solutions would give fewer false positives. Approximately 10 mg of LISSA or FITC was dissolved in 25 ml of dry acetone. A drop of the stain solution was applied with a polyethylene dropper to a cross section, and the excess was wiped away immediately with a paper wipe. Approximately 10 mg of RB or DCF was dissolved in 25 ml denatured ethanol. A drop of the stain solution was applied with a polyethylene dropper to a cross section and the excess wiped away immediately with a paper wipe.

The nonfluorochrome Sudan black (SB) was applied as recommended by Johnson and Packard (1971). A 60% ethanol:40% water (v/v) solution was saturated with SB. Cross sections were immersed in SB solution for about 30 minutes, then soaked in 40% ethanol:60% water (v/v) for 1 minute, then soaked in water 30 minutes. The amido black AB2 stain, as described by Martin (1977), was used exclusively: 100 mg of amido black was dissolved in 45 ml of glacial acetic acid to which is added 45 ml of 0.1 M aqueous sodium acetate followed by 10 ml of glycerine. Cross sections were immersed in the AB2 solution for approximately 5 minutes, rinsed with water, then soaked in 5% aqueous acetic acid for 5 minutes.

3 RESULTS

Table 1 summarizes the staining results obtained from the samples examined and some of the results are illustrated in figures 2–13. Exact numbers of the number of staining attempts for each stain on each media, were not recorded. In fact, a particular stain was used to stain a particular media from one to 10
times because most the cross sections contained three or more known layers. With one exception, there was complete reproducibility of results when a particular stain was used to stain a particular layer. The exception, LISSA on pure linseed oil, sometimes yielded spotty pink blotches (fig. 7) while at other times it yielded a uniformly pink coloration of the media. The blotchy result seems to be related to the excavation of the surface of the sample.

TABLE 1 STAINING RESULTS

Fig. 2. Sample 1, schematic (43x). Sample consists of iron oxide red pigment in casein-lime binder on wood.

Fig. 3. Sample 1, autofluorescence in UV light (43x)
Fig. 4. Sample 1, fluorescence, stained with DC-C7A (43x).

Fig. 5. Sample 2, schematic (43x). Layers consist of gelatin and linseed oil.

Fig. 6. Sample 2, autofluorescence in UV light (43x).

Fig. 7. Sample 2, fluorescence, stained with LISSA (43x).
Fig. 8. Sample 3, schematic (43x). Layers consist of egg white, ZnO in linseed oil, and acrylic gesso.

Fig. 9. Sample 3, visible light, stained with Sudan black (43x).

Fig. 10. Sample 3, fluorescence, stained with FITC (43x).
4 CONCLUSIONS

The results obtained with SB are fully consistent with that obtained by Johnson and Packard (1971). SB will stain layers containing acrylic emulsion a blue to black color. The results obtained with AB2 are fully consistent with those obtained by Martin (1977). It fails to stain acrylic emulsion layers to any significant degree.

The results obtained with RB and DCF are fully consistent with those obtained
by Wolbers (1987). Layers containing acrylic emulsions are stained varying shades of red to yellow by RB and yellow-green to green by DCF. It has been pointed out that these results—using knowns—seem more consistent than the results typically found when stains are used with unknowns, especially from older paintings (Gifford 1991).

Both LISSA and FITC consistently yield a positive result when used to stain linseed oil containing certain pigments and with media based on acrylic emulsions. In fact, upon staining with FITC, a sample containing three layers: egg albumin over zinc white in oil, over acrylic gesso, left the albumin layer unstained, stained the zinc white layer bright green, and stained the acrylic gesso layer dim green. Similarly, LISSA consistently (tested three times with different lot numbers of the stain and delivery solvent) marked a sample very convincingly for protein. Yet this sample contained only linseed oil with whiting.

It was observed that the acetone delivery solvent used with LISSA and FITC would etch the surface of the young linseed oil samples used in this study. This fact may explain some of the discrepancy between these findings and those of Wolbers (1987, 1988). However, it cannot be the full reason as neither LISSA nor FITC would stain lead white or ultramarine containing oil layers. LISSA may have some value in detecting acrylic paints as it has consistently yielded a characteristic yellow-orange color with the acrylic paint samples analyzed in this study.

The fluorescent protein stains contain sulfonyl chlorides or isothiocyanates that are highly electrophilic functional groups. These materials react quickly and exothermically with nucleophiles such as hydroxyl groups (−OH), and in particular with primary amines (−NH2) and thiols (−SH) all of which are found in proteins. Sulfonyl chlorides react with water to form sulfonic acids and isothiocyanates react with water to form thiourethanes. One might conjecture that they would react with water that is adsorbed onto the surface of pigment particles and remain tightly bound to these particles in the same manner in which polar compounds are adsorbed onto the surface of the silica gel particles used in chromatography. It is interesting to note that manufacturers usually coat titanium oxide with silica and/or alumina to aid in its dispersion in the media and to improve the durability of the paint media (Whitehead 1978). The results of this study are consistent with the hypothesis that fluorochromes with electrophilic groups are reacting with water adsorbed onto the surface of the polar micelles present in acrylic dispersion paints.

DC-C7A is the only protein-selective, fluorochrome stain in this study to stain casein-based paint media (see figs. 2–4). Although it contains a sulfonyl chloride as its protein reactive functional group, it does not yield as many false positives with oil-containing layers as do LISSA and FITC. It uses an aqueous, alkaline delivery system that causes excavation of gelatin containing layers. However, this alkaline delivery system is advantageous in certain
circumstances, as it did not excavate the carbonate- or oil-containing layers examined in this study. It does not stain iron oxide pigment in either linseed oil or Elvacite 2044. DC-C7A appears to be far more reliable than the other fluorochrome stains, as it does not stain most linseed oil-containing layers to any significant degree. It would be prudent to confirm the presence of titanium oxide before drawing any conclusions as to the presence of protein or acrylic media. DC-C7A does not stain egg white to any significant degree.

ACKNOWLEDGEMENTS

The author wishes to acknowledge F. Christopher Tahk, Dan Kushel, and Christopher Augerson for their helpful suggestions and lively discussions.

REFERENCES


AUTHOR INFORMATION

JOHN M. MESSINGER II received his Ph. D. in organic synthesis from the State University of New York at Buffalo in 1986. Since 1986 he has held the position of assistant professor of conservation science in the Art Conservation
BINDING MEDIA IDENTIFICATION IN PAINTED ETHNOGRAPHIC OBJECTS

DUSAN STULIK, & HENRY FLORSHEIM

ABSTRACT—This article describes a binding media identification procedure for the analysis of 5 mg samples from painted ethnographic objects. It is based on modified medical diagnostic and forensic science tests and is designed to identify vegetable oils, lards, simple sugars, tree gums, starches, animal glues, casein, eggs, and blood in paint layer samples. Flow diagrams for individual tests are described as well as a binding media identification procedure and a general binding media identification flow chart.

1 INTRODUCTION

Identification of binding media in the painted layers on ethnographic objects is an important step prior to any conservation treatment. The first attempts to paint with
colored materials were made without using any binding media or using only a temporary binding medium (water). Eventually craftsmen and artists realized that such procedures did not give satisfying or long-lasting results. They recognized the need for binding media that would hold pigment particles together and adhere the pigmented layer to the substrate.

The problem of identifying binding media in ethnographic objects is complex. Each culture and each time period had a set of favorite media. The range of binding media used on ethnographic objects is broad and covers a variety of materials from tree gums, salmon eggs and orchid juices to modern synthetic polymers. Binding media found on ethnographic objects are raw natural products (egg, honey, or blood), processed natural products (animal glue, casein, starch, or oil), or synthetic organic materials. This paper focuses on natural binding media that chemically belong to groups of lipids (vegetable oils, or lard), carbohydrates (honey, tree gums, or starches), and proteinaceous materials (animal glue) and on complex binding media (egg, blood, or fruit juices). For example, egg is a complex binding medium that contains proteins, oils, and carbohydrates. Blood contains proteins, oils, carbohydrates, and hemoglobin.

Several simple chemical tests have been modified for identification of binding media in paint layers of art objects. These tests are based on qualitative spot tests (Feigl 1966), microchemical analytical procedures (Schramm and Hering 1988), or chemical microscopy methods (Masschelein-Kleiner 1986). The literature mentioned serves as a good introduction to these methods and contains references needed for more detailed study.

The aim of this study was to develop a simple binding media identification system that would not require extensive training to master and would not use sophisticated chemical and physical instrumentation, which is beyond the means of many conservation laboratories. Because of their simplicity and widespread availability, commercial test kits developed for modern medical diagnostics are the basis for much of our work. Some additional tests were added using methods of qualitative analytical chemistry and forensic science. We have made every effort to include test reagents that are readily available worldwide. Some tests included in the binding media identification procedure give straightforward and reliable answers. In some cases, there is a need for a combination of tests to identify the binding medium class.

Each test was checked for possible interference from the other binders considered in this study. The possible effect of some pigments important in ethnographic art objects was studied; they include yellow and red ochre, kaolin, limestone, gypsum, ultramarine, charcoal, manganese dioxide, and “battery black” (an impure form of manganese dioxide extracted from old batteries by Australian and African ethnographic artists and used after World War II). Where interference was observed, it is noted under the comments for the individual tests.

2 TEST FOR TRIGLYCERIDES
Triglycerides (TG) used as binding media on ethnographic art objects can be categorized as oils or lards. Chemically, both oils and lards belong to a class of chemical compounds known as esters. Esters are produced when an alcohol and a carboxylic acid undergo a condensation reaction. Vegetable oils are obtained from seeds and nuts of certain plants. Lard is a solid fat prepared by rendering fatty tissue of animals. Both vegetable oils and lards are composed of triglycerides of fatty acids (esters of glycerol and higher saturated or unsaturated carboxylic acids). The number of carbon-carbon double bonds in the triglyceride affect the drying properties of the material. Drying oils contain a large concentration of polyunsaturated fatty acids (especially linolenic acid). Nondrying oils contain only very small amounts of this acid and consist of varying amounts of saturated and mono- or disaturated fatty acids. Lards are composed of palmitin, stearin, and olein (triglycerides of palmitic, stearic, and oleic acid, respectively). Hydrolysis of oils and lards produces glycerol (glycerine) and free fatty acids. The fact that glycerol is an integral part of all vegetable oils and animal lards serves as a basis for a laboratory proof of these materials in paint layers.

2.1 METHOD

The sample is dissolved in hot methylene chloride. Insoluble material is removed by centrifugation. The methylene chloride solvent is evaporated, and the presence of glycerol in the sample is determined by an enzymatic test. Triglycerides are first hydrolyzed by lipoprotein lipase to glycerol and free fatty acids.

\[
\text{TG} \xrightarrow{\text{Lipase}} \text{Glycerol + Fatty Acids} \]  \hspace{1cm} (1)

Glycerol is then phosphorylated by adenosine triphosphate [ATP] forming glycerol-1-phosphate [G - 1 - P] and adenosine-5-diphosphate [ADP] in the reaction catalyzed by glycerol kinase [GK].

\[
\text{Glycerol + ATP} \xrightarrow{\text{GK}} \text{G - 1 - P + ADP} \]  \hspace{1cm} (2)

G - 1 - P is then oxidized by glycerol phosphate oxidase [GPO] to dihydroxyacetone phosphate [DAP] and hydrogen peroxide [H2O2].

\[
\text{G - 1 - P + O}_2 \xrightarrow{\text{GPO}} \text{DAP + H}_2\text{O}_2 \]  \hspace{1cm} (3)

Hydrogen peroxide catalyzes the reaction of 4-aminoantipyrine [4-AAP] with sodium N-ethyl-N-[3-sulfopropyl]-m-anisidine [ESPA] to form a quinoneimine dye.
A pink to purple color of the quinoneimine dye indicates the presence of triglycerides in the analyzed sample (McGowan et al. 1983; Barham and Trinder 1972).

2.2 PROCEDURE

The flow chart for the triglyceride test is shown in figure 1. A finely ground paint sample (5 mg) is placed into a 3 ml screw-cap vial, and 0.5 ml of methylene chloride (CH2Cl2) is added. The suspension is sonicated in a hot water bath until the solvent begins to boil. This procedure should be conducted in a fume hood. The vial is removed from the water bath and allowed to cool to room temperature. The suspension is transferred to a plastic microcentrifuge tube and centrifuged for about 1 minute. The supernatant is transferred into a 3 ml flat-bottom vial; the sediment is saved for further tests. The solvent is carefully evaporated (in a fume hood) at the lowest heat possible. About 0.3 ml (5 drops) of Sigma GPO-Trinder (GPO-T) reagent (table 2) is added to the dry residue. After thorough mixing, allow the sample to stand at room temperature. A positive test is indicated by a pink to purple color change which forms in about 10-15 minutes.
Fig. 1. Triglyceride test flow chart

5 mg finely ground paint in a 3 ml screw-cap vial

+ 0.5 ml methylene chloride boil in fume hood (water bath or hot plate) cool to room temperature

to microcentrifuge tube; centrifuge 1 minute

solid

Pigments and CH₂Cl₂ insoluble binding media

liquid

transfer to 3 ml flat bottom vial evaporate solvent

dry extract

+ 0.3 ml (5 drops) of Sigma GPO-T let stand 20 minutes

PURPLE color large concentrations of TRIGLYCERIDES PRESENT

PINK color low concentration of TRIGLYCERIDES PRESENT

No color change NO TRIGLYCERIDES PRESENT

Cross-check for proteins and casein
2.3 COMMENTS

Paint samples containing drying oils, animal fat (lard), egg yolk, or unpurified milk casein give a positive color. The color intensity of the test varies with concentration of triglycerides in the sample. Egg yolk and whole milk (source of casein) contain some triglycerides and may give a very weak positive test. If weak tests are obtained, the sample should be tested for presence of protein and phosphorus. Paint samples treated with glycerine or with material containing glycerine might also give a positive test for triglycerides even without any triglycerides present.

3 TESTS FOR CARBOHYDRATES

Complex carbohydrates, (polysaccharides such as gums) and simple sugars (monosaccharides such as honey) have been used as binding media in ethnographic objects. In the past, the term “gums” was used as a general term to denote a wide range of compounds. To avoid confusion, it is advisable to use the term “gums” more specifically for plant polysaccharides found either in intracellular parts or as extracellular exudates. Aqueous solutions or dispersions of gums have suspending and suspension-stabilizing properties. Gums can also act as emulsifiers, adhesives, and friction reducers. Chemically, gums are made up of a number of different monosaccharide units linked by various glycosidic bonds to a central core composed mainly of D-galactose and D-glucuronic acid units.

Honey is the sweet, sticky material made from flower nectar by certain bees. Honey absorbs and retains moisture, thus retarding drying. Honey was used as a plasticizer to improve elasticity of other binding media (glues, or gums) or as a straight binding medium in certain ethnographic objects. All types of honey are rich in the simple sugars dextrose (D-glucose) and levulose (D-fructose). Detection of carbohydrates in paint samples is based on a sugar-specific chemical reaction.

3.1 TEST FOR SIMPLE SUGARS

3.1.1 Method

Simple sugars are extracted from the sample using hot water. Upon heating, o-toluidine reacts with aldohexoses (glucose) in the presence of acid to form a blue-green colored complex.

3.1.2 Procedure

The simple sugar test flow chart is shown in figure 2. About 5 mg of finely
ground paint sample or residue from the methylene chloride extraction (triglyceride test) is mixed with 0.5 ml of distilled water in a 3 ml flat-bottom vial. The resulting suspension is boiled for a short time on a hot plate at a low heat setting. After cooling to room temperature, the suspension is transferred to a microcentrifuge tube. After about 1 minute of centrifugation, 3 drops of supernatant are mixed in a 3 ml flat-bottom vial with 0.5 ml of o-toluidine reagent. The vial is placed in a boiling water bath for about 10 minutes. A positive test for simple sugars is indicated by the formation of a blue-green color (Hultman 1959; Hyvarinen and Nikkila 1962).

Fig. 2. Simple sugar test flow chart
3.1.3 Comments

This procedure tests for simple sugars (honey) as either a binding medium or a binding medium additive in paint samples. In the case of a very weak positive test, it is important to search for other binding media. Some complex binding media (milk, blood, egg, or plant juices) might contain enough carbohydrates to produce a weak positive test. In such cases, a combination of simple tests or the use of instrumental methods may be necessary. Some pigments (charcoal) were found to interfere with the test. Hence, the sample for the simple carbohydrate test should be obtained from nonblack paint layers of the object to avoid such a problem.

3.2 COMPLEX CARBOHYDRATE (GUM) TEST

3.2.1 Method

This method is identical to the test for simple carbohydrates with the addition of acid hydrolysis of the polysaccharide chains.

3.2.2 Procedure

The complex carbohydrate test flow chart is shown in figure 3. About 5 mg of finely ground paint sample is mixed with 0.5 ml of 0.5 M H2SO4 in a 3 ml screw-cap vial. The vial is closed tightly and placed in an electric oven preheated to 100°C for 2 hours. The vial is removed from the oven, and allowed to cool to room temperature. The contents of the vial are transferred to a microcentrifuge tube and centrifuged 1 minute. Three drops of the supernatant are placed in a 3 ml flat-bottom vial. One drop of 6N NH4OH is added, followed by 0.5 ml of o-toluidine reagent. The vial is placed in a boiling water bath for about 10 minutes. A positive test is indicated by the formation of a blue-green color.
3.2.3 Comments

This test identifies complex carbohydrates (natural plant gums) in paint samples. Battery black (impure manganese dioxide), yellow, and red ochres were found to interfere, giving a negative test. Samples containing different pigments (preferably white pigments) should be obtained for the complex carbohydrate test.

4 TEST FOR STARCHES

Starch is present in all plant cells. Primary sources for starches are potatoes, rice, corn, wheat, and arrowroot. The starch granules are separated from these plants by milling and washing in water. Starch granules contain two polymers, amylase and amylopectin. Chemically, the amylase is a large linear polymer of 1,4-anhydroglucose. Amylopectin molecules are also based on the same
anhydroglucose polymer, but they have a large number of short linear chains attached to the main polymer chain. The heating of dry starch to 160°-190°C produces dextrin. Both starches and dextrins are used as paste adhesives. In its more soluble form, starch can also be used as a binding medium for pigments.

4.1 METHOD

An aqueous solution of starch gives a blue or brown color in a dilute solution of iodine. The active fraction of starch is amylose. The amylose exists as a coiled helix of poly α-D-glucose into which linear molecules can fit. In the presence of starch, iodine ions (I⁻) form a long chain of I⁻5 ions that occupy the center of the amylose helix. It is this dark blue I⁻5-amylose complex that provides proof of the starch in the paint sample (Vogel 1989).

4.2 PROCEDURE

The starch test flow chart is shown in figure 4. About 5 mg of finely ground paint sample or residue from the methylene chloride extraction is mixed with 0.5 ml of distilled water in a 3 ml flat-bottom vial. The resulting suspension is heated to a low boil on a hot plate. It is boiled for about 2 minutes and then allowed to cool to room temperature. The suspension is transferred into a microcentrifuge tube and centrifuged 1 minute. Five drops of supernatant are mixed with 1 drop of starch test reagent. The presence of starch is indicated by an immediate color change to blue or brown.
4.3 COMMENTS

This test identifies starch as a binding medium or adhesive in paint samples. The resulting color complex is usually blue, but different shades of brown color also indicate the presence of starch. It is recommended to perform a parallel blank test with 5 drops of distilled water and 1 drop of reagent for comparison.
5 TEST FOR PROTEINS

Proteins are simple or complex polymers consisting of chains of amino acids. There are 22 naturally occurring amino acids that are bound together in proteins by peptide linkages (-CO-NH-). The molecular weight of proteins ranges from 104 to 107. Amino acids occur in varying proportions in different proteins. Several proteinaceous materials have been used as binding media in ethnographic art objects. Glue is obtained by drying solutions made from boiling animal skin or bones in water. Gelatin is a purer form of glue made from selected, cleaned animal matter. Egg has two protein-rich parts. Egg white is composed of different proteins (65% ovalbumin). Egg yolk is an emulsion containing water, lipids, proteins (15% livetine and phosvitine), and the phospholipid lecithin. The yellow color is due to the presence of carotene pigments. Casein is the main protein in milk. It is a complex mixture of proteins and phosphoproteins.

5.1 METHOD

The protein test is based on the formation of a color complex of proteins with an organic dye (Bradford 1976). In this test, a blue dye complex is formed between Coomassie blue (brilliant blue G) and small amounts of protein in an acid-alcoholic medium.

5.2 PROCEDURE

The protein test flow chart is shown in figure 5. About 0.5 ml of distilled water is added to 5 mg of finely ground paint sample or the residue from the methylene chloride extraction (triglyceride test) in a 3 ml flat-bottom vial. The suspension is boiled on a hot plate for 2 minutes. After cooling to room temperature, the suspension is transferred to a microcentrifuge tube and centrifuged 1 minute. Three drops of the supernatant are added to 0.5 ml of protein reagent in a 3 ml test tube and mixed well. A positive protein test is indicated by the immediate formation of a blue color complex.
5.3 COMMENTS

Protein-containing binding media (animal glue, egg, casein, or blood) are determined with this test. Yellow ochre pigment was found to cause a weakened or negative protein test. Binding media of low protein content (egg yolk, or blood) may give weak positive test results.
6 TEST FOR PHOSPHORUS

Certain binding media contain phosphoproteins. In such cases, the detection of phosphorus helps to identify the binding medium. Phosphoproteins are proteins with an ester bond between the side chain of a serine (one of the amino acids found in proteins) and a phosphate unit. Casein, milk, and egg yolk contain enough phosphoproteins that the phosphorus test can be used as a secondary test for binding media identification.

6.1 METHOD

Phosphoproteins are hydrolyzed using a strong acid. The hydrolysate is then reacted with ammonium molybdate in an acid solution to form phosphomolybdate. A mixture of sodium bisulfite, sodium sulfite, and 1-amino-2-naphthol-4-sulfonic acid (Fiske-Subbarow reducer) is used to reduce the phosphomolybdate to form a phosphomolybdenum blue complex.

6.2 PROCEDURE

The phosphorus test flow chart is shown in figure 6. About 8 drops of 6N HCl are added to about 5 mg of finely ground paint in a 3 ml screw-cap vial. The vial is closed tightly and placed into a 100°C preheated oven overnight. The vial is removed from the oven and cooled to room temperature. The vial's cap is removed, and the vial is placed again into a 100°C oven to evaporate the acid. This takes about 1 hour. About 0.5 ml of distilled water is added to the dry residue. The contents of the vial are mixed and transferred to a microcentrifuge tube. After 1 minute of centrifugation, about 5 drops of the clear supernatant are transferred to a clean 3 ml vial. About 5 drops of molybdic acid solution are added. The solution is mixed, and about 2 drops of Fiske-Subbarow reducer are added. The solution is mixed again. Color changes are observed after 10 minutes. A blue color indicates a presence of phosphorus in the sample (Fiske and Subbarow 1925).
6.3 COMMENTS

The test allows for identification of phosphorus in binding media. Casein gives a strong phosphorous test. If milk or egg yolk was used as a binding medium, the test is weaker due to their lower phosphorus content.
7 TEST FOR BLOOD

Several cultures have been known to use blood as a binding medium for painting. Although blood appears to be a simple liquid, it is actually a body tissue. The cells, instead of being joined together as in solid body tissues, are suspended in a fluid, called plasma. The cellular portion of blood consists chiefly of red blood cells, with a smaller number of white blood cells and platelets. Chemically, blood is made up of water, inorganic salts, proteins, lipids, polysaccharides, glucose, cholesterol, and hemoglobin. This blood test is based on detection of heme molecules in the paint sample and is used in forensic science to detect fresh or aged blood.

7.1 METHOD

The test is based on the peroxide-mediated oxidation of reduced phenolphthalein in which the heme molecule acts as a catalyst (Saferstein 1982).

7.2 PROCEDURE

The blood test flow chart is shown in figure 7. About 0.5 ml of distilled water is added to 5 mg of finely ground paint sample in a 3 ml flat-bottom vial. The resulting suspension is boiled for about 2 minutes on a hot plate. After cooling to room temperature, the suspension is transferred to a microcentrifuge tube and centrifuged for about 1 minute. One drop of supernatant is mixed with 3 drops of phenolphthalein working solution and observed for about 30 seconds. The mixture should remain colorless. Three drops of 3% hydrogen peroxide are added to the colorless solution. Development of a pink color within 30 seconds indicates the presence of blood.
7.3 COMMENTS

The blood test can be used to detect the presence of blood in red or black paint layers. Iron oxides and metal salts have been reported to give a false positive test (Saferstein 1982). Our tests with red ochre did not show such a problem. The color obtained when charcoal black-blood paint layers are analyzed gives a weaker positive test, possibly due to the heme adsorption on charcoal particles.
Pink or red color that develops after 3-5 minutes is due to the presence of other oxidizing substances or to peroxidase catalysts from certain plant sources (Saferstein 1982).

8 BINDING MEDIA IDENTIFICATION PROCEDURE

If there is previous knowledge of binding media used by a particular culture in a corresponding time period or in a given geographic region, the Binding Media Test Chart (table 1) can be used for binding media identification. An individual test or a series of parallel tests can be used to find which type of binding medium is present in a paint sample. A strong starch test indicates whether a starch binding medium is present. A strong triglyceride test indicates whether a drying oil or lard binding medium is present. (A solubility test might help differentiate between polymerized drying oil and non-polymerized lard.) A strong protein test, medium tryglyceride test, and weak phosphorus test determine the presence of an egg-based binding medium.

TABLE 1 BINDING MEDIA TEST CHART

If there is no previous knowledge about the character or type of binding medium used, a more systematic approach based on the Binding Media Identification Flow Chart (fig. 8) is recommended. Such an approach allows for separation of binding media, and multiple tests can be performed using a single sample.
About 5 mg of finely ground paint sample is placed into a microcentrifuge test
solvent begins to boil. Centrifugation separates the supernatant, which is tested for the presence of triglycerides (triglyceride test). The solid phase in the bottom of the test tube is boiled with distilled water for about 1 minute, mixed, and centrifuged. The resulting second supernatant is tested for the presence of blood, simple sugars, proteins, and starches. If all of the above tests are negative, a second sample should be tested for the presence of gums. Analysis of samples giving multiple positive tests should be interpreted using the Binding Media Test Chart (table 1).

9 CONCLUSIONS

Working with the proposed procedure is easy, and analytical methods for the individual tests or the whole identification system can be learned in a very short time. The procedure was originally developed for participants in “The Consolidation of Painted Ethnographic Objects,” a training course, held at the Getty Conservation Institute in June 1990. About 20 practicing conservators of ethnographic art worked with the system for 2 days. Regardless of their previous laboratory experience, all participants mastered identification procedures and were able to identify binding media types in test samples, painted facsimiles, and selected authentic ethnographic objects. The major advantage of the procedure is the fact that the majority of reagents, tools, and lab ware is readily available from laboratory supply houses (table 2); a kit can be assembled quickly and easily.

A systematic instrumental approach to the identification of binding media has been published recently (Erhardt et al. 1988). The approach outlined requires the availability of infrared, gas chromatographic, and high-pressure liquid chromatographic instrumentation. While these instruments are frequently not available to a museum conservator, they do provide advantages such as ease of documentation and a somewhat smaller sample requirement. They may also provide information that is not available by our less sophisticated procedure, such as the possible identification of specific proteins, gums, or oils.

Like any analytical method, our procedure is not universally applicable. Certain pigments interfere with some of the tests. Insufficient sample may be available to satisfy the requirements for some or all of the tests, or the analyst may require information concerning the presence of specific binders or drying oils. In such instances the reader is referred to the literature (Erhardt et al. 1988; Masschelein-Kleiner 1986; Mills and White 1987).

Our tests were designed to provide quick answers to binding media questions at low cost to a conservation laboratory. As such, they cannot provide answers to all binding media questions or solve complex binding media “puzzles.” They can play a screening role in these complex cases, and the test results can be used to guide further investigation. In such cases, it is necessary to apply advanced instrumental techniques, and there are instances when even the most sophisticated analytical methods cannot give straightforward answers.
Work is in progress to improve the analytical performance of the procedures, and we are constantly searching for new technologies that might improve detection limits for binding media tests, improve the selectivity of the tests, or simplify the analytical procedure.

IMPORTANT NOTE: When working with the binding media tests, it is necessary to become acquainted with material safety data sheets for all reagents and practice safe and responsible laboratory procedures.

ACKNOWLEDGEMENTS

We express our thanks to Frank Preusser, Neville Agnew, and Marta de la Torre of the Getty Conservation Institute for their support of the project; to Sue Walston of the Australian National Museum for numerous discussions and friendly advice; and to our colleagues Cecily Druzik and Karen Cole for their computer graphics work on text figures.

REFERENCES


Prentice-Hall. 272–76.

**AUTHOR INFORMATION**

DUSAN C. STULIK graduated from Charles University, Prague, Czechoslovakia, with B.S. and M.S. degrees in chemistry. He obtained a Ph.D. degree in physics from Czechoslovakia Academy of Sciences. He is deputy director of the Scientific Research Program and head of the Analytical Section at the Getty Conservation Institute. His current research is in the application of modern scientific methods in conservation science. Address: Getty Conservation Institute, 4503 Glencoe Ave., Marina del Rey, Calif. 90292.

HENRY A. FLORSHEIM received his B.S. and M.S. degrees in organic chemistry from the University of California at Los Angeles. His research interests involve the detection and identification of organic binders in paint layers. Address: Getty Conservation Institute, 4503 Glencoe Ave., Marina del Rey, Calif. 90292.
WITH PAINT FROM CLAUS & FRITZ: A STUDY OF AN AMSTERDAM PAINTING MATERIALS FIRM (1841–1931)

MICHEL LAAR, & AVIVA BURNSTOCK

ABSTRACT—Claus & Fritz was an Amsterdam-based firm that manufactured and supplied artists' drawing and painting materials from 1841 to 1931. Original sources have been used to document the founding of this company, its patronage by contemporaneous artists, the range of materials it supplied, and the quality controls it applied to its products. Claus & Fritz manufactured a range of its own oil-based paints, supplied in tin tubes. Analysis of the inorganic pigments and binding media of 41 different paints from its 1921 line was carried out in this study. The results of the analysis characterize the range of pigments and mixtures used, including extenders, and the use of additives such as beeswax and resin to the linseed oil binding media of the tube paints.

1 INTRODUCTION

On the backs of canvases and panels, as well as on frames and stretchers, helpful information can sometimes be found regarding the provenance, dating, and attribution of a painting. That valuable evidence such as labels, numbers, seals, and stamps should be preserved goes without saying. In 1993 two labels of the firm of Claus & Fritz, suppliers of artists' materials, were documented on the stretchers of two paintings by Gerrit Willem Dijsselhof (1866–1924) (fig. 1). Later that year, in the Van Beek artists' supplies shop on Stadhouderskade in Amsterdam, which is now nearly 100 years old, another piece of evidence relating to Claus & Fritz was found: a photograph of a handwritten testimonial dated November 30, 1900, and signed by 43 artists from Amsterdam and The Hague (fig. 2). The text reads as follows:

The undersigned, all Dutch painters, willingly declare that long-standing use of the paints prepared by the firm of Claus & Fritz in Amsterdam has convinced them that those paints belong among the best and most reliable products of their kind made both inside and outside the Netherlands. The factory was founded in 1841.
Fig. 1. Stamp located on the reverse of a painting by Gerrit Willem Dijsselhof in the collection of the Rijksmuseum, Amsterdam, acc. no. SK-A-3586. Photograph courtesy of the Rijksmuseum, Amsterdam

Fig. 2. Photograph of the handwritten testimonial to Claus & Fritz signed by 43 artists and dated November 30, 1900. Photograph courtesy of the Rijksmuseum, Amsterdam

Most of the signatories were members of Arti et Amicitiae, an artists' society in Amsterdam, or of Pulchri Studio, an artists' society in The Hague. Most were born in the 1850s. By far the oldest among them was Jozef Israels, who was probably the first to sign, since the date appears to be in the same hand as his signature. The other signatures were added at different times, and the artists need not be regarded as a single group at any one time or place.

The initiative was obviously a commercial one on the firm's part, but the idea was not unique; witness the presence on a mounting board in an empty frame in the Rijksmuseum of a printed label of the frame maker E. de Roos of Amsterdam, which dates from before 1870 and is signed by 16 artists (fig. 3). Here the commercial intentions are again very clear. The idea of such a recommendation by artists may have come from England, where in 1869 a similar recommendation, in this instance for “Improved Studio Easels,” was printed in an advertisement for Winsor and Newton (Field 1869, 38–39)(fig. 4). It is not inconceivable that the signatories also gained some sort of financial advantage, a discount on future orders, for example.
Fig. 3. Label of the firm E. de Roos, Amsterdam, from before 1870, adhered to a painting's backing board in the Rijksmuseum. Photograph courtesy of the Rijksmuseum, Amsterdam
Since the signatories of the Claus & Fritz testimonial must all have been among the firm's customers, we now know the names of 43 painters who certainly must have acquired their materials from the Amsterdam concern. The fact that a number of them lived in The Hague, and later became known as The Hague School of Painters, testifies to the firm's importance. Its reputation is also suggested by a letter of 1903 to the critic Albert Plasschaert from Willem Bastaan Tholen (1860–1931), who, in response to a request for biographical details, summed up his life as follows: “Born in Amsterdam in 1860 and not dead yet, paints with paint from Claus & Fritz” (De Jong 1994, 159).

2 THE FIRM OF CLAUS & FRITZ

The founder of the firm in 1841 was Pieter Claus Jr. (1778–1864), a painter of landscapes and townscapes. That same year it moved into the premises at 295 Herengracht, where it remained for more than 50 years (fig. 5). In 1853 Harmina Christina Louisa Claus (1834–99), (fig. 6), Pieter's daughter by his second wife, married the painter Johannes Fritz (1823–91) and from that year on the firm appeared as Claus & Fritz in the directory of the leading inhabitants of Amsterdam, although Claus also kept his own entry in the directory until his death. From 1856 on the entry read “Claus (P.) Art Dealers in Painting and Drawing Materials, Claus & Fritz, at the address given above.” The letter of recommendation indicates that the firm manufactured paints from 1841, but whether they and other artists' requisites were made at the same address as the
shops unclear. The premises there were certainly none too large. That the firm also dealt in paintings is clear from these entries as well as from the account books of Cornelis Springer (1817–91), from whom it bought six pictures between 1842 and 1862 (Laanstra et al. 1984, cat. nos. 42–3, 52–2, 52–5, 54–4, 54–16, and 62–5).

Fig. 5. 295 Herengracht, Amsterdam, shown in 1915, just before the house was torn down. The second house from the left has the name Claus & Fritz painted on the facade. Photograph courtesy of the Gemeente Archief, Amsterdam
After Claus's death the firm retained the name Claus & Fritz, as it did again after Fritz's death in 1891, when it was continued by the art dealer and painter from Gouda, Bartholomeus Johannes van Maare (1837–1913), who bought the Herengracht premises on Fritz's widow's death in 1899. In 1909 the descriptive “Art Dealers” was dropped from the firm's title, which now read “Makers of Oil and Water Colors in Tubes, Canvas, etc. Dealers in Painting and Drawing Materials” (fig. 7).

After Van Maare's death the firm was taken over by his sons Jacobus (b. 1866) and Dirk (b. 1868), who sold 295 Herengracht in 1913 and on January 1, 1914, turned the business into a limited company under the same name, although “Van Maare Brothers” was now added in brackets after the name Claus & Fritz in
paper, canvas, and panels for painters. An advertisement in the 1915 catalog of the Moderne Kunstkring in Amsterdam reveals that they also sold “study paint,” presumably a student grade paint of lower price. The firm finally went into liquidation in 1931, probably driven out of business by the competition not only from imported paints in the early 20th century but also from the firm of Talens, founded in 1899, which rapidly captured the lion’s share of the Dutch market in the 1920s.

Fig. 8. Invoice from Claus & Fritz to the artist Willem Witsen, 1917. Photograph courtesy of the Rijksmuseum, Amsterdam

3 THE CUSTOMERS

The growing demand for ready-made artists' materials in the 19th century was partly due to the rise in the number of amateur painters, who found it difficult to make paints for themselves as professional artists had done in earlier centuries. At the same time many professional artists began to paint out of doors, often in locations far from home, so that there was a need for well-packaged materials ready for immediate use. New technology also made it possible for artists' materials to be made by machinery. The question of who met these needs in the
Netherlands has scarcely been answered as yet (Pey 1987). By studying artists’ bills, notes, and inventories, however, it is possible to gain an idea of what materials were used and how and who provided them.

The notebooks of G. H. Breitner (1857–1923) (Rijksbureau voor Kunsthistorische Documentatie) show him buying paints from Claus & Fritz in 1900 and 1901, but more insight is provided by seven bills sent by the firm to Willem Witsen (1860–1923) between 1908 and 1920 (Stichting Willem Witsenhuis) (fig. 8). These bills list all manner of paints, watercolors, brushes, charcoal, chalk, paper, stretchers, panels, and “our own (red) canvases”—presumably a specialty of which little is known. It seems unlikely that canvases would have been prepared in the Herengracht premises, so the firm must have had another location for that. Witsen's purchases of varnish consisted of six bottles of painting varnish, three of retouching varnish, and three double ones of mastic varnish. He also bought nine bottles of Haarlem siccative and three of bleached linseed oil, most probably to use as a binding medium.

Two interesting references in Witsen's bills are those of 1918 and 1920 to Roberson's Medium (fig. 9), a binding medium probably obtained by Claus & Fritz from the trade printers, bookbinders, and arts supply shop A. J. Nuss of Reguliersbreestraat in Amsterdam (established in 1861), which imported it directly from Roberson's in London between 1915 and 1922 (Roberson Archive; Carlyle 1991). Witsen may have discovered this megilp when working in London from 1889 to 1891.

Fig. 9. Tube of Roberson's Medium illustrated in a catalog (1911–25) of Charles Roberson & Co., London. Roberson Archive, Hamilton Kerr Institute, Cambridge (HKI PB. 23–1993, 26)
4 THE PAINT

The Van Beek firm still possesses a tube of sap green paint from Claus & Fritz (fig. 10), while in Dijsselhof's paint box at the Drents Museum at Assen, in addition to a few tubes of the manufacturers Oud Hollandse (Scheveningen), P. Briault (Paris), Dr. Fr. Schoenefeld (Düsseldorf), H. Schmincke & Co. (Düsseldorf), and Schouten en Voskuyl (Amsterdam), there are at least 62 Claus & Fritz tubes containing oil paint in 34 different colors. The tubes come in four different sizes, and one of them, emerald green, is labeled “Study Oil Paint.” Since the tubes have been little used, Dijsselhof probably bought them toward the end of his life. The Rijks-prentenkabinet in Amsterdam also has a box with many Claus & Fritz tubes, which came from the painter Hendrik van Borssum Buisman (1873–1951), who was also curator of the Teylers Museum at Haarlem.

Fig. 10. Paint tubes from Claus & Fritz from the paintbox of Gerrit Willem Dijsselhof, Drents Museum, Assen, the Netherlands, and the sap green tube from the firm of Van Beek, Amsterdam. The tube of emerald green, lower left, carries the descriptive “Study Oil Paint.” Photograph courtesy of the Rijksmuseum, Amsterdam

A good idea of the range of colors sold by the firm is also given in a price list issued in January 1928 by the Amsterdam firm of A. J. van der Linde (fig. 11). The wide assortment listed under the name Claus & Fritz includes cadmium colors, modern pigments that only came into commercial production around 1910 (Gettens and Stout 1966, 149). They illustrate that Claus & Fritz offered modern pigments, while the firm's thoroughness is indicated by the presence of Antwerp, Prussian, and Berlin blue, pigments generally regarded as synonymous. Unfortunately, these three colors are not present in the paint boxes of Dijsselhof and Van Borssum Buisman, so it is not yet possible to discover the differences between them. Also characteristic of the firm's range are the colors...
price list, but neither Dijsselhof nor Van Borssum Buisman appears to have used it.

Fig. 11. Price list from the A. J. van der Linde artists' supply shop, Amsterdam, 1928, showing Claus & Fritz paints for sale. Photograph courtesy of the Rijksmuseum, Amsterdam
5 CONTROL

The letterheads of all Claus & Fritz's bills to Willem Witsen (Stichting Willem Witsenhuis) also mention “Restoration of Paintings,” an aspect about which nothing more is known since there are no extant archives of the firm. From 1917 onward there also appears the line: “Manufacturers of Oil and Water Colors. Under the control of Mr. van Ledden Hulsebosch.” This is a reference to the Amsterdam criminologist and scientific adviser to the Criminal Investigation Department, C. J. van Ledden Hulsebosch (1877–1952) (fig. 12), a celebrity in his day whom the newspapers dubbed “the Sherlock Holmes of Amsterdam.” Claus & Fritz evidently considered the quality of their products important enough to warrant taking on an independent controller, who presumably would have conducted regular tests to ensure the fineness, authenticity, and quality of the pigments. Van Ledden Hulsebosch carried out similar product control on the flavorings of Maggi in Amsterdam and the tubular lights made by Philips of Eindhoven.

Fig. 12. Photograph showing C. J. van Ledden Hulsebosch illustrated in the daily De Telegraaf, July 14, 1927. The caption reads: “The police expert C. J. van Ledden Hulsebosch in his private laboratory at No. 17 Nieuwendijk in Amsterdam, where he undertook investigation at the service of the police and courts, resolving many a crime. Here he is shown with his fascinating instrumentation for ultraviolet radiation.” Photograph courtesy of the Koninklijke Bibliotheek, The Hague

Van Ledden Hulsebosch was also interested in modern methods of examining works of art. In his popular Veertig Jaren Speurdswerk (Forty Years of Detective Work) (1945) he described how, after World War I, he brought the
radiation in order to discover signatures that were completely invisible in ordinary light. The difficulty was particularly severe when the painter had signed his name in one of the very luminescent types of paint such as zinc white or other paints containing zinc or in a nonluminescent paint on a luminescent ground (Van Ledden Hulsebosch 1945, 166).

In addition to acknowledging his services, Van Ledden Hulsebosch's name on the firm's letterhead also had a commercial intention much like the signed document of 1900.

6 RECENT ANALYSIS OF THE MEDIUM

The 20 Dijsselhof tubes and the sap green belonging to Van Beek were examined by J. J. Boon of the FOM Institute for Atomic and Molecular Physics in Amsterdam. They were analyzed with direct temperature-resolved mass-spectrometry with an JEOL SX-102A double-focusing mass-spectrometer (Boon 1992). With this method of analysis one obtains a picture of the oils, waxes, and resins in the paint in addition to information about polymer fractions such as the oil paint network polymer, proteins, polysaccharides, and metals like lead, cadmium, mercury, and iron (Boon et al 1995; Boon and Van Och 1996). The paint samples were dissolved and suspended in toluene:ethanol:ethyl acetate (40:5:5), whereupon a few micrograms of the paint suspension were placed on a platina/ rhodium filament probe and heated to a high temperature (800°C). The evaporation and pyrolysis products were analyzed using mass-spectrometry with low electron volt (eV) electron impact ionization (16 eV) at the mass range of 20–1000 atomic mass unit (M/Z).

Drying oil appears to be the main component in the 21 samples studied, albeit its precise nature is not clear because classification is normally based on saturated fatty acids in hardened paint while the samples had to be taken from not yet hardened paint (Mills and White 1994). In some cases irregularities were found that would indicate unusual oil components. The possibility that these were oxidation products of triglycerides is being studied further by Boon. In one semihardened sample taken from the outside edge of one tube, the determined palmitate/stearate (P/S) ratio (1:4) indicated linseed oil as the medium. In some tubes minimal amounts of beeswax and triterpenoid resin were indicated. Notable was the presence of zinc in a few cases, the purpose of which requires further research (zinc palmitate, zinc stearate, or zinc white as additives perhaps). Beeswax and zinc salts are both mentioned in the literature as preservatives for paint in tubes (Mayer 1991).

7 TECHNICAL EXAMINATION OF THE PIGMENTS

The initials “W. D.,” in pencil, had been written on the labels of all the paint tubes in the paintbox of Gerrit Willem Dijsselhof. On one of the tubes of Terre de sienne was written “Mei 21” (May 21). Because the tubes were still full and in good condition, it seems likely that they were purchased by Dijsselhof toward
the end of his life. It is tempting to attribute the tubes of Van Borssum Buisman to the same years due to the similarity of design and printing on the label.

Samples of the paint were prepared for analysis of the inorganic pigments using light microscopy and energy dispersive x-ray spectroscopy (EDX). Samples were taken by Aviva Burnstock at the Courtauld Institute of Art in London in January 1996. Particle characterization of selected samples was carried out using secondary electron imaging with a scanning electron microscope (SEM).

The results of the analysis are presented in table 1. The following discussion summarizes points of interest from the analyses of the paints.

**TABLE 1 RESULTS OF SEM-EDX RESEARCH ON CLAUS & FRITZ COLORS**

**7.1 ADDITIONS AND EXTENDERS**

Calcium carbonate (probably precipitated chalk) is the most extensively used addition to the tube paints in this series. It is added to the black pigments, all the paints based on iron oxide pigments and greens including terre vert, sap groen, cobalt groen (nos. 1 and 3), and ultramarin guimet (extra).

The proportion of chalk added varies, for example, brun d'mars contains a relatively small amount of chalk, while oranje d'mars contains a relatively high proportion. In general, the lighter shades of earth colors contain proportionally more chalk than the darker colors. This finding may suggest that chalk functions not only as an extender but is added to lighten the color of the paint. Another possibility is that more chalk was added to the light colors because it would be less noticeable than if added to the dark colors.

Barium sulphate, found in some of the oker colors (in addition to chalk) fulfills a similar role. Optically, particles are characterized by large, translucent glassy shards that have low birefringence in polarized light and an intermediate refractive index. On this basis they were identified as barite, the naturally occurring form of barium sulphate (Feller 1986). Paints that include barite without chalk are cobalt groen no. 3 and smaragd groen. Barite was used as an extender for paints from the last decade of the 18th century. Because it has low oil absorption, addition of barite to pigments that are highly oil absorbing may reduce the total oil content of the paint formulation. Drying of the paint is enhanced both by increasing the pigment volume concentration and by providing a relatively large particle surface area.

More transparent colors contain neither chalk nor barite. These include the lake pigments carmin fix de garance and donkere gekristalliseerde kraplak and the more transparent earth colors violet d'mars and paarsche dodekop. Other paints without extenders are cobalt (blue), the three white pigments—zincwit (zinc oxide), loodwit (lead carbonate), and cremswit (a mixture of lead carbonate and
zinc oxide), and the series of colors based on cadmium.

Silica in the form of quartz has been added to half gebrande geel oker.

Aluminum is added, probably in the form of aluminum hydroxide (Al(OH)3), to all pigments except the white pigments, cadmium rood, vert veronese, and cobalt groen no. 3.

7.2 PIGMENTS BASED ON IRON OXIDE

The range of oil colors offered by Claus & Fritz include paints made using a variety of grades of natural and artificial pigments based on oxides of iron. In general, the paints made using natural iron oxides (including the range of okers, siennes, and ombers, and paarsche dodekop) contain coarsely ground particles of variable size and shade, while the artificial iron oxide pigments used for the mars colors contain submicron-sized particles of a uniform color.

Colors based on natural earth pigments can be grouped according to proportions of trace elements revealed in semiquantitative EDX analysis: Okers contain a relatively high proportion of silica, trace amounts of potassium, and occasionally titanium, and terre de siennes contain similarly small proportions of potassium and silicon. Ombers are distinguished by the presence of manganese, and most of the mars colors contain trace amounts of silica without potassium. Terre vert was also identified as containing the characteristic silicates of aluminum, magnesium, potassium, and calcium, used together with other pigments to make a range of green colors (discussed in more detail below).

The range of shades was achieved in some cases by mixing two grades of earth color. For example, the medium brown shade of bruin oker contains a mixture of brown and yellow particles, and roode oker is made with a proportion of finely ground red (similar to the mars pigments) with coarser brown earth pigment.

A variety of shades of the same combination of pigments has been achieved by adding different proportions of the various extenders. For example, geel oker, the palest shade of iron oxide yellow, contains additions of both chalk and barite, the darker shade gebrande geel oker contains chalk, with only traces of barium and sulphur, while the middle color (half gebrande geel oker) contains chalk and silica. Similarly, ombre contains chalk and barite, while the darker gebrande ombre is extended with a little chalk only.

Zinc white has been added to two of the iron oxide colors, ombre and paarsche dodekop, presumably to modify the shade. While ombre contains both extenders as well as a significant amount of zinc white, the more transparent paarsche dodekop is made from an iron oxide pigment similar in color to that found in violet d'mars, with little zinc white and no other extenders.
7.3 PIGMENT MIXTURES

A few paints were made using combinations of pigments with different qualities in order to extend the range. **Engelsch rood** contains a combination of an artificial red iron oxide with a red lake pigment to give a red paint with transparency between a pure lake and the relatively opaque red earth colors. **Chineesche vermilloen** contains a proportion of cadmium red in addition to red mercuric sulphide, perhaps designed by the manufacturer to create an attractive darker shade of vermilion that could be marketed in addition to a more orange shade of pure artificial red mercuric sulphide.

All the green paints contain mixtures of pigments. **Terre vert** contains a small proportion of viridian, and the darker shade, **gebrande terre vert**, contains umber. **Sap groen** contains a mixture of **terre vert** (green earth), bone black, and yellow ochre. **Smaragd groen** contains viridian modified with some red earth pigment, while **cobalt groen** no. 3 is differentiated from **cobalt groen** no. 1 by the addition of viridian to the main component, cobalt green, a combination of cobalt and zinc oxides (CoO.ZnO).

The blue paint, **ultramarin guimet (extra)** contains not only French ultramarine but additions of cobalt blue and red iron oxide.

7.4 PIGMENTS BASED ON CADMIUM, CHROMIUM, COPPER, COBALT, AND ANTIMONY

In addition to the iron-containing yellow pigments described above, the Claus & Fritz range included six pigments based on cadmium ranging from pale yellow (**citroen cadmium**) to red (**cadmium rood**). Shades of yellow are made from cadmium sulphide with varying particle size and hue. **Cadmium rood** contains a selenium in addition to cadmium and sulphur and, unlike the yellow paints, contains no added aluminum.

Pigments based on chromium include **smaragd groen** (chromium oxide viridian, discussed above) and a barium chromate yellow, **paryt geel**.

**Vert Veronese** was found to consist of emerald green (copper aceto-arsenite) without added aluminum or extenders.

**Donker Napels geel** contains lead and antimony, identified as Naples yellow and lead antimonate. The blue paint **cobalt** was found to be cobalt aluminate, and **cobalt groen** (nos. 1 and 3) consists of cobalt green, made by calcination of a cobalt salt with zinc oxide (**McCrone et al. 1979, entry 935**).

7.5 LAKE PIGMENTS

**Carmin fix de garance** was identified as carmine lake. Based on the identification of the combination of elements calcium, aluminum, and sulfur, the
lake base was deduced to be aluminum and calcium hydrous oxide (Ca.Al2O3. H2O.CaSO4) as described by McCrone et al. (1979, entry 931).

Donkere gekristalliseerde kraplak contains a pink lake pigment that produced very low counts in elemental analysis. The proportions of the peaks suggest that the lake base is similar to that used for carmin fix de garance. This pigment was mixed with a small proportion of a red iron oxide pigment. Engelsch rood (discussed previously) is a mixture of a red lake with red iron oxide.

7.6 BLACK PIGMENTS

Two black pigments were included in the Claus & Fritz range. One was a carbon black, wijngaard zwart, which contain finely ground aggregates of carbon with a proportion of a black earth pigment. Ivoor zwart is brownish and contains calcium phosphate, bone black.

7.7 ANOMALOUS TRACE ELEMENTS: GERMANIUM, TIN, AND COPPER

Vleesch oker, paarsche dodekop, cadmium, lichte cadmium no. 1, and cobalt contain traces of the element germanium. Gebrande omer, oranje d'mars, jaune d'mars, paarsche dodekop, donkere gekristalliseerde kraplak, and ivoor zwart contain traces of copper, and several other colors contained traces of tin. Analysis of the metal tubes suggest that they are predominantly tin or (larger tubes) tin with lead. It is possible that traces of copper and possibly germanium may be associated with the metal tubes, although there may be a relationship between trace elements and the pigments or the process of manufacture of certain paints, which was not examined in detail.

8 CONCLUSIONS

It is hoped that this study will not only contribute to all aspects of 19th-century Dutch painting studies, thus materially assisting future restoration work, but also stimulate the examination of other paints used in the Netherlands and elsewhere in the 19th and 20th centuries.

ACKNOWLEDGEMENTS

Special thanks to Patricia Wardle, Monique Berends-Albert, and Elisabeth West FitzHugh. With thanks also to Hero Boothroyd Brooks London (for fig. 4); the Stichting Willem Witsenthuis, Amsterdam (for fig. 8); and Sally Woodcock, Roberson Archive, Hamilton Kerr Institute, Cambridge (for fig. 9). The ownership copyright of material in this archive is held by the Fitzwilliam Museum; it is published and quoted herein by permission of the Syndics of the Fitzwilliam Museum. Some of this material was first published in Dutch (van de Laar 1995).
REFERENCES


Rijksbureau voor Kunsthistorische Documentatie, The Hague.

Rijksmuseum, Amsterdam.

Rijksprentenkabinet, Amsterdam.

Stichting Willem Witsenhuis, Amsterdam.


AUTHOR INFORMATION


AVIVA BURNSTOCK is a lecturer in the Department of Conservation and Technology at the Courtauld Institute of Art, London, where she completed a Ph.D and a diploma in the conservation of easel paintings. From 1986 to 1992 she worked in the Scientific Department of the National Gallery, London, after a year as a practicing conservator in Australia with the Regional Galleries Association of New South Wales. She has a B. Sc. in neurobiology from the University of Sussex, England. Address: Courtauld Institute of Art, Department of Conservation and Technology. Somerset House, Strand, London WC2R 0RN, England.