Educ. quím., **22**(3), 191-197, 2011. © Universidad Nacional Autónoma de México, ISSN 0187-893-X
Publicado en línea el 25 de abril de 2011, ISSNE 1870-8404

Chemistry and Art: Ancient textiles and medieval manuscripts examined through chemistry

*Mary Virginia Orna**

ABSTRACT
The socio-historical value of examining ancient textiles and medieval manuscripts is illustrated by specific examples from the author's experience. Materials examined included pre-Columbian Peruvian textiles and Armenian and Byzantine medieval manuscripts, with connections made to present practice in both fields. Synthesis of pigments using recipes taken from medieval artists' manuals pointed to the strong relationship between modern chemistry and the artistic endeavors of the Middle Ages. While chemists always seem to have been more interested in the interface between their discipline and art, as evidenced from the discussion below, the last section of this paper will discuss a recent lively interest on the part of some artists, especially with respect to the chemical changes that take place in a "finished" work of art.

KEYWORDS: pigments, dyes, textiles, manuscripts, analysis, synthesis

RESUMEN
El valor socio-histórico de examinar textiles antiguos y manuscritos medievales se ilustra con ejemplos específicos de la experiencia de la autora. Los materiales examinados incluyen textiles peruanos precolombinos y manuscritos medievales de Armenia y Bizancio, con conexiones hechas a la práctica actual en ambos campos. La síntesis de pigmentos con recetas tomadas de manuales de artistas medievales apunta hacia la fuerte relación entre la química moderna y los esfuerzos artesanales de la Edad Media. De la discusión que se presenta deriva el interés de los químicos por el punto de contacto de la química y el arte; no obstante, en la última sección de este trabajo se discute el reciente interés vívido de parte de algunos artistas sobre los cambios químicos que tienen lugar en una obra de arte terminada.

Palabras clave: pigmentos, tintes, textiles, manuscritos, análisis, síntesis

Figure 1. A diorama depicting a typical ancient Peruvian gravesite. Museo Nacional de Arqueología, Antropología e Historia del Perú, Lima, Perú. Photograph: M. V. Orna.

Introduction

While thinking about how to introduce this paper on chemistry and art, it struck me that there is nothing in art that does not have something to do with chemistry. All art objects are material substances, and as such, are subject to the laws and to the manipulations of chemistry. At the same time, chemistry, in some limited instances, can also be subject to the manipulations of the artist. According to Hill and Simon (2010), art is a mirror of culture and of a culture's values. Using the materials available to them, artists can interpret their experience from a variety of perspectives: historical, socio-historical, symbolic, cultural, behaviorist, communal, environmental, functionalist, and structuralist. Thus, when examining a work of art, a chemist must keep these factors in mind and not concentrate solely on the material substance. Otherwise it would be possible to miss understanding the cultural context out of which the object came, and thus reduce the examination of art to an exercise in analytical chemistry rather than an appreciation of the cultural value of the object in question.

* Department of Chemistry, The College of New Rochelle.
New Rochelle, New York, USA.
E-mail: mvorna@cnr.edu

Keeping this cautionary note in mind, I would like to narrate the tale of this particular chemist's encounter with various works of art and of the cultures out of which they arose — all with a view to developing a course on the interface of these two disciplines for undergraduate non-science majors.

Analysis of pre-Columbian Peruvian textiles

In 1978, I was invited by Prof. Max Saltzman to participate in the analysis of colors impregnated on threads taken from Peruvian mummy bundles. The objects were from a recent excavation done by the University of California at Los Angeles (UCLA) on the south coast of Peru, home of the Nazca culture. For three thousand years, the art of weaving was the most important artistic and cultural expression of the many highly developed Pre-Columbian societies, including the Nazca. The Nazca people believed strongly in a life after death. This belief drew them to mummify their corpses (Figure 1) and wrap them with the finest textiles they could produce which, after 2000 years, still look as if they were woven yesterday.

In the Nazca times (200 BCE – 600 CE), as in many other pre-Inca civilizations, textiles played an important societal role, and thus were made with great art and skill: among other things, textiles were an index of the wealth and status of an individual. Prof. Saltzman and I developed an ultraviolet-visible spectrophotometric method for determining the nature of the dyes by comparing the spectrophotometric curves of known with unknown materials. In this way, we were able to distinguish among the various principal red dyes (cochineal and relbunium), as well as blue indigo and shellfish purple dibromoindigo (Saltzman, 1978). Figure 2 illustrates the Nazca use of the colors we found by analysis.

Figure 2. Nazca Textile. This weaving was made by the Nazca people of what is now coastal southern Peru. The pre-Columbian cultures of the Andes made exquisite textiles, which often depicted mythical stories and were sometimes used as markers of status by their owners. This piece is a patchwork made of camelid fibers and dates from 800-1300 AD. Museo Arqueológico Rafael Larco Herrera, Lima, Peru. Photograph: M.V. Orna.

Figure 3. "San Rafael," bulto. José Armijo, Española, New Mexico, 1999. Collection of Taylor Museum, Colorado Springs Fine Arts Center, Colorado Springs, Colorado. Used with permission.

Development of post-contact coloring of art objects in the American Southwest, Mexico, and Peru

Skipping ahead about seven centuries, a 2001 exhibit put on by the Smithsonian Center for Materials Research and Education documented the scientific study of the materials and techniques used by 17th to 20th century artists steeped in the tradition of crafting sacred images called *santos*. Using a variety of instrumental techniques, such as X-ray diffraction and X-ray fluorescence spectroscopies, chromatographic analysis, and scanning probe microscopy, the exhibit provided information about the evolution of this art form in separate areas where the artists used the materials that were close to hand. For example, José Armijo, a *santero* from Española, New Mexico, with whom I had personal contact, told me that he gathered his colors sometimes from natural sources, and sometimes by purchasing them from local supply houses. His yellows came from both the chamisol bush and from a gathered mineral (yellow ocher), his green came from local clay, as did his red pigments. His purple came from cochineal beetles obtained locally, whereas his blues, both azurite and indigo, were purchased (Orna, 2001). An example of his work is shown in Figure 3.

Figure 4. Navajo Dye Chart. Courtesy of Toh-Atin Gallery, Durango, Colorado; © Ella Myers. Used with permission.

How the information on these coloring materials, chiefly from plants, can be used either as an engaging entrée to understanding chemical concepts or as research projects in the classroom is described by Hayes and Perez (1997). Figure 4 is an evocative visual catalogue of the traditional plant dyes and their sources as used by the Navajo nation.

Moving farther south, it is worthwhile to visit, either in person or online, the Museo Textil de Oaxaca, Mexico (Museo Textil de Oaxaca, 2010) to view how this museum supports and encourages local artisans who use traditional coloring materials and techniques in their weavings.

Figure 5. Chinchero, Perú. A demonstration of dyeing of wool fibers with cochineal at varying pH of the dyebaths. Photograph: M.V. Orna.

Figure 6. Chinchero, Perú. A bowl of cochineal scale insects from which the red dye is prepared. Chemically, the red dye is carminic acid. Photograph: M.V. Orna.

Returning full circle to Perú, one can visit the village of Chinchero to see weavers and dyers in action using the traditional naturally occurring textile coloring materials and see how they vary the colors by using mordants and pH changes in their dyebaths (Figures 5, 6, 7).

Although I came away with samples of all of these colors, no chemical analysis has been done on them. A recent paper by Brooks, *et al.* (2008) documents analysis of mural pigments from northern Peru, where the blue was found to be azurite [$Cu_3(CO_3)_2(OH)_2$], the green was atacamite [$Cu_2Cl(OH)_3$], the yellow was goethite [$HFeO_2$], and the red was cinnabar [HgS]. The mordanting mineral mined from the Peruvian mountains and described by the Andinos at Chinchero as “qollua” has defied identification, although from its pale yellow color one would suspect that it might be an alum.

The range of colors obtained from minerals in Peru is not limited to textile colorants. The ancient Peruvians of the varying cultures, for example, the Moche and Paracas cultures, were highly adept at ceramic production, and knew how to vary the colors of a glazed ceramic piece by using either an oxidizing or reducing atmosphere in their kilns.

The identification of the colorants used in these artifacts is of great value to museum curators since any information obtained from the artifacts of a preliterate society helps us to understand them. Another very important reason for determining the nature of textile dyes is related to the conditions under which they may be exhibited in a museum setting. The work done by Padfield and Landi (1966) and Henry Levison (1976) gives us a reasonable amount of information about the lightfastness of these natural dyes, which for the most part is very poor. Knowing these facts can help the curator or conservator to make decisions regarding exhibition light-

Figure 7. Pisaq, Perú. A display of coloring materials used in the production of modern Peruvian textiles. The purple, blue and green colors are described as coming from minerals; the garnet and pink colors are from cactus flowers; the orange is from the sunflower; the red is from cochineal; the black is from the ragwort plant; and the yellow is from the broom plant. Photograph: M.V. Orna.

ing, conditions of storage, and safety of conservation treatments.

Analysis of Armenian and Byzantine medieval manuscripts

Following that initial encounter (and subsequent follow-ups) with art, I took up residence at the Conservation Center at the Institute of Fine Arts at New York University where I had the opportunity to work with an art historian, Prof. Thomas Mathews. We began a project to study the pigments used in medieval illuminated manuscripts using small particle analysis techniques. We started with Armenian manuscripts, which offered a special advantage in that most of them were dated and located by inscriptions; we then expanded our scope to include Byzantine and Islamic manuscripts as well. Our work shed light on several art historical problems, including tracing lines of influence and interconnection between medieval centers of manuscript production and clarifying periods of known usage of several important artists' pigments. Manuscripts from the following museums and centers have been sampled and analyzed: the Walters Gallery of Art (Baltimore, Maryland), the Freer Gallery of Art (Washington, D.C.), the Pierpont Morgan Library (New York, New York), the New York City Public Library, the special collections at UCLA and the University of Chicago, the Armenian Patriarchate of Saint James in Jerusalem, and the Monastery of San Lazzaro, in Venice. The data and results have been published in representative books and journals (Orna, 1981; Orna *et al.*, 1989; Lang *et al.*, 1992; Merian *et al.*, 1994). Figure 8 illustrates how a typical manuscript page was documented after sampling in order to keep track of the origins of each of the samples.

Figure 8. Documentation of an Armenian Manuscript Page Selected for Analysis: The Visitation of Mary to Elizabeth, p. 312 of the *Glajor Gospel Book* of UCLA (early 14th century). The circles indicate locations from which samples were taken for analysis. **B**, **Y**, and **G** indicate the hues: blue, yellow, and green; the other numbers are x-y coordinates in millimeters measured from the bottom left corner of the page. Photograph: M.V. Orna

The analysis of pigments contained in illuminated manuscripts can be approached in a variety of ways. The final decision regarding approach must be made on the basis of availability of samples and equipment and the amount of information that can be gained. There are many so-called non-invasive methods involving such instrumentation as energy-dispersive X-ray fluorescence (XRF) analysis, whole-manuscript neutron activation analysis (NAA), electron spectroscopy for chemical analysis (ESCA), and more recently, terahertz spectroscopy (THz). These methods require the availability of these sophisticated instruments, and sometimes, the information gained is not sufficient to identify the actual pigments present. Therefore, we opted for particle analysis of samples abstracted from the manuscripts examined using polarized light microscopy, X-ray diffraction, and microscopic Fourier-transform infrared (FT-IR) spectroscopy.

Armenian Manuscripts – Results

The principal pigments found in the Armenian manuscripts ranging in date from the 10th to the 16th centuries were indigo, a widely used material of vegetable origin containing the blue coloring matter, indigotin; ultramarine, a pigment extracted from the powdered mineral lapis lazuli, with a lye solution used to remove foreign particles, and then extracted with successive washings; gold, virtually pure metal beaten into very thin sheets and burnished onto the vellum; organic red lake, usually the red coloring matter (alizarin and its derivatives) extracted from the roots of the madder plant or from the lac insect of India and the Far East and precipitated with alum; vermilion, the red sulfide of mercury with the chemical formula HgS; white lead, a basic lead carbonate with the chemical formula $2PbCO_3Pb(OH)_2$; and orpiment, a sulfide of arsenic with the formula As_2S_3. It may be noted that the manuscripts from Melitene in eastern Turkey were noticeably poorer, lacking gold, lead white, and ultramarine, and this may be attributed to the dislocations of Armenian populations upon the arrival of the Seljuk Turks in Anatolia. Moving into properly Byzantine territories in Cappadocia, the painters relied more heavily on the organic colors being used by their neighbors. In post-Cilician painting, in eastern Armenia in the fourteenth century, the Cilician palette survived more or less intact, but the quality of ultramarine was less uniform, and azurite, a copper blue pigment in use in contemporaneous Persian manuscripts, was added.

Byzantine Manuscripts – Results

To the naked eye, colors in Byzantine manuscript painting appear more restrained than in Armenian painting. Borders may glow with enamel-like reds and blues, and skies may shine with gold, but the figures are painted in pastel shades against muted backgrounds. The difference in tonality seems to have its basis in the palette employed. Pigment analysis of Byzantine manuscripts of the twelfth and thirteenth centuries has discovered a much broader reliance on organic pigments, which generally yield weaker and more transient colors. The chief mineral pigments used were ultramarine and vermilion, but virtually all of the other pigments (orange, yellow, green, purple, and brown) were organic in origin. Although organic pigments can be quite brilliant when first applied, they tend to decompose gradually over long periods of time, thus losing their original brilliance and intensity. This process can explain the more subdued effects found in Byzantine manuscripts.

From the chemical analyses described above, we can see where the art in question indeed mirrored the historical, socio-historical, cultural, and environmental circumstances in the manuscripts' creation.

Further work with manuscripts: Medieval artists' manuals as an index of pigment synthesis and use

It is one thing to actually sample manuscripts (and works of art in general) as the most direct way of determining what materials were used in their creation. However, not everyone has access to every work of art of interest nor does one necessarily get the permission to examine works of art directly, whether by so-called "destructive" means such as sampling, or by non-invasive techniques such as the various types of spectroscopy already mentioned. Given this limitation, I, together with my mentors at the Institute of Fine Arts, New York University, decided to look into the literature surrounding pigment synthesis to see what artists may have used in ancient and medieval times. As early as the first century A.D., Pliny the Elder describes pigment use, although the earliest syntheses do not appear until the eighth century when Theophilus (1979; p. 40) describes the preparation of artificial cinnabar (HgS). By the ninth century, synthesis of artificial pigments is in full swing, and to my great surprise, most of the effort seemed to have gone into making blue pigments. In an extensive literature search on this matter (Orna *et al.*, 1980), I discovered that this interest stemmed from the fact that during the Middle Ages, blue as a pigment was in short supply. Egyptian blue, copper(II) sulfide, and azurite were the only inorganic blue pigments known in the ancient Roman empire. Egyptian blue, which can be traced back to the early bronze age and to the third millennium B.C. in Egypt, was the first pigment to be subjected to modern chemical analysis beginning with the trial preparations of Sir Humphry Davy (1815) and continued by Tite, *et al.* (1984). The latter showed through laboratory reproduction that the ancient Egyptian blue mineral ($CaCuSi_4O_{10}$) was formed as a result of the solid state reaction between silica, lime, and copper(II) oxide. Copper(II) sulfide occurs naturally as the mineral covellite, although it too can be prepared synthetically (Society of Dyers and Colourists, 1975), but it was probably not much used in antiquity because it is not durable, decomposing slowly and spontaneously to black copper(II) oxide unless protected by varnish. The third ancient blue pigment, azurite, is a basic copper carbonate closely related to the green pigment malachite. It has the formula $2CuCO_3{\cdot}Cu(OH)_2$ and occurs naturally as a monoclinic crystalline materials throughout Europe and the former Soviet Union. It was the most important and most widely employed blue pigment throughout Europe in the Middle Ages (Gettens & Stout, 1966; p. 95).

The use of a fourth blue pigment, natural ultramarine, derived from the semi-precious mineral lapis lazuli, can be traced to sixth and seventh century wall paintings in Afghanistan, and was eventually introduced to European artists following the journeys of Marco Polo, but it remained for centuries, until its eventual synthesis, a rare and costly commodity. After the introduction of synthetic ultramarine and also synthetic azurite, both pigments became the mainstay of European artists, but until that time, they were constrained to use the expensive and rare natural versions. Hence, the great incentive to produce synthetic blue pigments during the Middle Ages (Orna, 1996).

And produce them they did! The earliest trials used copper mixed with vinegar, a simple procedure resulting in several crystalline forms of copper(II) acetate. Then the recipes got a little more complex, utilizing copper with lime and vinegar; copper, lime, vinegar, and ammonium chloride (called "sal ammoniac" in the recipes); copper, lime, vinegar, and potassium carbonate (called "oil of tartar" in the recipes). The pigments manufactured from these recipes presented a very complicated chemical profile: some resulted in rather chemically pure products, and others resulted in mixtures that defied analysis. In our laboratory, a compound harvested from a mixture resulting from carrying out a recipe in one of major medieval artists' manuals, the *Mappae Clavicula* (Smith & Hawthorne, 1974), turned out to be identified as calcium copper acetate hexahydrate, an exotic compound whose crystal structure was first determined in 1967 (Langs & Hare, 1967). What we found remarkable in following the chemical pathways of these medieval artists was the degree of sophistication they attained long before the advent of modern chemical theory that would provide a theoretical basis for these syntheses.

For a review of the coordination chemistry of the pigments and dyes cited in this paper, please see reference (Orna *et al.*, 1994).

Modern developments at the interface of chemistry and art

Although artists and chemists alike have always been deeply involved with the use of materials, particularly with respect to their transformation into other forms, artists seem to have neglected, or even shied away from, the application of chemical theory and practice to their artistic endeavors, even though chemistry is, in fact, the scientific discipline most closely related to artistic practice. Spector and Schummer (2003) attribute this marginalization of chemistry to a culturally rooted "chemophobia", but they also give examples of many artists who are willing to experiment with the new materials that chemistry offers, and also with the fact that their work may indeed be a "work in progress" given that chemical reactions within the work may continue over long periods of time after the work of art was presumably "finished".

One artist who has boldly experimented with copper reactions in her works is Cheryl Safren; she has produced works of great beauty without the use of any paint, allowing chemistry to assume center stage. Changing color through reaction, crystallization, fusing, and solidification are a few of the ways chemistry informs her works. "Chemistry", she says "is sometimes the subject of my work, often its inspiration, and always the method or means of its creation. The dynamic process that forms my current work involves copper, chemicals, and extreme heat. Light hits the copper and cascades into a burst of fiery color and then, just as suddenly, tapers off into cool serenity. Mood and thought change as light and color shift rhapsodically. When the light dims or strikes at certain angles the color becomes saturated, majestic, and even reverential. Shifting light on the copper surface and viewer movement are the kinesthetic forces altering perception, allowing us to discover new and interesting things each time we view the work." Figure 9 is a beautiful example of her method.

Figure 9. Safren, Cheryl: *Creation 17*, 2002, 24" ×36", chemistry on copper. Used with permission.

Safren continues: "Many hours of research and experimentation have allowed me to control and manipulate chemicals in order to create these images. While biology and the environment have influenced the subject of these works, it is the chemical interactions that give full expression to the images." Safren (2010) is one example of a developing new world where chemistry is art and art is chemistry!

Concluding remarks

The topic of "Chemistry and Art" is necessarily broad since all art works lend themselves to chemical examination. This paper has outlined several very narrow areas where the two disciplines have interfaced with one another. This interface is continuing to grow as more opportunities arise for dialogue between artists, chemists, curators, and conservationists. It is hoped that all parties, in coming to understand better how a works of art were produced and what their material vulnerability may be, may be better prepared to not only preserve these works for future generations, but also to come to some understanding of the cultures that produced them.

References

Brooks, William E.; Piminchumo, Victor; Suárez, Héctor; Jackson, John C. and McGeehin, John P., Mineral Pigments at Huaca Tacaynamo (Chan Chan, Peru), *Bulletin de l'Institut Français d'Études Andines*, **37**(3), 441-450, 2008.

Davy, Humphry, Some Experiments and Observations on the Colours used in Painting by the Ancients, *Philosophical Transactions*, **105**, 97-124, 1815.

Gettens, Rutherford J. and Stout, George L., *Painting Materials: A Short Encyclopædia*. New York: Dover Publications, 1966.

Hayes, Janan and Perez, Patricia, Project Inclusion: Native American Plant Dyes, *Chemical Heritage*, **15**(1), 38-40, Fall 1997.

Hill, Patricia; Simon, Deborah. "Chemistry, Art, and Cultural Diversity," paper presented at the 21st Biennial Conference on Chemical Education, University of North Texas, Denton, Texas; 3 August 2010.

Lang, Patricia L., Orna, Mary Virginia, Richwine, Lisa J., Mathews, Thomas F., and Nelson, Robert S., The Visible and Infrared Microspectroscopic Characterization of Organic Red Pigments Removed from Three Medieval Byzantine Manuscripts, *Microchemical Journal*, 46, 234-248, 1992.

Langs, D. A. and Hare, C. R., The Crystal Structure of Calcium Copper Acetate, *Journal of the Chemical Society, Chemical Communications*, 890-891, 1967.

Levison, Henry W. *Artists' Pigments: Lightfastness Tests and Ratings*. Hallandale, Florida: Colorlab, 1976.

Merian, Sylvie L., Mathews, Thomas F. and Orna, Mary Virginia. The Making of an Armenian Manuscript. In: Mathews, T. F. and Wieck, R. S. (Eds.), *Treasures in Heaven: Armenian Illuminated Manuscripts*, pp. 124-142. New York, NY: The Pierpont Morgan Library and Princeton, NJ: Princeton University Press, 1994.

Museo Textil de Oaxaca. Can be consulted in the URL http://www.museotextildeoaxaca.org.mx/, last retrieval 18 October 2010.

Orna, Mary Virginia; Low, Manfred J. D.; Baer, N. S., Synthetic Blue Pigments: Ninth to Sixteenth Centuries. I. Literature, *Studies in Conservation* **25**, 53-63, 1980.

Orna, Mary Virginia and Mathews, Thomas F., Pigment Analysis of the Glajor Gospel Book of U.C.L.A., *Studies in Conservation*, **26**, 57-72, 1981.

Orna, Mary Virginia; Lang, Patricia L.; Katon, Jack E.; Mathews, Thomas F.; and Nelson, Robert S., Applications of Infrared Microspectroscopy to Art Historical Questions about Medieval Manuscripts. In: Allen, R. O. (Ed.), *Archaeological Chemistry – IV*. Washington, D.C.: American Chemical Society, 265-288, 1989.

Orna, Mary Virginia; Kozlowski, Adrienne W.; Baskinger, Andrea; Adams, Tara. Coordination Chemistry of Pigments and Dyes of Historical Interest. In: Kauffman, George B. (Ed.), *Coordination Chemistry: A Century of Progress*. Washington, D. C.: American Chemical Society, 165-176, 1994.

Orna, Mary Virginia, Copper-Based Synthetic Medieval Blue Pigments. In: Orna, Mary Virginia (Ed.), *Archaeological Chemistry: Organic, Inorganic, and Biochemical Analysis*. Washington, D.C.: American Chemical Society, 107-115, 1996.

Orna, Mary Virginia, Chemistry, Color, and Art, *Journal of Chemical Education*, **78**, 1305-1311, 2001.

Padfield, Tim and Sheila Landi, The Light-Fastness of the Natural Dyes, *Studies in Conservation*, **11**, 181-196, 1966.

Safren, Ch. Chemistry on copper. Can be visualized in the URL http://www.safren.com/series/chemistryoncopper/, last retrieval 18 October 2010.

Saltzman, Max. The Identification of Dyes in Archaeological and Ethnographic Textiles. In: Carter, G. F. (Ed.), *Archaeological Chemistry – II*. Washington, D. C.: American Chemical Society, 172-185, 1978.

Smith, C. S. and Hawthorne, J. G. *Mappae Clavicula: A Little Key to the World of Medieval Techniques*. Philadelphia, Pennsylvania: Transactions of the American Philosophical Society, New Series, **64**, Part 4, 1974.

Society of Dyers and Colourists, *The Colour Index*, 3rd Ed., Revised. Bradford, U.K., 4668, 1975. In the following URL http://www.colour-index.org/ can be found some updated information on the Society and *The Colour Index International*. It was retrieved on October 18th, 2010.

Spector, Tami I. and Schummer, Joachim, Chemistry in Art, *HYLE – International Journal for Philosophy of Chemistry*, **9** (2), 225-232, 2003.

Theophilus, *On Divers Arts* (*De Diversis Artibus*), trans. Hawthorne, J. and Smith, C. New York: Dover Publications, 1979.

Tite, M. S., Bimson, M., and Cowell, M. R., Technological Examination of Egyptian Blue. In: Lambert, J. B. (Ed.), *Archaeological Chemistry – III*. Washington, D.C.: American Chemical Society, 215-242, 1984.