Rethinking the History of Artists' Pigments Through Chemical Analysis

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Abstract

Following a brief overview of the history of analysis of artists' pigments, I discuss the illustrative example of lead-tin yellow. Recent advances in our knowledge of artists' use of red lakes, glassy pigments, and metallic pigments in works of cultural heritage, particularly European paintings, as determined from chemical analyses are described.

1. INTRODUCTION

Results from chemical analyses inform us about not only the aesthetic aims of artists and artisans of the past but also the science and technology of their times and cultures. The specific pigments found in art and artifacts shed light on the technological development of materials and the trade and exchange of both technical know-how and the colorants themselves; their identification also helps researchers explore the role of color in societies. Determination of the exact nature of the pigments can help us imagine the original appearance of works whose colorants have deteriorated over time. Technical investigations provide a concrete buttress for historical research that has proven fascinating (1).

Scientific and technological innovations led to the creation of new pigments from plant extracts and the preparation of synthetic substitutes for minerals, and innovation in artistic practice is demonstrated by the layering and mixing of colors and binders. Thus, developments in chemical and artistic pursuits have always been intertwined. In 1910, Laurie (2, pp. 4–5) wrote that "[t]he development of the potter's art and the discovery of various colored glazes would naturally result in the attempt to use such glazes ground fine as pigments. . . . Discoveries connected with mining and metallurgy would also result in adding fresh pigments to the artist's color-box. . .and the additional results of the fermentation of the grape and the production of vinegar [was necessary] before white lead and verdigris could be added. . . . The painter also owes much to the art of the dyer." Laurie termed these crafts the sister arts.

Current chemical analysis has greatly illuminated the history of painters' pigments and the interconnection between painting and other crafts. This interaction did not end in the Renaissance: New colors, both inorganic and organic, flooded the market for artists' materials in the eighteenth and nineteenth centuries. The emergence of a robust dye industry in the late nineteenth century and the development of synthetic organic chemistry, spurred in part by the desire to produce new colors for the textile industry, provided artists with an abundant range of bright, high-chroma compounds, termed coal-tar colors, used for paint making (3). Chemical variants abounded (4), and many were commercially available for only a few years. Although these compounds were notoriously unstable, many artists employed them for their vivid (if fleeting) hues. Their identification can present challenges to the analyst due to their instability and high tinting strength, which results in low concentrations in paint (5). The role of the sister arts in expanding the painter's palette remains strong today; artists choose esoteric colorants such as nacreous and flip-flop pigments designed for specialty uses such as car paints (6, 7).

2. EARLY HISTORY OF PIGMENT ANALYSIS

Rees-Jones (8) summarized the earliest scientific work on pigment analysis. The scientists Humphry Davy (1778–1829), Jean Chaptal (1756–1832), and Michael Faraday (1791–1867), along with the German chemist Martin H. Klaproth (1743–1817), were among the first to publish analyses of pigments used in works of art and cultural heritage. Their work laid the foundation for studies of Greco-Roman and European art. In 1910, Laurie (2) published analyses of Egyptian pigments, which became the basis for current studies. The growth of conservation science as a discipline promoted a surge in interest and understanding of artists' materials and methods. *Painting Materials: A Short Encyclopaedia* by Gettens & Stout, first published in 1942 (9), was seminal, and Joyce Plesters and her successors (10) at the National Gallery, London, paved the way for further discoveries through their many publications in the *National Gallery Technical Bulletin*. The landmark study (11) on the palette used by the Venetian painter Giorgione (1477 or 1478–1510) also set an example for today's studies. Flieder (12) was the first to make a comprehensive analytical study of manuscript painters' materials.

Crown (13) and Easthaugh et al. (14) have produced useful compendia of pigments and their history. Our knowledge of the use of materials in African and Asian art remains much less well developed, but that situation is gradually changing as more analyses are undertaken (15–20). Our understanding of the materials of the painter's palette also derives from old treatises and prior analyses. One method of investigation informs the other, and the combination is powerful.

Until the 1940s, old terms for yellow pigments, such as masticot, giallorino, and giallolino, were assumed to refer to lead monoxide, either massicot or yellow litharge. Jacobi's (21) careful observation of higher-than-expected levels of tin in samples of yellow paint and his dogged persistence in explaining the results despite his peers' skepticism led to the rediscovery of the use of lead-tin yellow as a painters' pigment and fundamentally changed our understanding of the nature of the colorants used by painters. Two types were identified: (*a*) lead-tin yellow type I ($PbSnO_4$), a binary oxide of fixed composition, and (*b*) lead-tin yellow type II, which was described as either $Pb(Sn,Si)O_3$ or $PbSn_2SiO_7$. This example illustrates the power of analytical chemistry to improve our knowledge of materials used by artists and artisans. We now know that lead-tin yellow was used for centuries and across geographical boundaries (22) until the mid-eighteenth century, when it disappeared. In Section 5, I provide some details about the use of lead-tin yellow type II. The family of yellows collectively known as giallorino is described in Reference 23.

3. GENERAL HISTORY OF COLORANTS IN ART AND ARTIFACTS DETERMINED FROM THEIR ANALYSIS

Table 1 presents a simple classification of colorants. Among the colorant materials that have traditionally been difficult to analyze, three types of pigments are emphasized in this review. These three classes have become better characterized chemically, and the knowledge of the distribution of their use is becoming better grounded through analysis. They are lake pigments, glassy materials, and metals.

3.1. Sampling

The age-old conundrum for analytical chemists—"Is the sample representative of the whole?"—is very important to consider, although it is often difficult to ascertain when dealing with objects

Table 1 General classification of pigments according to technological requirements for preparation

Broad classes of colorants	Examples
Crude materials (inorganic and organic compounds)	Found earths, asphalt, native minerals, blood, plant juices, and exudates
Minimally worked up materials	Earths and minerals purified by levigation, charcoal, colorants extracted from plant roots and bark
Metal salts and complexes	Ionic compounds (e.g., lead white), transition-metal complexes (e.g., aureolin), dyes rendered into pigments by reactions with inorganic salts (lakes)
Metals and alloys	Tin, silver, gold, copper, brass, bronze, bismuth filings; copper, silver, gold in lusterware
Completely synthetic, unnatural materials	Glasses (other than obsidian); so-called coal tar colors; other classes of organic colorants, organometallic complexes, and heteropoly blues

of cultural and artistic heritage. The artifacts are extremely inhomogeneous and comprise many original materials and their degradation products. Samples are limited not only in size but also in scope and site; replicate analyses are usually impossible to obtain. Therefore, scientists working on pigment identification are extremely circumspect regarding the choice of samples.

SEM-EDX: scanning electron microscopy coupled with energy-dispersive X-ray analysis

Minute samples are removed near existing losses and damages through the use of tungsten needles or scalpels such as those used by eye surgeons. Scrapings can be transferred to appropriate sample holders for analysis with glass fibers, eyelash picks, or extremely fine brushes. Various techniques are used for examination. In the past, optical microscopy was invaluable; today, it is less frequently used because the detection limits of other analytical methods have become much lower and optical microscopy requires a great deal of experience. Investigators remove cross sections of paint from works with sharpened tungsten needles or scalpels by gently encouraging propagation of extant cracks into the paint structure to excise microscopic chips, which are lifted (by use of the tools mentioned above) and placed into molds for embedding into a suitable medium for workup; this process may include polishing or microtomy. The layer structure is amenable to study through many techniques, such as scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM-EDX), IR mapping, micro-Raman analysis, and microfluorescence spectroscopy.

3.2. Instrumental Methods for Pigment Identification

Modern instrumental analytical methods have improved researchers' ability to identify and characterize pigments. Detection limits have significantly decreased, which has allowed the practical application of these methods to very small, precious, irreplaceable samples. Many papers emphasize this point by employing the prefix micro-, which often suggests that a microscope was part of the instrumental setup. Current interest in understanding artists' materials and methods has broadened the scope and application of analytical approaches. Synchrotron studies have further reduced the required sample size and have provided improved determination and quantification of impurities, which can reveal the sources of raw materials and the manufacturing processes used in the production of colorants (24).

Currently, all classes of pigments can be identified if the samples and choice of analytical method are appropriate. Changes in the design of instruments have allowed them to be used for pigment characterization without sample taking (termed noninvasive); thus far, these methods have been easier to apply to the characterization of inorganic compounds. X-ray fluorescence spectrometers were among the first open-architecture instruments used to examine artworks (25, 26). X-ray diffraction; PIXE (particle-induced X-ray emission) (27); fiber-optic reflectance spectroscopy (28, 29); and infrared, Raman, and surface-enhanced Raman spectroscopy (SERS) (30–33) have helped address the limitations imposed by restrictions on sampling. Raman spectroscopy is useful for distinguishing the crystallographic forms of a compound; for example, the rutile and anatase forms of TiO_2 are easily recognized. Copper-based green compounds can be identified, thereby allowing the researcher to discriminate among copper chlorides, sulfates, and phosphates used as pigments.

Chemical imaging based on spectroscopic methods is becoming increasingly sophisticated and permits the mapping of the distribution of colorants throughout an artifact (34, 35). Although these methods remain difficult to apply to heterogeneous systems that contain an unknown number of phases—some of them unexpected—improvements in spatial resolution and mathematical analysis of spectra are leading to improved characterization and identification. Mass spectrometry offers great sensitivity and discrimination among analogs; this technique is being applied to natural organic pigments and modern synthetic pigments with increasing success (36–39).

4. RED DYES AND LAKES

A range of red (and yellow) colorants are derived from plant leaves, roots, or wood. Madder, from the root of *Rubia tinctorum*, and brazilwood, from the wood of various trees such as *Caesalpinia* spp., were and still are widely used as dyes and pigments. Insects, too, have offered red colorants to the artist: Lac, kermes, and cochineal can be obtained from various species. Specific identification of the colorants in works of art depends first on analysis of the natural product (which can be challenging in itself) and then on the appropriate methods for analysis of the materials in paint. Madder, kermes, cochineal, lac, and related colorants are substituted derivatives of anthraquinone (40, 41). The use of other red colorants is not as well characterized; among them are dyes from fruits and flowers such as pomegranate, safflower, rhubarb, lichen, and dragon's blood. Dragon's blood is exuded by or extracted from trees of the Dracaenaceae family, although the name of this substance has probably been applied to other natural products. The name was initially used by Pliny in the first century CE and is found in lading bills from the fourteenth century onward (42). Despite this pigment's frequent mention in treatises, until recently it had not been positively identified in works of art. It has now been conclusively identified in oil paint in the St. Ansgar panel (located in St. Peter's Church, Hamburg, Germany), dated 1457, but it was used mostly in a translucent glaze to make the white metals tin and silver appear golden (43). Our knowledge of the use of this pigment is scant, and there remains much to learn about its origin and use.

The colored molecules derived from stalks and leaves of plants are somewhat thermally unstable and very light sensitive; therefore, these pigments are usually identified in manuscripts or drawings that have been bound in books or stored away from light and heat. Rhubarb has been found only once so far, in a painting on paper by a fifteenth-century German miniaturist (44).

The colored essence of brazilwood dye is brazilein, the light-sensitive oxidation product of brazilin. Although its use has often been cited in treatises and artists' manuals, chemical analyses have seldom detected it in oil paint, perhaps because of its instability. However, this colorant has apparently been used a great deal in watercolors ever since the Middle Ages (45), and there is evidence that it was stocked in large quantities by Renaissance-era color sellers. Brazilwood has been found in a painting by Raphael (1483–1520), *The Ansidei Madonna* (1505) (46)—although it is still not clear whether this is an atypical use or a rare example of an unchanged sample in a painting—and its use in paintings by van Gogh has been confirmed (47). This pigment and its relatives (logwood, redwood, and sappan) have a long history that is still being unraveled.

Organic dyestuffs can be converted into pigments by reaction with metal salts to yield insoluble metal complexes. It is also through this process that dyes can be fixed. Such products are termed lakes, and the reaction is known as mordanting or laking. Aluminum (Al^{3+}), obtained from alum [$KAl(SO_4)_2$], is the oldest and most common agent used to make pigments, but dyes can also be laked with tin, iron, chromium, and other metal ions or tartaric or oxalic acid to extend the range of possible hues. The history of these colorants' use as dyes is older but, surely, intimately connected to the history of their use for making pigments.

The invention of lakes involved a great deal of chemistry. Dyes were extracted from roots, leaves, or insects; mordants were procured or manufactured; and finally the reactions to make lakes were performed, which may have required a pH change or buffering before the products could be purified and worked up for use. All this chemistry was undertaken by artisans engaged in artifact and art making. The earliest known use of madder is on a Middle Kingdom (ca. 2124–1981 BCE) Egyptian leather quiver (48).

Our understanding of the range and scope of use of various red pigments dramatically improved when high-pressure liquid chromatography (HPLC) superseded thin-layer chromatography due to the smaller sample size required and the consequent increase in the number of samples that could be analyzed (49). In 1996, Kirby & White (50) published the first wide-ranging compilation of analyses of red lakes found in easel paintings. Perhaps not surprisingly, madder, kermes, and cochineal were the predominant colorants. Interestingly, many Italian artists used cochineal before its introduction from the New World; prior to then, European artists used Polish cochineal from a scale insect, *Porphyrophora polonica*, that lives on the roots of various plants. At the same time, northern European artists had a preference for madder, the dye extracted from *Rubia tinctorum*. However, some artists, such as Lorenzo Lotto (ca. 1480–1556), used both cochineal and madder and/or kermes. Fluorescence microscopy of a sample from the red dress depicted in Lotto's *St. Catherine* (1522) shows that the artist alternately layered red paints of different luminescence. By using HPLC to identify and separate the colorants derived from Polish, Armenian, or Mexican insects, researchers have revealed that the New World colorant supplanted its European-derived counterpart over a few decades after 1540 (51).

Although liquid chromatography–mass spectrometry provides the most complete chemical characterization of red lakes (**Supplemental Figure 1**; follow the **Supplemental Material link** from the Annual Reviews home page at **http://www.annualreviews.org**), spectroscopic methods of analysis provide important information that is sufficient to classify the source of lake colorants. Advances in spectroscopic techniques allow the identification of very small amounts of material and can even by used in standoff (or open or in situ) modes. Raman spectroscopy has been very useful in the quest to characterize ever-smaller pigment samples. The inherent difficulty of analyzing red lakes with this technique (because of their luminescence) is being overcome through the development of SERS for such analysis (52). There have been attempts to perform SERS directly on a paint surface. SERS has been used to discover the earliest known occurrence of lac in an occidental artifact (52a), an Ottoman carpet; this finding pointed to the role of trade, and perhaps the centrality of Constantinople, in the movement of colorants throughout the world (53).

UV-visible and luminescence spectrophotometric analysis can be used on scrapings and cross sections and is being developed as a nonsampling method for pigment identification (54–56). Establishing standards and the chemometric analysis of spectra of solid-state, heterogeneous samples, wherein aggregated species may contribute to the signal, demand further attention (57).

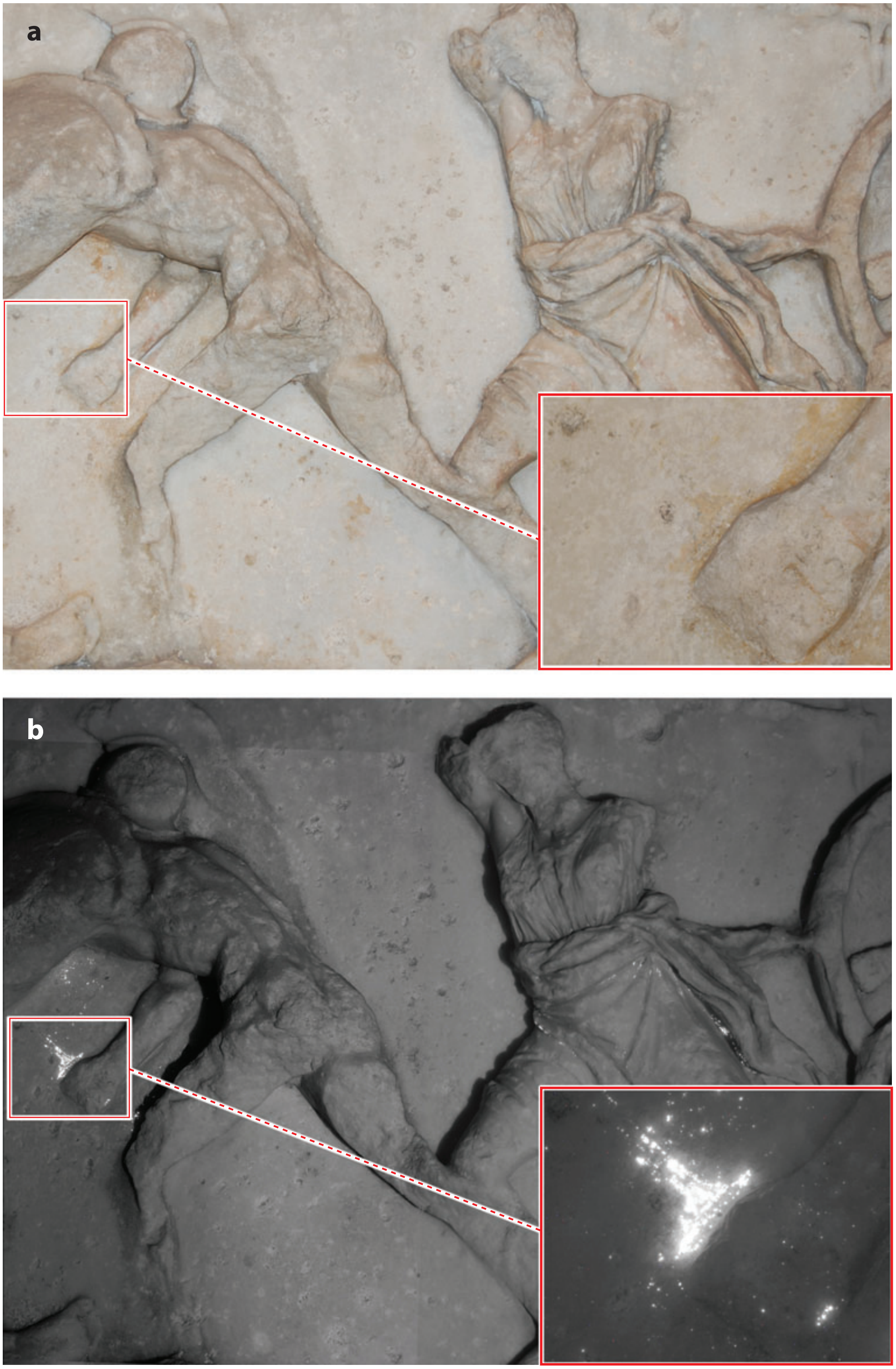
5. GLASSES

The pigment known as Egyptian blue may be among the first synthetic colorants. Laurie (2) stated that it is made from nothing more than crushed blue glass, but he was not entirely correct. The blue is the copper silicate cuprorivaite ($CaCuSi_4O_{10}$) (58). It is similar to two pigments used in Asia for thousands of years, Han blue and Han purple (59), which, astonishingly, were also used millennia later in Europe (60, 61). A striking characteristic of Egyptian blue is its intense photoinduced luminescence in the IR (62). This phenomenon allows Egyptian blue to be detected even when it is barely visible to the naked eye, revealing not only where but also how it was used. The newly appreciated ubiquity of this pigment clearly indicates the extent of polychromy in marble statuary and buildings (**Figure 1**) (63, 64).

Since at least the late eighteenth century (65), the blue glass known as smalt has been recognized as an important pigment on the easel painter's palette. Today, the term smalt universally signifies

Figure 1

The intensity of the visible-induced IR luminescence of Egyptian blue ($CaCuSi_4O_{10}$) allows it to be easily visualized with IR imaging. Shown is part of the Amazon frieze of the Mausoleum at Halicarnassus (British Museum 1847.0424.4) both (*a*) in visible light and (*b*) in IR. (*b*) The presence of Egyptian blue on the sword of the warrior and in the garment of the Amazon warrior is revealed. Image used with permission from the Trustees of the British Museum.


a
b

XRD: X-ray powder diffraction

a cobalt-colored blue potash glass; however, there are tantalizing hints in treatises on painting that so-called smalti for painters could come in other colors. In fact, it has been well known since approximately 1940 that, in addition to blue smalt, painters used an opaque yellow glass known as lead-tin yellow type II (Section 2), and artists' use of colorless or pale glass in oil paint has been recognized since the 1970s. Both blue and yellow smalts have been used for hundreds or thousands of years in colored glass and in glazes for ceramic ware. EDX analysis of the frit in a crucible found in a medieval Merovingian site in Switzerland revealed that the glassy lead-tin yellow pigment is different from the glass it was used to color (66). Antimony, alone or in combination with tin, has been used for millennia to color glasses and glazed pottery.

The history of use of yellow and blue glasses as pigments in paint requires more investigation, but such use may follow the technological history of glass making and pottery glazing, wherein recipes were lost or superseded and then rediscovered. Sixteenth-century Italian writers and artists specifically mention giallo in vetro (yellow glass) and zalolin da vasari (potters' yellow) (67, pp. 249–50; 68, p. 212). On the basis of the idea that the colorant in lead-tin yellow type II can be described as $PbSnO_3$ with a pyroclore structure, an early study used X-ray powder diffraction (XRD) to identify this pigment in two sets of paintings: fourteenth-century Italian paintings and Venetian paintings from the last quarter of the sixteenth century (22). A later study using SEM-EDX on a greater number of samples suggested that lead-tin yellow type I ($PbSnO_4$) replaced the glassy type II pigment on the easel painter's palette in the mid-fifteenth century; this new product may have been brought to Italy from Germany (69). Raman spectroscopy has proven useful in distinguishing the two major forms of the pigment. Recent work (70) shows that lead-tin yellow type II does not necessarily have a fixed stoichiometry. Although its formula is given as $Pb(Sn,Si)O_3$ or $PbSn_2SiO_7$, new analyses indicate that a diversity of species are used for such pigments. SEM shows that these glasses are suspensions of crystallites in glassy matrices. It is possible that various lead-tin compounds may be present, tin oxide may be included, and some variants may contain antimony in addition to tin; some related pigments are glasses or frits colored only by yellow lead antimonate.

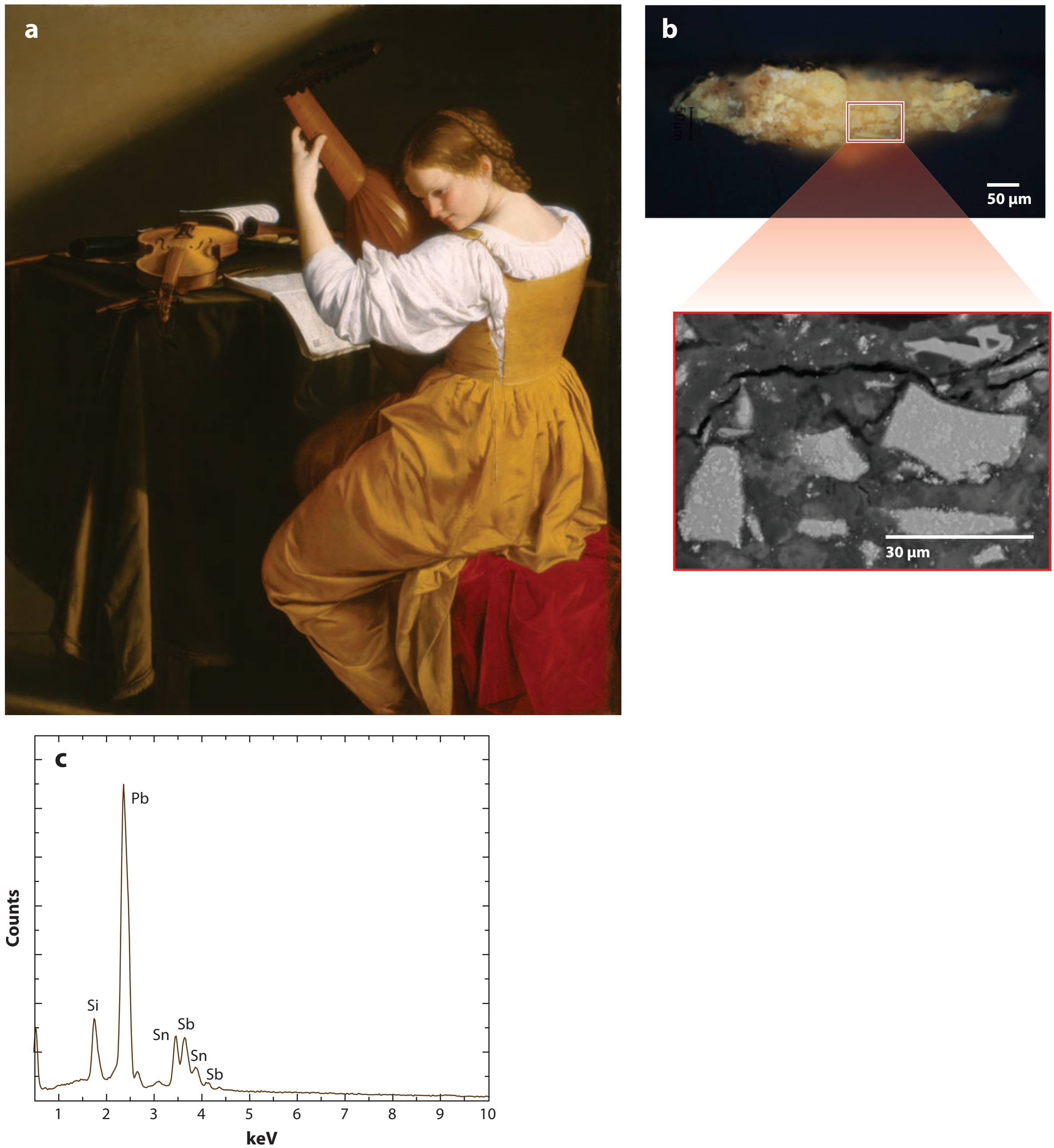
In 1998, Roy & Berrie (71) used XRD to characterize the opaque glassy pigment used by several seventeenth-century Italian artists as a ternary oxide of lead, tin, and antimony ($Pb_2SnSbO_{6.5}$). The paint for the yellow dress in Orazio Gentileschi's (1563–1639) *The Lute Player* was made from this pigment (**Figure 2**). The limited number of samples seemed to suggest that the colorant was used predominantly in Rome in the mid-seventeenth century. Since this study was published, however, this compound has been characterized in many works, and it is now clear that it was used more widely (72–74). The earliest use known to date was in a 1497 altarpiece by Marco Palmezzano (ca. 1460–1539), located in the Pinacoteca Communale, Faenza, Italy (75). Although the glassy character of the pigment has not been proven in this case, it is fascinating that this altarpiece was created in Faenza, one of the most important centers for ceramic production at that time. Electron microprobe analysis of tesserae from St. Peter's Basilica in Rome offers a good

Figure 2

Between approximately 1612 and 1620, Orazio Gentileschi painted the yellow dress in (*a*) *The Lute Player* (1962.8.1 Ailsa Mellon Bruce Fund, National Gallery of Art, Washington, DC), using yellow glass colored by $Pb_2SnSbO_{6.5}$. This pigment, here used in oil paint, is associated with colored glass and ceramic glazes. (*b*) Bright-field (with polarizer) image of a microscopic chip of yellow paint from the dress. (*Inset*) The back-scatter electron image of the area in the rectangle. Shards of leaded glass (*medium gray*) colored by the yellow compound $Pb_2SnSbO_{6.5}$ (*light gray*) are distributed through the paint film. (*c*) An EDX (energy-dispersive X-ray spectroscopy) spectrum of a point within one of the shards shows the presence of both tin and antimony with lead and silicon. (Oxford INCA spectrometer and SuperATW detector on a Hitachi S-3400N scanning electron microscope at 20 kV.)

comparison between the glass maker's products and those used as pigments in easel paintings (76), and Raman spectroscopy has identified the presence of the ternary oxide in ceramic glazes (77).

Flakes of colorless or pale-hued glass have been found in translucent red paint made from organic pigments, such as lac and cochineal, as well as other paints. Until sustained investigations of the painting methods of the Italian artists Pietro Perugino (ca. 1450–1523) and Raphael were



XRF: X-ray fluorescence analysis

performed, only a handful of examples of such glass had been identified. The results of SEM-EDX analyses of cross sections of paintings by Perugino and Raphael indicate that these artists frequently incorporated a particular soda-lime glass into paint made with red lakes (78, 79). X-ray fluorescence (XRF) analyses of a group of paintings by contemporaneous artists who had passed some time in Florence show that many added manganese-rich glass to their red lake paints (80). A wide-ranging study (81) has revealed that the apparent localization of the practice of incorporating glass into translucent paint may have arisen from study of Italian and French paintings, given that German painters also added glass to paint. Especially interesting is that this analysis shows that the glass artists used generally had a formulation typical of the region where they worked. Thus, German artists added potassium-rich forest glass, whereas Italian artists incorporated soda-lime glass, either common glass or cristallo. A high-lead glass was added to azurite-colored paint in Raphael's *Alba Madonna* (ca. 1510) (82). To date, no other occurrence of this specialty glass has been reported; however, this glass is similar to the glassy matrix of lead-tin-antimony yellow used in Gentileschi's *The Lute Player*.

The role of the glass in the red lake paints is debated and being investigated. Is it a drier? Does it play a role in the optical properties of the paint? Certainly, red lake paints dry slowly due to the antioxidant effect of the anthraquinone dye or colorant. A colorless or pale-hued additive such as glass [or silica, which has also been found in red paints (81, 83)] would decrease the weight percent of the antioxidant pigment without altering the tone of the color or decreasing the desired translucency of the paint. The presence of manganese in the glass may hasten drying. Also, depending on the size of the flakes of glass, such additives may have a beneficial effect on the paints' rheological properties. Some artists painted with multiple thin layers, which would decrease the likelihood of formation of paint-film defects from slow drying.

Of glass in paint, Merrifield wrote in 1849 that "[i]t is probable that they [smalti or enamels] were in general use for painting on glass in Italy during the fifteenth and sixteenth centuries (84, p. 333). Stained glass was created through the application of frits or enamels made with high concentrations of flux; the image was then fired. The binding material, often gum or resin, burned off, and the frit melted into the glass substrate. The materials for painted glass were different because the work was not refired, and many artists used oil paints that comprised pigments typical of those found on the panel painter's palette. However, Hahn et al. (85) have shown that reverse-glass painters of the sixteenth century used materials from the traditions of both stained glass and easel painting. Specifically, to create the thin black outlines that were painted first, the reverse-glass artists eschewed carbon-based pigments in oil paint, instead using a high-lead iron-copper black glass. That reverse-glass painters freely incorporated materials and methodologies of easel painters while maintaining many of their traditional materials is another example of artists' innovative and experimental attitudes, more of which remain to be discovered through chemical analysis. Quantitative analysis of minute glass shards embedded in matrices remains a challenge for analysts, but its reward is a greater appreciation of the complexity and sophistication of mixing artists' paints and the influence of the sister arts, glass making and ceramic decoration, on painters' pigments.

6. METAL FOILS AND FLAKES

Application of gold leaf backgrounds and gold decorations (chrysography) to icons and early panels is readily recognized, and although gold seems to have been the most commonly used metal used in art, it was by no means the only one. Its apparent preponderance is probably a reflection of its inert chemical behavior. Given the cost of gold, other metals were used in its place. Silver or tin could be used unadorned for their luster or with translucent coatings to imitate gold or to yield gem-like effects. However, silver becomes black, and tin oxidizes to powdery white tin dioxide, so the artist's intention of depicting light and luxury is lost over time. Nevertheless, XRF and SEM-EDX analyses reveal wide use of other metallic foils.

The cloth of honor hanging behind the Virgin in *Madonna of Humility* by the Florentine artist Masaccio (1401–1428) was decorated with the sgraffito technique. Each black line in the rich textile was once sparkling silver. Raphael used a similar technique to sign the center panel of *The Mond Crucifixion* (ca. 1505), scraping through a brown glaze to "write" his name in silver. The signature is hardly visible now but has been confirmed with SEM-EDX. In this painting, Raphael also used silver leaf for the moon at the top of the crucifixion (46).

A laminated silver-gold foil, known as parti gold in English, oro di metá in Italian, and Zwischgold in German, appears to have been more prevalent than had previously been assumed. Gold-wrapped threads predominated in brocades and tapestries woven before the thirteenth century; subsequently, parti gold was used extensively to wrap silk threads. Parti gold was probably more common than gold because it is thicker and easier to wrap around a thread (86). Parti gold was also widely used in prints. XRF analysis showed that it was employed, along with pure gold and silver leaf, in devotional prints on paper in Germany during the fifteenth century (45).

The fourteenth-century painter and writer Cennino Cennini described gilded or golden tin in his oft-cited treatise (88). Once thought rare, analysis is suggesting that the use of gilded tin for decorations such as halos and raised lines on drapery was not uncommon. Tintori (89) discussed some early discoveries of golden tin in thirteenth century frescoes. Giotto (1266/1267–1337) used gilded tin extensively in frescoes (90) and in one panel painting, *The Pentecost* (ca. 1305) (91). In some cases, the gold leaf was adhered to a thicker tin foil substrate with a resinous adhesive; in other instances, the gold was apparently beaten onto the tin, and a kind of amalgamation may have occurred. The chemistry of this material has not been completely elucidated. In any case, the thick but relatively soft tin foil allowed deep, decorative punchwork on frescoes and wall paintings.

Pure tin foil has been used for centuries. Thick (40-μm) foil was used for decorations on carved and painted brocade on twelfth-century French polychrome sculptures (92). Tin foil was used to create paste prints, a rare art form preserved inside and on book covers (93, 94). A fascinating example of the use of tin metal is found in the soldiers' armor in Giotto's fresco and in representations of other metallic objects, such as cups, knives, and swords (95). Tin may also have been used more extensively in northern Europe than we currently know, given that it was abundant in England and Germany. Further analyses will tell.

Painters used metal foils covered with oil glazes to create sparkling effects and illusionistic gems. The frame of an altarpiece attributed to the mid-fourteenth-century artists Allegretto Nuzi and Puccio di Simone is badly worn and damaged, and although it has been reworked, the method of the original decoration can be seen. The silver foil, covered by translucent red or green glazes, remains remarkably untarnished in places where the oil glaze has remained in good condition. The combination of colored glazes over the foil was used to depict fanciful zoomorphic decoration. Another example is *Bianca Maria Sforza* by Giovanni Ambrogio de Predis (1455–ca. 1508), which may be a wedding portrait of its subject, showing her bedecked in jewelry (**Figure 3**). The gems on the placket of her bodice and in her hair were once much more brilliant. They were painted with layers of tin foil covered by a translucent, deep red glaze. The foil has corroded and the glaze has darkened somewhat, so the original luminosity is lost (96).

The decorative border around Giotto's *Crucifix* (ca. 1290) in the church of Santa Maria Novella contains an interesting amalgam of tin and mercury as the substrate for a translucent yellow glaze used to mimic gold. SEM-EDX analysis showed that mercury was located in particularly silvery granules in the alloy (97). The recipe used for making the amalgam may have been similar to that employed by the medieval monk Theophilus for a silvery fluid ink for use with a quill or brush

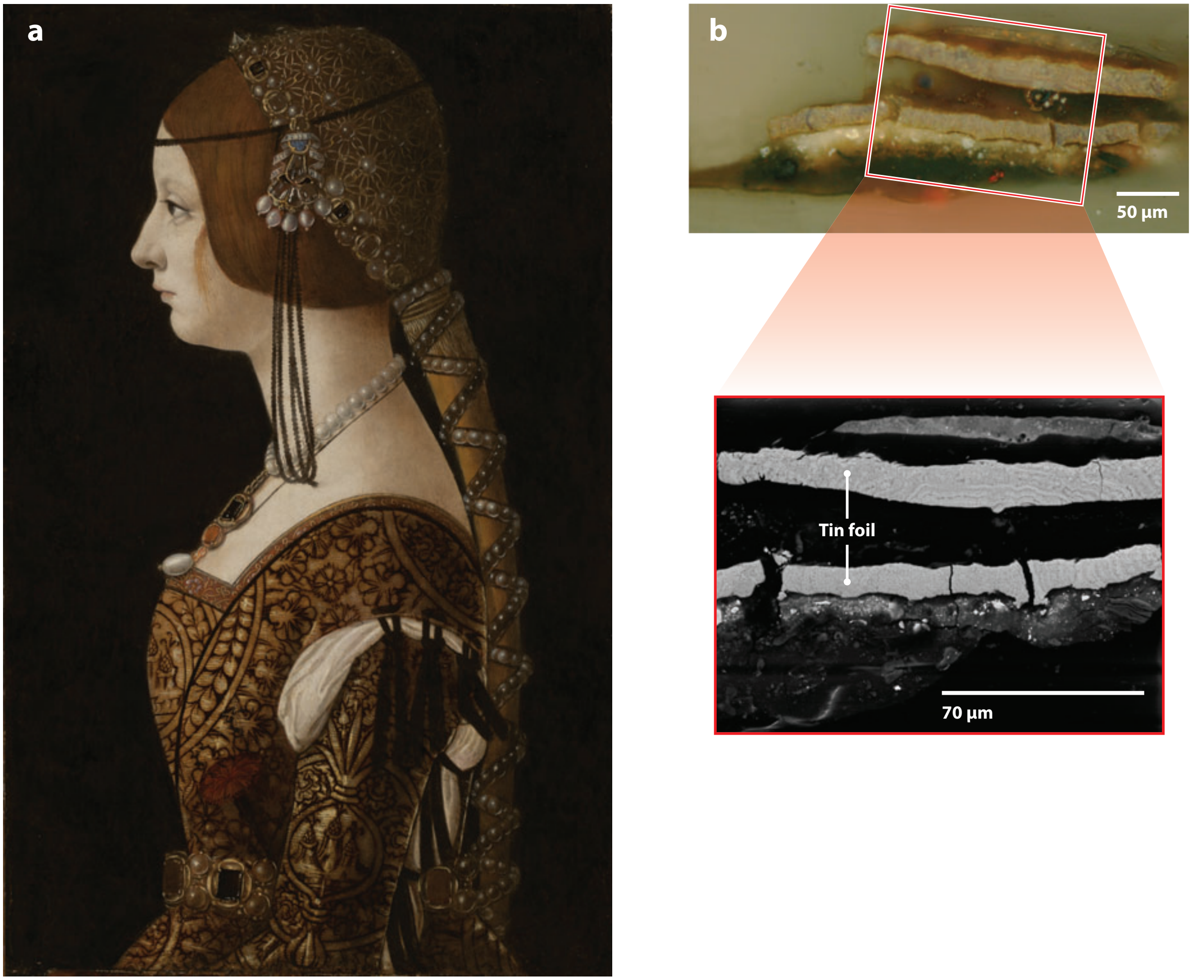


Figure 3

Metal foils served as a reflective underlayer for translucent, colored glazes of paint in (*a*) *Bianca Maria Sforza* (1493) (1942.9.53 Widener Collection, National Gallery of Art, Washington, DC). Ambrogio de Predis used tin foil under red glazes to imitate a garnet or ruby embellishing the snood over Bianca Sforza's hair. (*b*) A cross section (photographed in bright field with polarizer) from the jewel showing two campaigns for making it. A layer of tin foil was laid on a sticky mordant, and a translucent red glaze was applied to the foil. Perhaps because the foil cracked, a second layer of foil was put down and covered with a red glaze. (*Inset*) The back-scatter electron image of part of the sample; the tin foils are visible as horizontal light gray lines. (Oxford INCA spectrometer and SuperATW detector, on a Hitachi S-3400N scanning electron microscope at 20 kV.)

(97). This occurrence long predates the apparent date of introduction of the tin amalgam mirror (98) and raises questions about "who knew what, when" about these materials.

Metal flakes or filings have been used in paints for centuries; to date, we know that gold, silver, copper, bronze, brass, tin, and bismuth have been employed for this purpose. Aluminum powder has been used by painters since it was first produced in the nineteenth century. Powdered gold, termed shell gold for the container in which it was stored, was extensively utilized for painting, drawing, and writing (i.e., chrysography). Powdered gold and silver have been found in Islamic paintings, but brass and copper, although described in early treatises, have not yet been found in

Islamic miniatures or paintings (99). In general, although bronze or brass filings may have had the same color and luster as gold and may have been an oft-used, inexpensive substitute, they are rarely found today. These metals corrode and react with fatty acids over time, which turns them black or green because of the formation of various copper salts. Notably, a high-tin bronze was used by Perugino (who also employed other metal powders, including elemental tin) and Raphael (78).

Powdered metallic bismuth has a soft, light gray hue. It was discovered with air-path XRF in paintings by the Italian artist Fra Bartolomeo (1472–1517) (100) and in the predella of Perugino's altarpiece (1497) at Fano (101). XRD showed conclusively that a gray used in several paintings by Raphael, and by Francesco Granacci (1469–1543) for the armor in *Portrait of a Man in Armour* (ca. 1510) (102), is bismuth. Measurements of the infrared reflectivity of bismuth compared with that of BiS_3, another possible pigment, showed that they behave quite differently; therefore, near-IR spectroscopy in conjunction with XRF would help discriminate between them (102). Raman spectroscopy is also a good tool for confirming the presence of bismuth (103). This element has been found in miniatures by the French artist Jean Bourdichon (1457–1521) (**Figure 4**) (104, 105). The German artist known as the Master of Cappenberg used bismuth for the black patterning in the decorative edging of a sumptuous cloak in *The Coronation of the Virgin* (ca. 1520) (106). Bismuth was produced from mines in Schneeberg, so there may be many more occurrences of this metal to be discovered in German paintings.

The metallurgist Georgius Agricola (1494–1555) offers an early description (1530) of bismuth and its characteristics (107), but we know little about when it was first isolated. Its use as a pigment in the late fifteenth and early sixteenth centuries may indicate a fascination with a recently available material that was not yet known as a new element.

Burnished bismuth powder was employed as the background for painting in the decorative arts collectively known as Wismutmalerei (108). Small caskets and boxes dating from the fifteenth through eighteenth centuries are the best preserved examples of the art form, but bismuth may have been used more widely.

It is ironic that a great national treasure of Japan, Ogata Korin's (1658–1716) double-screen painting *Red and White Plum Blossoms* (1712–1713), was not created with metal leaf, as had been assumed. It was thought to have a gold leaf background, and the dark stream running between the trees was believed to be corroded silver leaf. However, XRF analysis showed that the gold content in the background is not high enough to be gold foil and that there is no silver at all in the stream. The artist created an image that looks as if it were painted using precious metal leaf, but he eschewed the usual materials and methods. The imitation gold foil was painted with shell gold and an organic pigment, and the river with only organic pigments. Korin's masterpiece is important both aesthetically and because it shows how great artists adopt new techniques (109).

7. FUTURE ISSUES AND RESEARCH AREAS

To glean as much information as possible from art and artifacts, it would be advantageous to employ analytical methods that can perform simultaneous analyses for the identification and mapping of colorants over the macro- to molecular scales. A significant advance would be to acquire information not only in two dimensions but also extended to the third dimension, so that chemical characterization of the materials used throughout the layers of paint can be achieved. Chemical imaging methods would be key in this development. Improved discrimination among and simultaneous analysis of the various materials in a heterogeneous sample such as paint require the application of robust chemometrics.

Figure 4

Raman spectroscopy showed that metallic bismuth was used for gray color in this miniature (1498–1499) by Jean Bourdichon, *The Presentation in the Temple* (tempera and gold on parchment, 24 × 17 cm) (The J. Paul Getty Museum, Los Angeles, MS 79b verso.[1]) See Reference 105.

[1]All the digital image files supplied by the Getty Museum for this review have been carefully color corrected and are a close match to the original artwork. They were produced in a tightly color-controlled environment using industry-accepted color management procedures. Color and tone evaluation of Getty digital files should ideally be on a computer monitor in a room with neutral gray walls of 60% reflectance or less. Ambient light should be 5,000 K and very dim (<32 lux). The monitor white point should visually correspond to the white point of your viewing booth. Monitor luminance should be set to a minimum of 100 cd m^{-2} and preferably 120 cd m^{-2} for an LCD monitor; luminance of a CRT should be as high as possible. Once printed, these image files will be converted from their native Adobe 98 RGB color space to CMYK or gray scale, which may produce unpredictable results.

Apart from the advantages that improved instrumental methods would provide, there is another consideration for future work. As noted by Laurie (2) and shown by the examples discussed in this review, artists' use of color was related to innovations in the so-called sister arts. Our progress in conservation and cultural heritage science depends on new work in other scientific fields. Just as it required effort, determination, and originality for master painters to meet and overcome the challenge of artfully using new materials, we need to address the challenges of incorporating findings from the sister sciences. Scientists' knowledge about the chemistry of entire classes of chemicals used for coloring underpins the identification of colorants from plants in the arts; ceramics scientists' analytical expertise complements our knowledge of colored glasses, frits, and pottery. The study of cultural heritage can be so much more than merely applying an analytical technique: When analysts have an opportunity to delve deeply into historical material, to push the limits of analysis, to explain apparent anomalies, to reconcile inconsistencies, and to contextualize the results in terms of the history of technology and use of materials, then we can be as creative and inventive as the artists whose masterworks we study.

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