Common Medieval Pigments

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I. Introduction

Within the period of time formerly known as the "Dark Ages" there existed a production of numerous objects of art containing brilliant and glorious colors that illuminated the medieval mind and so deeply reflected the content they embellished. This glimmer in the medieval world owes much of its brilliance to simple elements such as clay, natural minerals and insects, common ingredients in the pigments used in the production of medieval illuminations. The pigments used in medieval manuscripts varied by geographic location, time period and materials available. This paper offers an introduction to the common medieval palette used in illuminated manuscripts before 1500. The different methods that have been utilized for the identification of these pigments will be discussed, with encouragement to further develop and research nondestructive methods of testing.

A. Medieval Manuscripts

Soon after the primary sacred text in the Christian church came to be called the Bible, or "the book", many manuscripts based on this content were produced (Diringer 21). All books during this period were written by hand, until the invention of the printing press in the 15th century. Book illumination, or the illumination of manuscripts, is the art of embellishing parchment manuscript books with painted pictures, ornamental letters and designs. The technical term for "illuminated" refers to being "light up" with bright colors. John W. Bradley writes, "Perfect illumination must contain both colors and metals"(Diringer 21).

There is not a clear distinction between illumination and illustration, though it has been suggested that illumination refers solely to beautifying the object of devotion and illustrating deals with clarifying the contents of a text. Ancient examples of book illustration include the *Ramesseum Papyrus* and the *Book of the Dead*. Both Egyptian works dated as early as the 20th century B.C. The earliest illuminated manuscript extant of Western Christianity is the *Quedlinburg Fragment* from Northern Italy dating back to the 4th century A.D. (Diringer 22). Illumination in the full sense of the word has been commonly accepted to originate in Europe around the 6th c. A.D (Diringer 23). The elements discussed are some of the more common pigments used in medieval manuscript illumination in the period before 1500.

B. Medieval Pigment

Most of the information on pigments from the medieval period comes from technical treatises on technology and painting from the 1st to the 15th centuries. Included in the descriptive techniques of Roman wall painting found in Vitruvius' *De Architectura* and in Pliny The Elder's *Naturalis Historia* are some characteristics and various uses of certain pigments. The well known medieval study of technology, the *Mappae Clavicula*, was produced around1130 A.D. and in addition to containing the first recipe for soap, these manuscripts include procedures for the making and mixing of pigments (Smith et al.). Other well known sources include the treatise by Theophilus, a German monk who wrote an exhaustive account of the techniques of almost all the known crafts of the early12th century in *De Diversis Artibus* and Cenino Cennini who produced a treatise on painting in the early 15th century, the *Libero dell'Arte*.

Pigment is defined as the coloring agent in paint. Pigments come from various sources of animals, plants and natural minerals. The powdery pigment is mixed with a binding medium (which can range from honey to earwax) into a workable medium that can be applied as paint. Common media used as a binder were egg-tempera and gum-arabic. Early scribes prepared their own pigments, and their recipes differed in the techniques and materials used, making it difficult to replicate an exact color. There is evidence that in the early 13th century some scribes began purchasing ingredients from stationers and some standard colorants began to emerge.

Medieval manuscript illuminations today have some preservation issues which have been dealt with differently over the ages. A main issue is the consolidation of flaking pigments. An important key to the proper treatment of illuminations is the identification of what pigments are present. For example, some consolidants will affect the visual appearance of pigments differently, making them more opaque or translucent. The identification of pigments is also used to form a better understanding of the way in which the original artist was working, matching colors for restoration, identifying compatibility with chemical treatment, and identifying authenticity. This identification can be done in a destructive way, requiring a sample of the pigment for analysis, or in a non-destructive manner that does not require a sampling from the work. Cheryl Porter stresses the need to develop more straightforward and non-destructive tests for pigment identification than currently exist (2001). A goal of this paper is to provide an introduction to common medieval pigments, encourage the use of non-destructive identification

and highlight the importance to research more extensively non-destructive techniques for pigment analysis.

II. Common Medieval Pigments

Common Medieval pigments can be broken into four categories: Earths, minerals, manufactured and organic. Included in the following breakdown are the common name of a pigment, physical and chemical characteristics, means of identification and any special significance in the Middle Ages.

A. Earths

The earths have been described as the "workhorses of the palette." They are not bright or flashy, and were inexpensive (Porter). The main compounds were iron, clay, manganese dioxide, alumina, and silica. Categorization of these pigments refers to the origin of the materials being "dug from the earth." This category includes the siennas and umbers as well as the ochres, which were "evidently not attractive to the illuminators of the later Middle Ages" as stated by Ross (6).

Terre Verte

K[(AI,Fe^{III}),(Fe^{II},Mg](AlSi₃,Si₄)O₁₀(OH)₂

Green earth is derived from the minerals glauconite and celadonite and is one of the oldest pigments. Their colors range from neutral yellow green to pale greenish gray to dark

matte olive green. In the Middle Ages green earth could also have been known as *prason*. One of the most well-known uses for green earth was in the underpainting of flesh (Fig. 1) as described by Theophilus and Cennini. Cennini also mentions the use of green earth for bole, stating that the ancients "never gilded except with this green." He also described terre verte as a "fat" color, by which he most likely meant the powder absorbed much of the binder media when mixing (Feller, vol. 1).

The pigment is easily identifiable under the microscope due to the characteristic appearance of celadonite and glauconite. The particles are greenish gray, mottled and striated. A destructive



Figure 1. detail of *The Virgin and Child with Saints Dominic and Aurea* showing green earth underpainting. (http://www.essentialvermeer.2 om.com/palette/palette_green_ earth.htm)

chemical test for the detection of ferrous ions can be done by treatment with concentrated acid solution to positively identify this pigment.

B. Natural Minerals

Ultramarine

$Na_{8\text{--}10}Al_6Si_6O_{24}S_{2\text{--}4}$

Ultramarine in Cennini's words is, "a color illustrious, beautiful, and most perfect, beyond all other colors; one could not say anything about it, or do anything with it, that its quality would not still surpass..." (Hoeniger 2). Ultramarine is famous for having been the most expensive pigment. It was more expensive than gold during the Renaissance and also highly exotic because of its origin. First used in 6th century Afghanistan, the pigment was used most extensively in the 14th and 15th century illuminated manuscripts and Italian panel paintings. It was often reserved for the cloaks of Christ and the Virgin (Douma). The pigment is made from the precious stone *lapis lazuli*. The stone was also used as a medieval cure for melancholy. The source of the mineral in the Middle Ages was from the Badakshan mines in Afghanistan. Even the best lapis lazuli has impurities of calcspar and iron pyrites. Thirteenth century recipes describe the best methods for extraction. The powdered lapis lazuli was mixed with pastille of pine resin, mastic, wax or linseed oil boiled together. The mass was soaked, then kneaded in lye until the blue color was extracted (Ross 11). The purest, deep blue was extracted in the first batch and sold for the highest price. As the process was continued, the subsequent batches of pigments were slightly less pure; the final batch being a transparent blue gray called ultramarine ash.

There have been few cases of ultramarine turning a gray or yellowish-gray from "ultramarine sickness." It has been proposed that atmospheric sulfur dioxide and moisture are the cause for this discoloration (Feller vol. 2).

Ultramarine shows a high stability to light, but is readily decomposed by acids. Hydrochloric acid will rapidly destroy the blue color and is a useful but destructive chemical identification test. Heating to redness was an early identification method to determine ultramarine from azurite, which would turn black around 300 ° C. Under the microscope natural ultramarine usually shows crystalline mineral impurities which are mainly colorless particles mixed in with the blue crystals of lapis lazuli. This aids in distinguishing natural ultramarine from the synthetic, first made in 1828 (Ross 11).

Infrared photographs of Ultramarine are also used to identify the pigment in a nondestructive way. In normal light a painting depicting the Virgin and child shows Mary's robes painted in ultramarine as a deep, dark blue. In an Infrared photograph the same robes appear light because of the high reflectance of ultramarine for infrared light (Fig. 2). Color infrared film is also used to distinguish ultramarine from azurite as discussed in the section on identification methods.



Figure 2. Detail from a triptych by Duccio. National Gallery, London, No. 566. The image in panchromatic (left) and infrared (right) light.

Azurite

2 CuCO₃ · Cu(OH)₂

Evidence has shown this pigment was used most often from the 14th to 17th centuries and is often considered the most important medieval pigment because of its frequent use. Azurite is a copper carbonate prepared by grinding the lump form, then washing and levigating to separate the color from impurities. Coarsely ground azurite produces a dark blue, while finely ground azurite produces a lighter tone.

Azurite is stable to light and normal atmosphere, but is known to turn green, reverting to the chemically similar malachite. This is commonly seen in many medieval works containing azurite. The pigment gives off water and carbon dioxide when heated to 300°, turning black with the formation of cupric oxide. It also darkens when warmed by alkalis and with exposure to

sulfuric fumes. Azurite is recognizable microscopically by its crystal morphology, color and refractive properties with little difficulty unless the sample is very finely divided (Feller vol. 2). Under the microscope azurite crystalline fragments appear pale, colorless or slightly purplish blue. It is very similar to ultramarine and can be distinguished from the pigment by heating to 300° or using color infrared film to test for reflectance.

Orpiment

As_2S_3

Orpiment is also known as king's yellow and is found in natural and artificial form. It is difficult to differentiate between natural and artificial orpiment, except that the artificial form is more finely ground. The first mention of this form of orpiment is by Cennini in the 15th century. Orpiment has been identified in objects of the 31st century B.C. in Egypt, some suggesting that the pigment was used in Egyptian cosmetics despite its toxicity. The Chinese used the toxic properties of Orpiment to repel insects from book rolls, as described in 5th century treatises (Feller vol. 3). The pigment is described as a lemon or canary yellow but can range from golden to brownish yellow. Orpiment shows severe color loss after exposure to ozone in the absence of light, converting to arsenic trioxide. The pigment decomposes slowly in water, and is soluble in hydrochloric acid and sodium hydroxide.

Orpiment is incompatible with lead and copper pigments and will darken them when in close proximity. The pigment outgases, and the orpiment vapors will creep over to the lead color and revert it to a lead-gray color. This process can creep at a couple of inches in a few months. It also has a corrosive action on binding materials, often decaying and coming away from the parchment (Ross 16). Orpiment's incompatibility is mentioned in the *Mappae Clavicula* from the 12th century, specifically referring to its corruption of white and red lead. By the 15th century it was known that verdigris and orpiment should not be used together. Eastern sources from the 11th century state it was common to mix orpiment and indigo to create a green color. In Europe orpiment was later mixed with azurite to make a green commonly used in medieval miniatures (Feller vol. 3).

One can identify between orpiment and the similar arsenic disulfide *realgar* with a destructive burn test. Both realgar and orpiment produce arsenic trioxide when heated, but only realgar burns with a blue flame (Feller vol. 3). Orpiment can also be confirmed with a test for arsenic. Under the microscope orpiment particles have high refringence and appear as needle

shaped crystals. This may suggest other pigments such as litharge, chrome yellow and strontium yellow, but all these will test negative for arsenic.

Silver and gold leafing

Gold was often used in gilding manuscripts with decorative borders or laid in gold leaf form. First, a base adherent or bole was put on the desired areas. Next, the gold lead was carefully positioned on the page. It was allowed to dry and the excess was removed with a tool like a soft brush. Silver was used less often because it easily tarnishes due to oxidation. Artificial gold pigment is known as mosaic gold, arium musicum, or ormolu. Also known as stannic sulfide [SnS(2)] it was manufactured to resemble mineral gold. This scaly yellow crystalline powder was used as a pigment in bronzing and gilding wood and metal work as well. Another artificial metal pigment was purpurinus. This artificial tin sulfide was prepared by melting equal parts of tin and mercury and adding sulfur and sal ammoniac as described in treatises of the 14th century (Ross 20).

C. Manufactured Pigments

Lead White

$2PbCO_3 \cdot Pb(OH)_2$

This pigment has been used since classical times, and was prepared by suspending strips of lead above vinegar or urine in a vase, sealing it and burying it in a dung heap for several days. After a few days the artist scraped off the crust formation on the lead and ground it for use. The pigment is poisonous when ingested or inhaled, but medieval ladies found it to be a useful cosmetic nonetheless. Lead white tends to darken when exposed to air and is incompatible with verdigris and orpiment. Bone white was often an alternative choice when working in proximity with these two pigments (Ross 2, 4).

Lead white is a basic lead carbonate soluble in dilute nitric and acetic acid. Lead white shows remarkable permanence and is unaffected by light. Hydrogen sulfide in the air can cause the pigment to turn black perhaps because of the formation of lead dioxide. The black formation can be converted to a more stable state using hydrogen peroxide, as shown in the treatment of certain wall paintings (Feller vol. 2. 72). A positive test for the presence of lead is usually

acceptable for identification, usually done with water and KI to form the precipitate PbI₂. Optical characteristics include high opacity and high density.

Red lead

Pb_3O_4

The orange red tetroxide of lead is produced by heating white lead until the heat expels water and carbon dioxide from the crystals in the form of gas. The pigment was called "minium" and from its frequent use in the small independent illuminations found in manuscripts, these illuminations became known as "miniatures." Thinned down red paint was also used as a writing ink for rubrics (the headings on medieval pages). Dilute nitric acid turns red lead into brown lead peroxide, which is the last stage to which white lead may be oxidized. Under great heat red lead becomes a light violet, and when cooled again it becomes a yellowish red (Feller vol. 1).

Lead-Tin Yellow

Type I Pb₂SnO₄

By gently roasting white lead the pigment known as litharge or lead monoxide is produced. The addition of tin produces two types of lead-tin yellow. The more commonly used is type I, and was mostly used before the 18^{th} century. Forms of lead-tin yellow are mentioned in the Italian manuscripts of the late Middle Ages which refer to is as "massicot" and Cennini refers to the pigment as "giallorino" (Feller vol. 2, 70). Under a microscope there is a distinct difference in particle morphology between type I and II. The pigment is toxic because of the high lead content, is unaffected by alkalis. It blackens with hydrogen sulfide promoting the formation of lead sulfide. Lead-tin type I exhibits compatibility with almost all pigments and was commonly mixed with verdigris, azurite and white lead (Feller, vol. 2, 72). It is distinguished from chrome yellow by testing for CrO_4 and Pb. Chrome yellow should be positive in both tests, while lead-tin yellow will test negative for CrO_4 and positive for lead.

Verdigris

$Cu(OH)_2 \cdot (CH_3COO)_2 \cdot 5 H_2O$

Infamous for being destructively reactive, this popular pigment consisted of the basic acetates of copper in which the amount of acetate determined the greenness of the product.

Verdigris was produced by the corrosion of strips of copper with vinegar fumes. After the pigment was scraped from the plate, it was mixed with wine and allowed to thicken. Salt green was made from smearing the copper with wine, honey or vinegar and calcined salt before corroding. If the copper was smeared with soap before being suspended it was known as "rouen" (Ross 19). Also known as Spanish green, the pigment is incompatible with white lead and orpiment as well as many media and surfaces. Verdigris is destructive and will degrade cellulosic materials and parchment. In some Persian miniature paintings the presence of saffron appears to mitigate the harmful effect of the verdigris. The major chemical mechanism responsible for this behavior is the saffron solution serving as a buffer. Research by Barkeshli shows results that verdigris mixed with saffron did not char the paper support, and charring occurred only where the pure verdigris existed.

The color ranges from green, green-blue to blue and it exists in two types: basic and neutral verdigris. The neutral form seems to be the preferred verdigris pigment in the Middle Ages. Basic verdigris is formed when acetic acid vapor, water vapor and air act upon copper and copper alloys. Neutral verdigris, or *verde eterno*, is neutral copper acetate formed when basic acetates are dissolved in acetic acid, as recommended by Cennini. The basic pigment is composed of blue-green crystals that dissolve entirely in water and decompose when boiled. They dissolve in acetic acid, producing a dark green solution (Feller vol. 2).

Neutral verdigris particles are composed of tabular crystals with rhombic and hexagonal faces, resembling large chunks. The basic blue particles resemble bundles of long, fine needles.

Verdigris reacts destructively with its binding medium and binding surface. It is commonly known that the reflectance of verdigris pigment changes as it dries. Freshly applied verdigris differs from day old pigment and three month old pigment. Verdigris mixed with sulfur containing pigments in an aqueous media may darken due to the formation of copper sulfide. A test of verdigris pigment under three months of high illumination of fluorescent, xenon lamps and mercury vapor lamps showed no change, supporting the paints strong lightfastness, and also suggesting the brown discoloration that has been observed is not caused by light damage (Feller vol. 2).

Vermillion

HgS

Vermillion is formed from red mercuric sulphide obtained from cinnabar (Fig. 3), the principle ore of mercury, or artificially by heating sulphur and mercury together. The best cinnabar is known to originate in Spain. Artificial Vermillion was common knowledge by the 15th century. To produce this dye differing proportions of sulfur and mercury were put in a well-luted (sealed with clay) jar and heated until a blue vapor emitted or one heard the noise of the "two uniting." Vermillion was frequently mixed



Figure 3. Mineral cinnabar (www.webexhibits.org/pigments)

with red lead and sometimes with yellow in medieval painting (Ross 5). In D. V. Thompson's opinion "no other scientific invention has had so great and lasting effect upon painting as the invention of this color." (Ross 8). The only defect of this color is that it is slightly toxic and also can darken to a black substance. Since Roman times it has been known that specimens of vermilion darken when exposed to light. Some tests have shown that impurities in the alkali polysulfides used to "digest" the pigment lead to this instability. This catalyzes the transition of the red to black. It has also been found that the darkening of vermilion occurs mainly in paintings using egg tempera binder (Rose).

D. Organic

Organic pigments refer to pigments whose components are found in nature, but not in mineral form, such as plants or insects. Lamp black is made from the soot produced from burning linseed or other oils, pitch, candles, or resin. It was used in ancient Egyptian pottery, and was frequently mixed with gum and used for ink. Vine black, a charcoal made from grapevine twigs, was one of "the most perfect colors" according to Cennini. Saffron is an organic yellow made from the dried stamens of Crocus plants, then infused with glaire or gum water. Less popular pigments made from organic matter include yellow lakes, blue turnsole and dragon's blood.

Lac and Kermes

The term "lake" in the Middle Ages applied to red pigments that were extracted from organic dyestuffs. The term now refers to any dye-based pigment. Lake comes from the Indian

"lac" or "lakh" meaning "a hundred thousand" referring to the large number of *Laccifer lacca* found on tree branches. These insects secreted a sticky resin that was harvested then ground into a fine powder. The powder was boiled in urine or lye with the addition of alum, then the liquid was poured off and the remaining matter was allowed to dry and harden. A binding medium was added to the pigment, and the former insects then contributed their brilliant color to sacred iconography in various illuminations.

Kermes is produced in a similar way from the dried bodies of the female *Kermes vermilio* that are found in great numbers on the scarlet oaks of Europe, the best quality growing in the Orient (Ross 6). Cennini notes that kermes was a highly prized dye in 15th century Florence. It produced a dark hue resembling blood and kermes is the linguistic root for the English word "crimson." A similarly colored pigment was madder, a natural dye from the root of the *Rubia tinctorium*. It was more common than kermes, and not as highly prized (Ross 6).

Brazil or Verzino

These pigments were prepared from the wood of the *Caelsalpinia braziliensis*, also known as brazilwood, and produced a splendid rose color. The color was obtained by boiling wood shavings in lye or urine and then soaking them in hot egg white or hot lye. Powdered alum was added for more transparent colors. To make a more opaque color required that the mix be precipitated onto a base of travertine, marble dust, chalk white lead or powdered eggshells. The treatises writers gave a lot of attention to this color. Despite being known as an inferior dye it was probably more popular because it was cheaper, more abundant and easier to use than other red dyes (Ross 8).

Indigo and Woad

These are organic blues from the *Indigoferra* and *Isatis tinctoria* plants. Treatises writers distinguished the two by referring to indigo as "bagadel indigo." Besides this distinction indigo and woad were basically interchangeable. Woad plants are indigenous to Europe, and were introduced in larger quantities in the 17th century. The pigment was made from the froth or "flower of woad" that rose to the top of the dyer's vat. It was skimmed off and combined with any variety of white bases (Ross 14). The pigment has been used since ancient times, perhaps by the early inhabitants of Britain to dye their skin blue (Ross 13). The first mention of the trading of indigo is seen in a12th century accounting book of a European merchant. Synthetic indigo was

not produced until 1870. The difference between natural and synthetic indigo is determined by the amount of the isomer *indirubin* present in the pigment. The isomer can be removed by boiling the substance in ether, resulting in pure indigo. An ancient test for indigo is described in the 1st century *Historia Naturalis* stating, "Indigo is tested on hot charcoal, for pure indigo gives a flame of a fine purple color." (Feller, vol. 3, 87)

Indigo is characterized as having a good light resistance, but there have been examples of changes in the spectral reflection of Japanese indigo exposed to "soft white" fluorescent lamps (Feller, vol. 3, 87). Indigo is insoluble in water, dilute alkali solutions and acids. The dye is more readily soluble in cholorform and may bleed in an oil medium. Mixing orpiment and indigo to produce shades of green was seen in the Islamic world of the 14th century and Cennini also mentions this as a popular practice in 15th century Florence.

Under the microscope indigo particles are very fine and opaque. The refractive indices of indigo and phthalocyanine blue are similar, so a bleach test with Chlorox (NaOCl) is used to distinguish the two. The blue color in indigo will bleach out, and the phthalocyanine blue will not be affected (Lab, 147).

These pigments are only some of the more commonly used in illuminated manuscripts produced before the 16th century. Since the 16th century many artificial pigments have been produced. As more technological advances in testing become available to scientists more pigments from illuminated manuscripts are being analyzed. The analyses suggest that medieval illuminators used varying colorants from very creative sources in their paint, some of which have yet to be identified. Analysis of a sample from a 15th century German manuscript suggested one of the red colorants was Rhubarb (Scott et al.). Krekel and Polborn reported the discovery of a pigment, named lime blue, or blue verditer that has not yet been reported in chemical literature (2003).

Some pigments are easily confused by the naked eye and can even appear similar under a microscope. Over the years methods and chemical tests have been developed to distinguish pigments from one another. These methods include those that require an actual sampling of the pigment and tests that can analyze the pigment in a non-destructive way.

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III. Identification

There are many different characteristics that are used to distinguish pigment particles from one another. The crystal or particles' morphology, its optical properties, the chemical composition, and the molecular structure are all characteristics used for identification, or rather, steps to confirmation since conclusions should depend on more than one method in determining an unknown. The conservator is limited by what instruments are at his/her disposal and how much time is available, as well as what type of sampling is allowed. Identification is important in deciding what materials to use for consolidation of flaking paint, testing to see if a treatment on the parchment or paper is incompatible with the painting media, as well as understanding any reactions between the pigments with the binding medium or parchment.

A. Destructive Methods

Microchemical tests are done to detect a particular element of functional group. In this process the sample paint chip is tested with various solvents, other elements, or by heating. A positive test for the presence of an element is usually more dependable than a negative test that only proves the absence of the element. Positive tests can also mean different things. An unidentified orange pigment that shows a positive KI test for lead could be white lead tinted with earth pigments or a whiting medium mixed with litharge. All tests should first be done with a

known sample to minimize error. Flow charts can be used to identify a sample through a series of tests, the results of which guides one to the appropriate pigment (Fig. 4). Some charts may be inconclusive, including the possibility that the unknown is not one of the options, or the pigment is not purely one type, but a complex mixture of many types.

Microscopic examination of pigments is used to identify physical

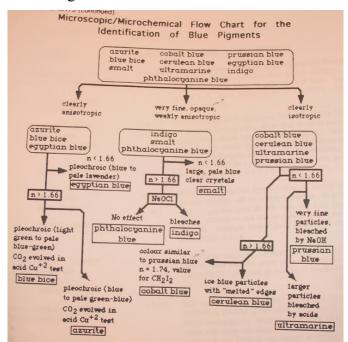


Figure 4. Flow chart for the identification of blue pigments. (Lab Manual, 149)

characteristics such as particle shape, surface structure, opacity and color. Kohler illumination is the standard used in optical tests for birefringence, in measuring refractive indices, and analyzing the appearance of particles in polarized and transmitted light. The refractive indices of pigments are a common property used in identification. The refractive index can be defined as the speed of light in one material divided by the speed of light in another material (usually air, water or a vacuum). By definition the refractive index of a vacuum is 1, air is 1.0008 and water has an index of 1.330.

In X-ray diffraction the sample is scraped and attached to a thin glass rod smeared with Vaseline. It is mounted in the center of an X-ray camera, which is lined with photographic film. As x-rays pass through the sample, the layers of atoms in a crystalline substance reflect wave trains in phase with each other. This is recorded on the photographic film. Identification of the pigment is done by comparison of the results with known standards. There are unique series of cocentric circles for each crystalline substance (Ross 22).

Gas chromatography, thin layer chromatography and IR spectroscopy are also used for identification of specific functional groups and elements in a pigment. They require a small sampled from the object for measurement. Strong absorption bands for pigments can be found for individual pigments in sources such as *Artists Pigments: A Handbook for their History and Characteristics* (Feller vol. 1, 2, 3). GC-MS is also commonly used for identifying the binding medium used in paint.

B. Non-Destructive Methods

Much can be learned about a pigment by inspection with a low powered binocular microscope, which does not require any destruction to the sample. Other non-destructive methods of testing include analysis by x-ray fluorescence (XRF), particle induced x-ray emission (PIXE- α), Raman spectroscopy, and observation under UV, IR and visible light. Raman spectroscopy produces a vibrational spectrum from a small spot diameter (approx. 0.5 to 1.0 mum) on the actual work. The spectroscopy does not usually work well with organic compounds but most informational sources on pigments include the strong absorption bands for the sample using Raman (Clark 1995).

A technique to distinguish two visually similar pigments, azurite and ultramarine, is the use of color infrared film or "false color film" (Hoeniger 1). Although both pigments appear

blue in normal light, with the infrared light ultramarine will appear cherry red, while azurite appears bluish.

There are some ways that conservators can reduce the level of destruction to the piece being analyzed. It is encouraged to use extremely small sampling sizes, invisible to the naked eye, if destructive analysis must be used. Using the offset of pigments when possible, as seen in the analysis of the *Codex Amiatinus* by Bicchieri et al. (2001), is another suggested choice to minimize destruction to the original illumination.

IV. Conclusions

There are many resources available on the identification of medieval pigments, including Feller's three volumes of *Artist's Pigments*. A more recent resource is a website providing information on the chemical and physical properties of pigments that also gives a short history of their use (www.webexhibits.org/pigments). Flowcharts are other useful tools in pigment identification. An idea for future research would be to develop a flowchart that uses all non-destructive methods of testing and suggests a destructive test only as a last resort. Learning more about the substances used for embellishing medieval manuscripts not only prepares the conservator for a possible treatment concerning these materials, but hopefully elicits some appreciation for the myriad of pigments used in this time period and encourages conservators to support research for non-destructive methods of testing.

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