The Art Detectives

Science brings a new perspective to the study of art

By STEFI WEISBURD

After critics gave disastrous reviews to Millet's "The Captivity of the Jews in Babylon" in 1848, the painting disappeared. Art historians long assumed that the canvas had been cut to pieces. But when scientists X-rayed another of Millet's paintings, "The Young Shepherdess," to see what was causing a lumpiness on its surface, they were delighted to find the long-lost "Captivity" painting beneath.

Was Gauguin cheated by the Paris dealer who sent him his paints while he lived in Tahiti? X-ray fluorescence reveals a high level of barium sulfate in the lead-white pigment in his paintings, an indication that the paint was of low quality. Perhaps Gauguin was just too poor to afford better pigments.

At first glance, the Vinland Map looks like a medieval document (circa 1440), showing, among other things, the North American coastline discovered by Leif Ericsson in the 11th century. But using electrons and X-rays to probe the map, scientists found that its inks contain particles of a decidedly modern white pigment, titanium dioxide, which was introduced commercially in 1920.

Art historians and curators traditionally have sketched out the histories of artworks by scrutinizing styles and techniques and by poring over letters, diaries, receipts and other documents. But with increasing frequency many are also finding that techniques used by chemists, physicists, biologists and geologists can add revealing shadings to their research palette. A wide spectrum of scientific methods – from electron microscopy to carbon-14 dating, from isotope analysis to biologic staining – is helping the art world detect forgeries, discover lost works and better preserve paintings and other art forms.

"There's a trend among art historians now, especially in Europe, to work in collaboration with scientists," says chemist Barbara Berrie at the National Gallery of Art in Washington, D.C. Scientists help to trace the technical evolution of individual artists, to see how groups of artists influenced one another and to unearth the origin of stones, ores and pigments that individual masters formed into sculptures, pots, plaques and paints.

"To describe an artist's style only in terms of the shapes or draftsmanship of a painting is to miss one of the most important ingredients," says art historian Thomas F. Mathews at New York University. "Artists differ from one another not only in how they draw noses and ears but in the choices they're making in the pigments that shade these in. Chemical techniques [that identify the type and quality of pigments] give you a very immediate sense of knowing what the artist was doing. It's like looking over his shoulder and seeing what he's putting on layer by layer."

Special Collections, University Research Library, UCLA

Of the five artists responsible for the 14th-century Armenian manuscript containing this illustration, the one who painted this page had access to the best pigments. Chemical analysis revealed that this artist used the highest-quality ultramarine as his blue pigment, whereas the other painters used less expensive azurite and poorer-quality ultramarine for theirs.

In addition to helping curators understand where and how artworks were made in the past, scientists help them preserve these works for the future. Considerable work has gone into studying the effects of light, humidity, heat, oxygen and air pollutants on works of art. In a collaborative effort with two other art conservation institutes, researchers at the Smithsonian Institution's Conservation and Analytical Laboratory (CAL) in Suitland, Md., are investigating the effects of fumigants – which are used extensively in museums – on dyes, pigments, resins, waxes, metals and other materials. And at the Mellon Institute Research Center on the Materials of the Artist and the Conservator in Pittsburgh, Robert L. Feller and his colleagues have developed an improved protective varnish for coating paintings and have studied the phenomenon of fading. Some of Feller's work prompted curators at Washington, D.C.'s National Gallery of Art to cover the museum's entire skylighting system with ultraviolet filters to prevent works from deteriorating.

Archaeological and historic artifacts also benefit from scientific analysis. Two years ago, when curators at the Smithsonian Air and Space Museum in Washington, D.C., wanted to restore the Wright

National Gallery of Art, gift of Mrs. Mellon Bruce

X-rays, used to detect the presence of lead-containing pigments, reveal an image of a young man beneath Jean-Honoré Fragonard's "A Young Girl Reading."

1903 Flyer — the first plane successfully flown by the Wright Brothers — they engaged metallurgists, chemists and other researchers from a number of Smithsonian labs to document the plane's condition and composition, to identify original parts and to recommend treatments. Scientists at the Freer Gallery in Washington, D.C., were even asked to take X-rays of the threads on the plane's connecting rods so that conservators would know which way to turn them when they disassembled the plane.

Science has been an important partner in the study and restoration of paintings, and it continues to help decipher the technology of making bronzes, ceramics and other objects. But until recently there was one form of art it had not touched: illustrations found in medieval manuscripts.

"Up to this point no one was quite certain that [direct] chemical analysis would yield any important information," notes Mary Virginia Orna, a chemist at the College of New Rochelle (N.Y.) who works with art historian Mathews. "What people had been relying on with respect to manuscripts was what was written about them [in historical texts] — that's secondary information. We're getting the primary information by doing the analysis ourselves. And we're finding that in many instances secondhand information doesn't go along with the primary data."

In general, too, manuscript illustrations are more difficult to study than oil and other paintings because the paint is laid down in a very thin layer and the paintings themselves are so small that it's difficult to get samples of any size or weight, adds Mathews. "So manuscripts have posed a different set of problems for the chemist."

So far, in their pigment studies of Armenian, Byzantine and Islamic manuscripts, Orna and Mathews have uncovered two forgeries, traced lines of influence among medieval centers of manuscript production and clarified when several important pigments were used.

A number of scientific techniques exist that can be used to study pigments. Some researchers have followed recipes in old painters' manuals, cooking up pigment samples and painting them on parchment. Then by using polarized light and other techniques to compare the microscopic structure of the painted samples with that of a manuscript, scientists can sometimes identify some of the manuscript pigments.

There are also a host of nondestructive techniques that can be used to examine a manuscript or painting as a whole. X-rays, for example, can reveal paints containing lead and other heavy metals. Since artists often used paints like lead white to sketch out their ideas, X-rays can show how an artist's ideas evolved.

A technique called autoradiography can detect many other chemical elements. Autoradiography bombards a painting with low-energy neutrons, which make some of the elements slightly radioactive. By monitoring the radioactive decay of these elements on a series of photographic emulsions, a researcher can map the elements' distribution throughout the painting.

Orna and Mathews, however, choose not to study the medieval manuscripts with such methods because they identify only elements, not complete compounds. Moreover, these techniques are largely oblivious to organic pigments, and they often require that the whole manuscript be removed from a museum.

Instead, Orna and Mathews used a fine surgical scalpel to remove tiny pigment samples, ranging in diameter from 4 to 100 microns. By subjecting their samples to polarized-light microscopy and X-ray diffraction, they can clearly identify the compounds in the pigments. They also used Fourier-transform infrared spectroscopy — which measures the vibrations of parts of molecules — to identify organic compounds. Working with such tiny samples has been a challenge. Ideally, the researchers would like to use chromatography or other methods to separate the organic components from the inorganic materials in their small

Pigments by the book

Suppose a curator asked you to vouch for the authenticity of a painting or to find just the right pigment for restoring a tiny patch of paint that has been chipped off. Where would you start? A good place would be *Artists' Pigments: A Handbook of their History and Characteristics* (National Gallery of Art, 1986).

In it, you'd learn how to identify Indian yellow, a pigment derived from the urine of cows fed mango leaves, and you'd discover that this pigment has been unavailable since 1908, when the government of India banned its manufacture on humane grounds. Or you'd see how to chemically distinguish and prepare the red pigments called carmine that are made from different species of scale insects.

The handbook, which took 10 years to put together, details how to identify 10 historically important pigments using a variety of scientific techniques to probe a pigment's chemical makeup and particle shapes. It also discusses the history, important usage, painting qualities, toxicity and common impurities of these pigments.

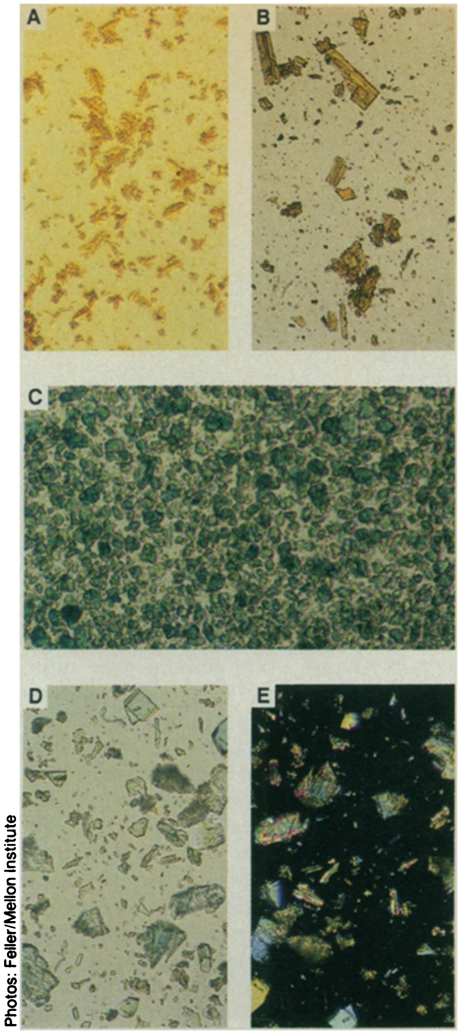
"The purpose of the handbook is to tell an art historian everything they'd want to know about a pigment used in a painting," says Mellon Institute's Robert L. Feller, who edited the handbook. Three more volumes are in the works, and Feller hopes the series will eventually cover all the important historic pigments, about 60 in total.

The kinds of information contained in the handbook should be a standard part of any description of a work of art, says art historian Thomas F. Mathews at New York University. "Unfortunately, people still describe all the colors of painting in terms of fruits and flavors — raspberry pink and banana yellow. That language is suggestive, but it doesn't help you when you want to know how the artist made the work." — *S. Weisburd* samples, in order to get "cleaner," more precise identifications. But, says Orna, "no one has come up with a technique yet of doing that without losing the sample altogether."

From their studies, the researchers have discovered that Byzantine painters mostly used organic materials mixed with lead white to produce pastel shades, while Armenian pigments were made almost entirely from minerals, which gave the manuscripts vibrant colors. "One could always see the difference visually between these two kinds of manuscripts, but to know exactly what causes the differences is important to both the art historian and the conservator who must preserve them," notes Mathews. Because Orna and Mathews found that the Byzantine organic pigments are not lightfast, for example, they've advised curators to display Byzantine manuscripts as little as possible.

They've also noted differences between Byzantine and Armenian manuscripts and those produced in Europe. They found that natural ultramarine, for example, was extensively used in the Near East. But because the pigment came from mines located in what is now Afghanistan, it was hard to come by in Europe, where it was often valued more than gold and had to be contracted for separately in a painting's commission. On the other hand, Byzantine and Armenian painters don't seem to have had a true green pigment to work with, and instead mixed together blue and yellow pigments. European artists had been painting with a range of green pigments based on copper acetate since the 13th century, and the Chinese had been using malachite since the 9th century.

By studying the kinds of pigments used in different manuscripts, Orna and Mathews can determine when an artist started to experiment with new paints and which artists had access to the best pigments. In a 14th-century Armenian manuscript painted by five different artists, for instance, they found that one painter used a much higher-quality ultramarine — as judged by the density of blue particles in the pigment crystal matrix — than the others.



Photos: Feller/Mellon Institute

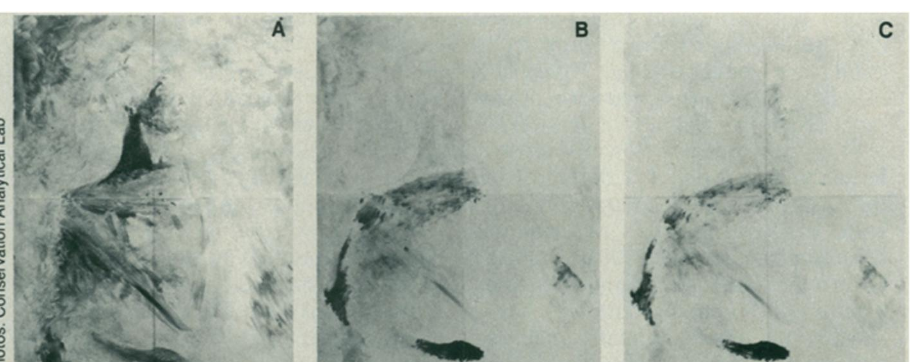
One common way of identifying a pigment is to look at it under an optical microscope. Here are micrographs showing (A) the leaf-like crystals of cobalt yellow, a pigment used primarily in the 19th century for watercolors, and (B) orpiment (arsenic sulfide), a poisonous mineral used since classical times. Micrographs also show that crystals found in modern pigments, such as the chromium oxide green shown in (C), are far more uniform in size than the ground-up particles found in ancient mineral pigments such as malachite green, a basic copper carbonate (D). Micrograph (E) shows how malachite green looks under polarized light.

Orna and Mathews have also helped to expose two forgeries. One is the 12th-century "Archaic Mark," so called because it contains the gospel of Mark written in an archaic form of Greek. The researchers were able to confirm the suspicions of University of Chicago art historian Robert S. Nelson that it (and possibly a similar manuscript now in Leningrad) is not what it seems.

Using infrared spectroscopy, Orna found the distinct signature of Prussian blue, the first known artificial pigment, originally made in Berlin in the 18th century. Since there's no written record of the history of this manuscript prior to the 1930s, when it was acquired by the University of Chicago, the researchers suspect that it was part of a large number of Athenian forgeries that came to market in the 1920s. In a similar fashion, Orna and Mathews discovered that a 16th-century Persian manuscript was in fact made at least three centuries later, because it contains chrome green, a modern synthetic pigment.

Often, however, science can play only a supporting role in ferreting out forgeries. For one thing, says CAL Director Lambertus van Zelst, forgers can read the science/art literature too, and, depending on the medium, can become as sophisti-

Courtesy of the National Museum of American Art, gift of John Gellatly



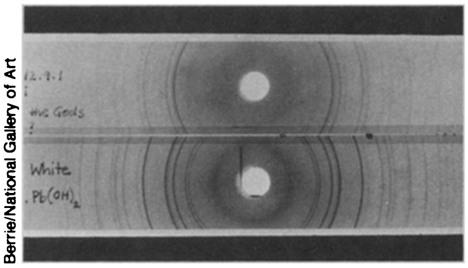
Photos: Conservation Analytical Lab

At the Smithsonian Institution, art historian Susan Hobbs uses autoradiography to study the painting techniques of turn-of-the-century American artist Thomas Wilmer Dewing. Autoradiographs of Dewing's "Portrait of Alma Thayer" (left) reveal the distribution of different chemical elements. The first in the series above shows that zinc and barium were used in the flesh-toned pigments of the neck and face (A), and from the autoradiograph patterns, Hobbs can tell that the artist painted this region with tiny horizontal and vertical brushstrokes. Other autoradiographs show the location of pigments containing antimony (B) and mercury (C).

cated as some of the scientists who test for forgeries.

For example, a technique called thermoluminescence can determine the time elapsed since a piece of pottery was last fired. By measuring the amount of light emitted from a ceramic object when it's heated, scientists can get an idea of the amount of radiation to which it has been exposed – a measure of its age. According to van Zelst, forgers in Italy are now taking recent pottery pieces to their dentists for a dose of X-rays that will make it look as if the pot has been exposed to radiation since antiquity. If done right, he says, this procedure could fool a routine thermoluminescence test.

And even when scientific evidence of forgery is presented, the art world doesn't always listen. Perhaps the most famous example of this is a series of paintings passed off during World War II as being works of 17th-century Dutch Master Jan Vermeer. In spite of the fact that traces of 19th-century pigments were detected in the works and that the real artist, a Dutch painter named Han van Meegeren, insisted the paintings were his, many collectors simply refused to believe they were fakes. Van Meegeren, who was on trial for collaborating with the Germans by selling them some of these works, finally settled the issue by creating a new painting while in jail. Looking at these paintings today, says van Zelst, one would find it hard to believe they were Vermeer's, but at the time that's all the collectors who had bought the works could see.



Berrie/National Gallery of Art

The pattern X-rays make when they are diffracted by a crystalline material can be used to "fingerprint" different pigments. From the diffraction patterns shown here, scientists know that the sample of white paint (above) taken from Giovanni Bellini's "Feast of the Gods" is made of basic lead carbonate (below).

While science is only one of many tools in the art historian's box, it is a tool that is becoming more precise and powerful as innovative techniques from the traditional fields of science gradually find their way into the art world. Working with immunologist Rose Mage at the National Institutes of Health in Bethesda, Md., for example, chemist Barbara Berrie has developed a series of antibodies, labeled with colloidal gold, which will tag egg yolk. This immunological approach can help them decide if a picture was painted in egg tempera rather than with oils – information that is important to a conservator, who must choose the proper kinds of solvents for cleaning the painting. It may also aid art historians who are trying to trace how rapidly oil painting spread from the 15th-century northern European painters, who perfected oil techniques, to schools of artists elsewhere in the world.

In addition, many curators and conservators are interested in using digital image analysis of paintings to detect and record the slight differences that come from aging, fading and preservation in order to document and better understand how artworks deteriorate. This computer technique, which divides a painting into hundreds of tiny zones, could also be used to compare the different kinds of information gleaned from a variety of imaging techniques such as X-ray and infrared analysis. One CAL researcher hopes to use this approach as a way to catalogue and look for underlying themes in the designs painted on Hopi Indian pottery. At the Freer Gallery, Thomas Chase wants to use holography to study how lead solder joints on metal objects degrade as a function of temperature and stress, and he'd like to see more nondestructive techniques developed to determine how fast metals cooled and other microstructural details of how objects were made.

Such tools might be applied to modern materials as well. "Often modern pieces are falling apart already because people are using materials that haven't been shown to stand up to time," says the National Gallery of Art's Berrie. "Some artists also mix together materials that adversely affect one another's longevity. . . . [Only a portion of artists today seem] interested in making their art last a long time without having to rely on old tried-and-true materials such as oil paint."

And modern materials in art are not the only ones that could stand the scrutiny of science. Some of the items for study on van Zelst's agenda are the space suits at the Air and Space Museum. Like many 20th-century materials, the suits were not designed to last for eons in museums, he says. "They're crumbling and falling apart already, but we haven't had the resources to get to them yet."

As is often the case when any two seemingly disparate traditions merge, there have been those who are leery of using science in art. "Some art historians are quite resistant to [scientific information]," notes Berrie. "But then there are others who won't do a thing until [scientists] put their two cents in."

And just as the art world has opened up a bit to science, some scientists find themselves changed by working with art. Says Berrie, "I've learned to look much more closely at a picture once I've thought about how and from what it's made." □

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Crossing Open Ground – Barry Lopez. A collection of 14 essays by this award-winning author that explore the bond between humans and the land and humans' betrayal of that bond. These essays, originally published in various magazines, have been rewritten for inclusion in this collection. Scribner, 1988, 208 p., $17.95.

Let's Grow!: 72 Gardening Adventures with Children – Linda Tilgner. Dozens of projects to help parents, grandparents and teachers give children a knowledge of nature and a love of gardening. The well-illustrated book includes projects concerned with growing vegetables, flowers, herbs, indoor gardens, balcony gardens and window boxes. The projects range in complexity from those to be used with the very young (such as growing sunflowers) to those suitable for preteens (such as starting seedlings and creating a patchwork quilt salad garden). Family and group projects are included. Activities are classified by age group and season. Storey Comm Inc, 1988, 208 p., illus. paper, $10.95.

The Perfect Puppy: How to Choose Your Dog by Its Behavior – Benjamin L. Hart and Lynette A. Hart. Intended to help prospective dog owners select the breed and gender of dog best suited to their lifestyle and environment. Here animal behavior specialists look beyond appearance and size to the behavior of 56 popular dog breeds. Their profiles of each breed focus on 13 key behavioral traits, such as excitability, barking, ease of housebreaking, demand for affection and playfulness. W H Freeman, 1988, 182 p., illus., paper, $9.95.

Rationing Medicine – Robert H. Blank. The American health care system faces, according to the author, an ethical and economic crisis in the coming decades of immense proportions. New medical technologies, an aging population and changing attitudes toward medical care have increased the nation's already astronomical health spending. The author traces four aspects of health care – organ transplantation, treatment of seriously ill newborns, reproductive technology and fetal health – to illustrate the problems facing our health care system. Columbia U Pr, 1988, 290 p., $25.

The Scientific Companion: Exploring the Physical World with Facts, Figures, and Formulas – Cesare Emiliani. "Our world," says this geologist, "is an incredibly coherent system endowed with a rich braid of evolutionary paths from its fiery beginning 15 billion years ago to the evolution of humans on Earth." This well-illustrated book describes how our world originated and evolved, focusing on the quantitative to give the reader a feeling for the dimensions involved. Wiley, 1988, 287 p., illus., paper, $14.95.