FINE ART EXAMINATION AND CONSERVATION

1. Introduction

A small number of specialist scientists, called conservation scientists, work with museum curators and art conservators in examining, from a technical point of view, works of art. Characterization of materials and how they were incorporated to create a work of art has several purposes. Chemical and materials analysis is directly relevant to the treatment and preservation of fine art since its conservation is strictly dependent on the materials that were used in its creation. The knowledge of the materials and methods used by artists allows us to gain an insight into the original appearance and artists' intention. The results of the conservation scientists' research are used to specify appropriate environments for storage, exhibition, and to help choose appropriate cleaning of the works. Research into degradation of artists' materials is important so that the best environment for the work can be chosen. For example, low light levels for displaying works that have fugitive pigments or a dry atmosphere for objects made from iron can be indicated. The work of conservation scientists is important also for understanding the process of creation of a work. This knowledge can help identify forgeries, fakes, and imitations. It is also useful to art historians in addressing issues related to attribution. Studying the materials and methods used by artists provides a way to understand the technology of the times in which they created their work. The works of art themselves document

the science and technology of their time. Science is now seen as a vital contribution to the good care and understanding of our cultural and artistic heritage.

The evolution of the profession of conservation scientists is relatively recent although scientists have applied their expertise to examining fine art and archaeological objects as long as they have been practicing their field. The English scientists Michael Faraday (1791–1867) and Humphrey Davy (1778–1829), and the German chemist, Martin H. Klaproth (1743–1817), published work on the examination of fine art. Faraday was commissioned to study the indoor environment of the National Gallery, London as part of an effort to preserve the works. However, the emergence of the professional conservation scientist is more recent. The Royal Museum of Berlin was the first museum to have a staff scientist (1888). The British Museum in London hired its first scientist during World War I. The first museum scientist in America was hired at the Boston Museum of Fine Arts in 1929. The field remains small but vital. Feller (1) summarized the research goals of conservation scientists as "Transfer knowledge and tools from other fields; explore potential new techniques and methods; search for general principles; build foundations for further advances; fill in gaps; refine or enlarge upon current knowledge." These objectives are being implemented as the field expands to include more scientists and more venues for their work.

A subspecialty of art history known as technical art history involves the study of works to understand how artists achieved their effects and to learn how artistic practice developed. This work depends on information acquired through technical investigation. Scientists and art historians are involved in this pursuit, an interdisciplinary field by necessity. Perhaps the first practitioner of this was the Belgian chemist, Paul Coremans, who published a seminal paper on the painting technique of Jan van Eyck for the masterpiece "The Ghent Altarpiece." (2) How chemical and technical analyses are used to understand paintings is explained by Hours (3) and many examples can be found in the Technical Bulletin of the National Gallery, London. One of the early achievements of technical art history was the use of infrared(ir) reflectographs of paintings to study the underdrawings in paintings by Northern European artists such as Gerard David (∼1460–1523) and Jan van Scorel (1495–1562) (4). Since then, the technique has found wide application (5). Analysis of the materials used in paintings has been compared to early treatises and inventories. This helps in understanding the veracity of early chroniclers of painting methods. The descriptions of Cennino Cennini of how to paint, written ∼1390, were compared to actual paintings from that time period through technical analysis. The results allow us to appreciate even more the artistic skill of these artists and their works which have survived centuries (6). In a slightly different application, the color and pigments in paintings can be correlated with economic and technological aspects of the time period. For example, the use of blue pigments by Albrecht Dürer, established by technical analysis, can be examined in light of the inventories of pharmacists who supplied painting materials (7).

Today, most conservation scientists work in museums and museum support centers; some are based in the academic environment. Increased funding has helped build stronger foundations for the field. Government and private funding worldwide have provided more opportunities for scientists to apply their expertise to the examination of fine art and cultural property. This entry will use

works of art for its examples, but the methods described are equally applicable to archaeological finds, many of which are works of art. One difference is that statistical methods can be applied to the results of analysis of archaeological material such as pottery shards that cannot be applied to fine art.

2. Technical Investigation of Works of Art

The range of science and analytical techniques involved in fine art examination and conservation is very large since it not only covers the topics listed above, but is applied to works of art made in every medium: paint, paper, photography, stones, glass, metals, plastic, etc. The works themselves may be classed as fine art, decorative art, cultural property or ethnographic material. The work of the conservation scientist depends also on information from the fields of art history, conservation studies, and the history of technology.

Appreciation of art and the desire to explore it using scientific methods has been a strong motivation for many scientists to apply their expertise to studying art as long as modern science has existed. The first published results of the application of science to the examination of fine art date to the late 1700s (8). In the following sections, only a few of the methods used for examining fine art can be described. The techniques found most often in museums have been chosen. Many other techniques have been applied to this field. Papers discussing the application of some of the less frequently applied analytical procedures can be found in the online journals of International Institute for Conservation (9), and the American Institute for Conservation (10).

2.1. Methods for Investigation of Fine Art. Instrumental analysis of every type has been applied to studying fine art. The example of Willem Roentgen, the discoverer of X-rays, using his discovery to examine paintings is not unusual. Limitations often relate less to the desire to apply a technology to the investigation of art than to the hurdles of expense, moving art to the instrumentation, and other practical difficulties.

Nondestructive analysis in this field implies that no samples are removed from the object. There was a restricted range of techniques that were employed for nondestructive analysis of fine art until recently, when the development and refinement of many spectroscopic and imaging methods has changed this. Today, there is instrumentation for nondestructive analysis in many museums and more available to conservation scientists at research institutions. A useful description of these, including technical notes on examination of paintings in ultraviolet(uv), visible(vis), and ir radiation, has been published (11). Despite remarkable refinements in noninvasive analysis, there are many times when samples are necessary to analyze the materials used in fine art and to understand the structure of the work. When required, samples are obtained from works and may be examined with the entire range of instrumental techniques available to the conservation scientist. Acquiring samples from fine art remains a difficult issue for the conservation scientist and one that requires much thought. Aside from the fact that there is a natural reluctance to sample a work, there is the matter of relevance of a particular sample to the issues presented regarding understanding an object and its preservation. The history of

prior interventions on a work is unknown and a sample may reflect a past restorers' work rather than the artists' original material. Standards of aged and deteriorated materials are almost impossible to obtain and the original components of a work may be so degraded that they cannot be characterized by comparison to fresh material. There is also a problem in assuming that the material from a tiny sample can be assumed to be representative. Experience and working in multidisciplinary teams help deal with these difficulties.

Nondestructive Analysis.   Stereomicroscopy and Scanning.   Low power stereomicroscopy is one of the most important tools for first analysis of an object. Typically, magnifications of $\times 2.5 - \times 350$ are used. Microscopy of paintings can reveal surface defects in paint films, small cracks in surfaces, and through them the underlying layers of paint. At this level of magnification it is possible to resolve the larger pigment particles in pastels, pencils, and oils and watercolors. Wear, tool marks, and surface treatment of metals can be discerned using this type of microscopy.

Highly sophisticated imaging techniques have been used for the structural analysis of works of art. A system developed at INOA is capable of scanning the surface of a work of art with submillimeter precision generating a virtual three-dimensional(3D) object with the surface roughness, cracks, and holes all thoroughly documented (12). Michaelangelo's sculpture of David (1504) was scanned and analyzed during its recent treatment. High-level computer modeling of images captured in reflected and fluorescent light conditions were used to show where residual waxes from past treatments was located which helped in understanding the mottled surface appearance (13).

Colorimetry.   Measurement of color is beginning to find application in the field to identify pigments on the surface of a work of art and for matching the color of losses (14). Scientific color information is important for accurately documenting the current state of a work, specifically the tone of its paint, or an area of corrosion, or the yellowness of paper. Advances in fiber optics and detector sensitivity have allowed the technique to be used to measure the color of very small areas of paint and thus to determine the pigments present on the surface of a work of art. The technique has been used to identify the pigments on Japanese watercolors (15). The technique could be used to document patinas on metals.

Infrared Reflectography (IRR).   This technique used to examine the artists' drawings below the surface of paintings (underdrawings) was pioneered by van Asperen de Boer in the 1960s (16). Infrared radiation can penetrate the layers of paint due to the transmissivity of many pigments in the ir region. This is exploited to show the black underdrawings on white primings used for painting. Infrared photography revealed much of the underdrawing, an artist's first rendering of the composition on the support, but the use of vidicon detectors that have a range to 2.5 μ revealed drawing under more colors than photography. The use of focal plane array detectors provides a digital output that is more easily handled and provides more resolution than the television output of a vidicon detector (17).

Underpainting in dark tones can be visualized using ir radiography. Infrared examination of the painting by Jacopo Tintoretto, "Christ at the Sea of Galiliee" shows that the canvas had been used for one and perhaps two

compositions prior to the one we see today. In ir, the sketch of the portrait of a man can be seen because it was painted using umber (18).

Infrared reflectography can be used to identify the medium of drawings (19). Carbon based drawing materials, charcoal, bone black, soot, and lamp black absorb over the response range of ir detectors. In contrast, metalpoints, iron gall inks, and inks based on dyes have distinct near-ir spectra that can be used to distinguish them. Imaging techniques used for identification of ink in forensic applications yield important information for identifying materials used for analyzing art works. Changes to drawings that are not visible to the eye can be discerned using ir reflectography. The method has also been used to distinguish among blue pigments. Cobalt blue, ultramarine, and Prussian blue can be differentiated by their reflection spectra in the infrared (20).

X-Radiography. X-Radiography is an important tool for nondestructive analysis of works of art. An early publication describes how X-radiography is used as a tool for art historians (21). The X-ray tube voltage and current chosen depend on the nature of the object being examined. Low voltage is appropriate for studying low density works such as paintings, ceramics, and small sculptures made from organic materials such as wax. A specially selected protocol for imaging watermarks on paper at 5 kV with a helium flush has been devised (22). High voltage, "hot," units are used for examining large bronzes.

Lead white $(2PbCO_3 \cdot Pb(OH)_2)$ was the most usual white pigment used for painting until the 1970s. The high absorption coefficient of this pigment means that it is clearly evident in X-radiographs and where it was used can reveal changes in the artists' composition. Artists' abundant use of lead white is what allows us to see changes made in the composition of work as the artist painted. Pigments other than lead white that are made from heavy elements absorb similarly, eg, vermilion, (HgS), lead tin yellow $(PbSnO_4)$, and strokes of these paints are clearly imaged using X-radiography. X-Radiographic studies of paintings reveal artists' changes, damages, and repairs. Sometimes it is possible to tell from an X-ray if the canvas support for an Old Master painting is its original size. When canvas is first stretched onto a stretcher or a strainer, the weave of the fabric at the edges acquires a scalloped shape where the fabric is stretched most to the nails or string holes. When the support is sealed using glue, the induced deformations in the weave become permanent. The deformations, called cusping, can be seen in the X-radiograph especially when lead white is used to prime the canvas. When cusping is not visible, it often means the painting has been cut down from its original size. Brushwork of underlying layers of paint can be visualized and are often informative about an artist's working methods.

X-Radiography is used to investigate the way objects were constructed: joints in all sorts of media can be imaged. The way wooden objects or composite ceramic objects were assembled can be elucidated using X-radiography; the location of nails and screws can be found. X-Radiography is useful for revealing cracks and damages in objects of all sorts including 3D objects.

Obtaining X-radiographs of metal sculptures usually requires high voltage to penetrate the mass of metal. Since high voltages result in low contrast images, lead foils are used to attenuate the radiation impinging on recording film to provide higher contrast images and allow better definition. Aluminum, or copper, filters placed on the X-ray tubes have been proven useful when X-raying objects

using beam voltages >40 kV since the filters reduce scatter of low energy X-rays and provide images with better clarity.

X-Radiography of wax and/or plaster sculptures reveals the objects from inside out, and shows the construction methods used. Many examples are brought together in the investigation of wax sculpture in French collections (23). These examinations provide important information about the solidity of the object and help in determining its stability and condition. The metal and or wood armatures can be seen and filling materials such as clay, corks, or wood are observable. The wax sculptures of Edgar Degas have been examined using X-radiography. In the X-radiograph of the wax sculpture, *Horse Balking*, we see how Degas used materials at hand—possibly corks and rope, to build up the internal structure around which there is a metal armature, partly store-bought and partly modeled from wire (24). An investigation of how the artist worked and the armatures he used led to a proposed chronology for his sculptures of horses (25).

Neutron Activation Autoradiography (NAA).   This technique has been used to examine paintings and some other works. Paintings or other works are exposed to a flux of thermal neutrons produced in a nuclear reactor. These neutrons activate some of the elements in pigments to form radioactive isotopes. The radioactive atoms thus formed decay to a stable atom by emitting beta particles, X-rays, or gamma rays. The rate of decay depends on the half-life of the excited isotope. X-Rays and beta particles cause fogging of photographic film or sensitive plates. The film (or plate) can be placed in close contact with the painting. Since the radioactive isotopes of the elements have different half-lives, films left in contact with the painting at various times following exposure to neutrons reveal the location of different elements. Manganese, gold, arsenic, and antimony are among the most easily observed elements using this technique. Lead does not activate and is "invisible" to this technique, which makes it a complement to X-radiography. Rembrandt used a dark paint containing umber (a manganese-containing iron earth pigment) to sketch his compositions on a dark ground, and therefore they are impossible to discern using infrared reflectography or X-radiography. However, the presence of manganese in umber allows the sketches to be seen using NAA (26). The difficulty of bringing art to a reactor and the high cost of NAA limit its application in the examination of fine art. [NAA was used to investigate a painting attributed to the French artist Georges de La Tour] (27). Researchers at the Hahn-Meitner-Institut in Berlin have applied this technique to another painting by Georges de La Tour (28).

Raman Spectroscopy.   Raman has developed considerably since 1990. The advent of Fourier transform (FT) methods and open architecture have allowed the technique to be used for nondestructive analysis of works of art. Currently, Raman spectroscopy is best suited for identification of pigments, especially inorganic and nonfluorescing pigments. This analytical technique offers high spatial resolution ($\sim$1 μ), molecular specificity and a good range of applicability (29). The instrumentation has been most successfully applied to analysis of pigments in water-based media owing to the fluorescence of oil binders. Pigments in mediaeval manuscripts have been analyzed and the technique has been used to identify corrosion products on metals and weathering products on stone. Ultramarine was found as a colorant on a thirteenth century Iranian ewer,

where it was unexpected. Raman spectroscopy has been applied to minute samples, individual particles, providing identification of pigments with no change in appearance (30). A large library of spectra of pigments has been assembled (31).

X-Ray Fluorescence Spectroscopy. Air-path energy dispersive X-ray fluorescence spectrometry (XRF) is widely used in the examination of fine art. The instrumentation is designed so that works of art can be analyzed without taking samples and without any surface preparation at all. This makes XRF one of the most valuable tools for nondestructive elemental analysis of works of art. There are, however, several limitations to the method. XRF is a surface-analysis technique. The depth of analysis ranges from $\sim$20 μ for metals to >100 μ for objects of low density, eg, paintings, watercolors, and photographs. Other analytical techniques may be required to confirm that the surface composition is an accurate representation of the bulk composition. It might be necessary to remove samples from patinated or weathered metals to accurately characterize the alloy. In paintings and other painted works of art, elements from underlying layers of paint that are invisible to the eye contribute characteristic X-rays to the spectrum of the area chosen to be analyzed. The size of the contribution from pigments in each layer to the spectrum depends on the thickness and density of each layer. So, in the absence of sampling, the interaction volume of the analysis cannot be quantified, and the results need to be interpreted by a conservation scientist who has a good knowledge of artists' materials and methods and knows the history of their use.

Air-path XRF instruments have poor response to low energy X-rays, therefore it is difficult to detect elements lighter than chlorine. The detection limits for light elements can be improved by using a helium flush between the detector and the work under study. Matrix effects in weathered surfaces, paintings, ceramics, and other works that have an unknown layer structure are almost impossible to model, so quantitative analyses of these groups of objects are rarely performed. However, the technique is widely used in the museum field because the qualitative information obtained without sampling is so useful. Elements found may be classed as major, minor, or trace and useful inferential information can be easily and rapidly obtained. Among the easiest examples of pigment identification to note are the inference of the use of vermilion (HgS) when mercury is found in a red paint and the presence of the yellow pigment Naples yellow (PbSbO4), when lead and antimony are present in yellow paint. Although it is impossible to determine the presence of organic pigments or lakes (complexes of organic compounds with a metal ion, usually aluminum), glassy pigments, or ultramarine (a sodium sulfoaluminosilicate), using nondestructive air-path XRF, the technique is powerful for providing confirmatory information on many pigments.

Air-path XRF has been successfully used to study colorants on works of art of paper (and parchment) although there is usually low signal to noise and owing to the low density of the substrate, high background (Bremmstrahling), and ineleastic scatter of primary X-rays, and consequent difficulties in analysis (32). The light sensitive agent in photographs can be identified; in a study of Alfred Steiglitz' (1864–1946) photographs palladium prints could be distinguished from platinum prints, and those printed using a process that involved both palladium and platinum with mercury development could be identified (33).

Metal alloys can be qualitatively and, with the provisos noted, quantitatively analyzed. The presence of carbon in iron to make steel cannot be determined using air-path XRF nor can beryllium in bronzes, but aside from these types of restrictions XRF is extremely useful for alloy analysis. The technique has been used to identify the alloy used for casting Renaissance medals and plaques. The information was used to identify classes of alloys using cluster analysis (34).

Modifications to the XRF instrumental setup, giving total reflection XRF, have allowed conservation scientists to analyze small amounts of material (35). New, portable instrumentation is available and becoming widely used in the museum environment where it can even be taken on scaffolding to identify the pigments in murals and large installations.

Proton induced X-ray or gamma emission spectroscopy (PIXE or PIGE) provides information similar to that obtained using XRF but its use in the museum field is restricted by the lack of access to instrumentation. However, this analytical method is available at the Louvre Museum in Paris, France and other sites and a system under development at the University of Surrey, U.K., is designed to accommodate works of art. PIXE offers good spatial resolution and detection limits.

2.2. Analysis Requiring Samples. Obtaining samples from works of art is undertaken with the utmost consideration of several concerns including maintaining the integrity, both visual and structural, of the work. Conservators and curators are involved in the decision to acquire samples. Samples are removed from an object when it is agreed that the information obtained from them will outweigh the small damage that results from their acquisition. Sample sites are chosen in consultation with conservators and curators to answer specific issues relating to understanding the condition of a work, conservation treatment and analysis for understanding its appearance and preservation. They are usually removed from the edges of old losses or wide cracks (36). Surgical scalpels and tungsten needles are the two most common tools for obtaining paint and fiber samples and microspatulas have been used for this. Hypodermic needles giving cores were used for a time, but the friable nature of samples from many works of art, especially paintings, has rendered this method obsolete. Tiny brushes and pig eyelash picks are useful for transferring samples and obtaining powdery material, eg, efflorescence on murals or stray particles on pastels. Samples can establish the authenticity or inauthenticity of the top layers of paint. Modern pigments in the top layers of paint on old works clearly demonstrate that top layers are late additions and can be removed with confidence, bringing the work closer to its original state while the confirmation of the presence of pigments that are of the period indicate an extraordinarily careful approach to treatment must be pursued. This can occur when the top layers are damaged, eg, they are degraded smalt (a pigment made from an unstable blue potassium glass colored using cobalt), a copper salt that has changed from green to brown, or reactive lead white, each of which, although unattractive and unstable, is original and is preserved.

A useful and common approach to examining works of art is the study of minute cross-sections. Cross-sections from corroded metals, deteriorating stone sculptures, murals, and easel paintings all can reveal extremely useful informa-

tion on the condition of a work. Cross-sections are also used to study artists' working methods. Samples are removed as described above with scalpels or needles; they are ~1 mm^2 or less. They are mounted in a plastic medium: epoxy and polyester/methyl acrylate copolymers are the most used for this purpose. The samples may be polished wet using alumina or dry using silicon carbide cloths and examined using various techniques. Reflected light microscopy and scanning electron microscopy are the most frequently applied methods, but at research facilities cross-sections can be examined using Fourier transform ir spectroscopic mapping, time-of-flight secondary ion mass spectrometry, and other sophisticated techniques.

Cross-sections reveal the layer structures of objects. Samples from paintings show the preparatory ground and priming layers as well as the number and sequence of paint layers applied by the artist. Dirt between layers of paint suggests the passage of significant time between the application of original layers and the topmost layers. This can provide confirmatory evidence that changes were made to the work after the artist's time. Samples from metals can show the alloy and the thickness and nature of patina and natural corrosion layers on the metal surface. Likewise, sections from stone can show how deep deterioration layers are and provide important information on their nature.

Light Microscopy.   This technique is invaluable for the examination of fine art. In addition to the use of stereomicroscopes for surface examination, plain and polarized light microscopy has been used for the examination of paint cross-sections, pigments, and metallurgical analysis, as well as for fiber and wood identification. Reflected and transmitted polarized light microscopy remain the most versatile tools for a conservation scientist although the techniques require much experience (37). The methods developed for mineralogy and petrology are used for identifying mineral pigments.

By using optical microscopy, the thickness and number of paint layers can be measured, and evidence for anachronistic layers can be recognized in several ways. Later layers of paint might fill age cracks in the original layers; paint applied later than the original might be separated from the original ones by dirt and/or varnish. It is possible to identify a large number of pigments in the paint film from their appearance in cross-sections, in particular, using their color and morphology, but it is often better to examine the pigment particles using transmitted polarized light microscopy or another technique. Chemical microscopy and microchemical testing once found greater use in the field but have been superceded by instrumental methods, in particular scaning electron microscopy with X-ray microanalysis and microprobe analysis(SEM-EDS), FTIR, and Raman spectroscopy, which are all be used to examine particles and cross-sections. The addition of these detectors onto microscopes aids conservation scientists in the analysis of pigments and binding media in cross-sections.

Chromatographic Methods.   Early results from the examination of fine art inclined more to inorganic analysis since techniques for analyzing small samples were available (microscopy, in particular). However, thin-layer chromatography (tlc) was used for identification of binding media and dyes, but the comparatively large samples required for these analyses means that tlc has been replaced by higher-performance liquid chromatography (hplc) and other chromatographic methods. Over the last 20 years, advances in chromatographic

methods have allowed them to be used to analyze the extremely small samples that are available from works of art. The first analyses were of paint binding media (38). Paint samples are hydrolyzed and esterified. Drying oils are characterized by the ratio of palmitic (P) to stearic (S) acid. The oils typically used in artists' paint, linseed, poppyseed, and walnut oils, can be distinguished by their P/S ratio even after aging. It is, however, important to examine the entire chromatogram since fats and waxes were often added to commercial artists' paints to provide a desirable texture. The addition of beeswax will markedly affect the P/S ratio in a sample of paint (39).

Chromatographic methods for analyzing organic pigments and dyes have matured. Red lake pigments (colored organic moieties cast on or complexed with metal ions like aluminum or tin) and dyes from plants and animals can be identified using hplc (40). The red colorants madder, cochineal and brazilwood, can be distinguished (41).

Mass Spectrometry.   The high sensitivity of mass spectrometry makes it useful for analyzing artists' materials. Direct temperature-resolved pyrolysis mass spectrometry was used to investigate Joshua Reynold's paint that was found to contain beeswax, mastic, and Venice turpentine in addition to oil (42). Recent advances in the use of laser desorption−ionization mass spectrometry for analysis of natural and synthetic organic artists colorants have been published recently (43). This method is particularly interesting to conservation scientists because information regarding the distribution of pigments among paint layers may be acquired. To date, the best results of these techniques has been in the analysis of modern synthetic pigments.

X-Ray Diffraction (XRD).   This technique is used for characterization of crystalline materials. Most mineral pigments, eg, ultramarine, hematite, and azurite, are amenable to characterization using X-ray powder diffraction. Most synthetic inorganic pigments and many organic pigments can be well-characterized using XRD. The colorants in some ceramic glazes are crystalline and can be characterized this way. The extremely small size of samples has meant that until recently the most useful diffractometers were equipped with Gandolfi cameras and the most sensitive detector was photographic film. With very long exposure times (up to 18 h) samples of corrosion products and pigments barely visible to the naked eye could be identified. Open architecture of some systems allows them to be used for pigment identification in enamels and ceramic glazes without taking samples. XRD was used to show that a yellow pigment on a painting was not the arsenic(III) sulfide that was used by artists, but rather a form of arsenic(II) sulfide, which is most often found as a red-orange allotrope. Since the orange-red form of realgar is converted to the yellow form by light, the question is raised whether the artist used the yellow form intentionally (44). When an intermediate in the transformation process is found, it can be assumed that the pigment is photoconverting to the yellow form and the color of the work is changing.

SEM-EDS.   This technique finds application to the examination of samples from all types of fine art. One application is to the identification of pigments in dispersed samples and in cross-sections. Imaging samples using back-scatter electron detectors allows pigments to be differentiated according to their average atomic number and energy dispersive spectrometry can be used to identify phases in the sample. Element mapping is extremely useful for this purpose. A cross-section from the "Feast of the Gods" by Giovanni Bellini and Titian was

obtained from the edge of Apollo's cloak. Ultramarine blue used for the robe covers the orange paint of the cloak. Point analysis shows that a large particle in the sample is an orange arsenical sulfide. Phase analysis, however, shows that only a small proportion of the orange paint is colored using this pigment. Although the hue is very similar throughout the paint, EDS indicates that most of the colorant appears to be an organic dye cast on chalk.

Some pigments that are difficult to identify using polarized light microscopy can be characterized using SEM-EDS. When coupled with other scanning methods SEM-EDS has been used to investigate the deterioration of paint made using lead white (45) or lead tin yellow, or red lead (46). This technique was invaluable in characterizing a yellow pigment (lead tin antimony oxide) found most frequently, to date, in seventeenth century Italian paintings (47). This pigment seems to be a type of glass or frit. In this case, the pigment imaged using back-scatter electron detector shows the colored particles consist of the ternary oxide suspended in a glassy matrix.

3. Preservation Studies

Fine art and other objects in museums, in particular archaeological finds, may have been subjected to harsh environments or treatments and are in poor states of preservation. However, some works that are hundreds of years old, and made from inherently unstable materials, are in remarkably good condition. Conservation scientists work to ensure the condition of objects remains as stable as possible. In order to be preserved and safely exhibited, objects must be in the most stable condition that conservators and conservation scientists can obtain. The subspecialty of preservation studies is becoming more important in the field of conservation science.

3.1. Environment.   Stable temperature and relative humidity are very important for the preservation of art. Work in 1950s suggested that an indoor environment of 70°F and 50% RH could be achieved and maintained in diverse geographical locations, London and Bombay being cited (48). These values became the standard for the museum environment that remains in effect today (49).

It is important to keep the humidity constant for several reasons including maintenance of dimensional stability of materials that contain water, eg, wood and paper, control of bacteria and fungi, and slowing hydrolysis reactions. The following examples demonstrate why stable RH environments are extremely important for conservation of works of art.

Medieval potash (potassium) glazes and glasses, and other unstable glazes, dehydrate when the RH falls below ∼40% giving rise to potassium (or sodium) oxide structures within the glass (50). On a rise of RH these moieties absorb water and the resultant hydroxides create a highly alkaline environment. The glass becomes crizzled and then powdery or "weeping" depending on the conditions. When this type of deteriorating glass is in contact with metal, as is the case for enameled objects, the metal becomes corroded extremely quickly. When the RH cycles around the dehydration–rehydration point of these glasses, the problem continues unabated. Purple and blue enamels are among the most sensitive glasses. Constancy of RH is very important for storage and exhibition of these works.

Objects made from iron are stored at <45% RH. Gaseous anticorrosive compounds that were once suggested for militating against corrosion do not provide sufficient protection to compensate for the difficulty of their handling, including issues of the toxicity of many of these compounds. Collections of archaeological material, industrial machines, and armor have many objects made of iron and stabilization of rust is very important in these circumstances.

The response of paper and wood to changes in temperature and relative humidity is accompanied by dimensional changes. There are many examples of the damaging effects of these; a dramatic one is the splitting of the wood support of panel paintings. However, long before such obvious damage occurs, stress and strain can be set up in art created from composite materials. The response of wood, paint films, and glue layers to changes in RH are different from each other and the variable expansion and contraction of each layer can result in cracking and delamination of paint.

The change in dimensions of a sheet of paper as the RH changes can be large. A sheet glued down on all four sides will cockle (buckle) as its size increases or tear as it shrinks and becomes taut. This is why prints and drawings are attached to mats with hinges (made from weaker paper than the work of art) on one edge only.

3.2. Light.   Most artists' materials are sensitive to the effects of light. Pigments fade or discolor, paper yellows, natural varnishes and paints photo-oxidize, synthetic polymers cross-link, and embrittle. Inorganic pigments can change color: Vermilion becomes black under the influence of light and the red-orange pigment realgar becomes yellow (see XRD section). Organic pigments, in particular natural and early synthetic pigments and dyes, are susceptible to fading. It was shown that fading pigments in incompletely hiding paint occurs more rapidly than at mass tone. Adjacent strokes of pure and diluted pigments fade at different apparent rates leading to distortion of the artist's original intention. Ultraviolet light is particularly harmful in the degradation of varnishes and fibers. It is eliminated from the museum environment as much as possible through the use of glazing laminated, either internally or externally, with a uv filter (51,52). Conservators choose incandescent and fluorescent lamps for lighting displays with their spectral output in mind. Although cutting out uv radiation is the main goal, ir radiation can also be problematic. Infrared absorbing (dichroic) filters are used for lamps that illuminate sensitive objects.

3.3. Exhibition and Display Cases.   Scientific investigations have been undertaken to determine how best to pack and ship valuable works. Guidelines for packing to insulate works from shock as well as temperature and humidity changes have been developed (53). The design of exhibit cases is very important in the preservation of works of art. We have learned that materials used to fabricate display cases can cause damage to art. For example, oak (traditionally used for display cases) emits acidic gases that react with art, dramatically with objects made from lead; plywood and particleboard are as bad or worse. Treated fabrics used to line cases cause damage to some materials laid on them; polyvinylchloride emits HCl, which damages art. The fabrication of cases that meet aesthetic, cost, and conservation requirements involves much care. In 1973, scientists at the British Museum published a test that museum professionals could use to determine if the materials used for building exhibition cases would outgas compounds that are detrimental to the works exhibited in

them (54). The test, called the Oddy test, today involves a simple procedure of sealing foils of pure silver, lead, and copper with pure water in a flask that is placed in an oven at an elevated temperature. After 28 days the foils are examined and if they are corroded the exhibition material is deemed unsuitable for fabricating cases for works of art. This empirical test is very useful and can be carried out by any museum professional (55). However, it is limited by its lack of specificity. Conservation scientists are working on new instrumental methods for evaluating materials used for building exhibition cases.

An environment with a specific RH can be created by using silica gel pretreated in a humidity oven to a specific water content. Zeolitic molecular sieves are a second material that can be used to control the RH in exhibition cases (56).

3.4. Biodeterioration.   Biodeterioration of cultural heritage, including fine art, causes huge losses (57,58). Bacteria and fungi are microscopic agents that thwart the conservation scientists' goal of preservation. Frescoes and murals are often damaged by colonies of microbes. White powdery surfaces of frescoes are sometimes the result of attack by microorganisms. It has been shown that some bacteria are able to oxidize Pb(II) in the pigment lead white to Pb(IV) resulting in white paint turning brown. The best way to obviate the deleterious effects of bacteria and fungi is to maintain artworks in stable environmental conditions with well-controlled temperature and humidity and clean air.

Paper is very susceptible to damage by fungi. Foxing, the spotting that appears on drawings, prints, or in books, has been attributed to both fungi and transition metal impurities, but most cases now seem to be related to fungal activity. Conservation scientists have shown that some of the most efficacious fungicides react with the material used for creating the work. Sometimes the appearance of the work is altered; in other cases it has been shown that the fungicide initiates chemical reactions that ultimately cause chemical degradation. A guide to control of fungi has been published recently (59).

Pest control and cleanliness are important steps in preventing insect damage to works of art. Wood-boring insects cause damage to works of art including paintings on wood panel and insects such as moths and silverfish damage paper and textiles. Ridding a work of pests once it is infected is undertaken with the aim, of course, of killing the infestation, but the choice of method for accomplishing this is made with a view to the detrimental aesthetic effects that an insecticide might have on organic materials. Since conventional methods for killing the agent of destruction might cause damage to works of art or alter their appearance, scientists have worked to try to find the most innocuous methods for insect control. Agents such as methyl bromide, ethylene oxide, carbon disulfide and other sulfide compounds are now used very infrequently. Freezing has been shown to be effective for some infestations and storing works in anoxic environments for prolonged periods is one of treatments preferred for dealing with works of art that are infested by insects.

4. Materials–Methods for Treating and Cleaning Works

Conservators are constrained in the methods they use for treating and cleaning works of art by the tenets of the profession. Specifically, they aim never to

remove or alter any part of the artist's work. To preserve the quality of the artist's surface, they avoid harsh physical cleaning methods and chemicals that react with the surface. Cleaning procedures are, of course, designed to remove dirt, but when the term cleaning is applied to fine art it also implies the removal of old varnishes, protective coatings, and old restorations. When the term is applied to works on paper it can mean washing out acidic degradation products from the support or old mounting materials (such as acidic paper mats or wooden backings) that disfigure the work, and removing stains. Cleaning metal sculptures involves removing old and often ineffective protective coatings and corrosion products.

Conservators work with the "principle of reversibility", which is that any material used to treat an object can be removed in the future without causing any damage. So, glues and consolidants that can be removed in the future using solvents that do not damage the original material are preferred. This effectively precludes the use of materials that cure, such as RTV silicones or epoxies for many treatments of fine art unless there is no alternative. Conservation scientists search for materials that meet the principle of reversibility and are effective. This research includes studying the stability of materials for conservation. New materials should not only be easily removed from a work in the future if wished, but they should remain stable and effective for their purpose over long time frames. Typically, conservators seek materials that have longer lifetimes than the informal industry standard of "permanent" equating to only 15 years.

4.1. Adhesives and Consolidants.   Conservators use adhesives for the crucial tasks of repairing and consolidating works of art. The long-term stability of synthetic materials used for these purposes is being studied by conservation scientists, as are the immediate and long-term interactions between adhesives and the materials used for creating artworks. A survey of the adhesives used in conservation has been published (60). Adhesives with low refractive indexes for repairing glass have been studied (61). Paraloid B72 finds wide use as an adhesive owing to its stability and its optical properties.

4.2. Varnishes and Protective Coatings. *Paintings.*   Varnishes are applied to paintings for protective and aesthetic purposes. Varnishes have been applied to, in particular, perfectly dried oil paintings to provide an attractive gloss and to saturate and deepen colors. Subtle differences in the dark tones of aged paintings can be reestablished through applying a fresh varnish and varnishes on old paints help us distinguish between, for example, dark blue and black.

Historically, a variety of materials were used as varnishes, including so-called hard resins, eg, copal and amber. These materials are fused, ie, melted, in oil to provide coatings. Soft resins, especially mastic and dammar (*Dipterocarpacae*,) that can be dissolved in solvents such as turpentine giving "spirit" varnishes. In fact, these have remained the favorite since the middle of the 1800s after the introduction of dammar ~1829. Although they have excellent handling properties and provide a beautiful finish for paintings, natural resins are prone to yellowing and embrittlement over time. Indeed, the yellowing and degradation of these varnishes are the most common reasons for treatment of paintings in museum collections. Conservation scientists have been evaluating synthetic alternatives to the customarily used tree resin varnishes to provide

more stable materials with the qualities appropriate for picture varnishes. In the 1930s, polyvinylactate(PVA) polymers were proposed for picture varnishes, but their softness and tendency to imbibe dirt decreased their acceptability. Later, polyacrylates were introduced as picture varnishes. Early on, it was found that i-butylmethacrylates tend to cross-link and become insoluble in solvents suitable for use on oil paintings. An ethylmethacrylate methylmethacrylate copolymer, called Acryloid B-72, is a very stable synthetic polymer and a suitable varnish for paintings apart from its unacceptably high gloss. It is also used for inpainting losses in ceramics and glasses (and as an adhesive) and is widely used for coating metals.

With the lack of synthetic alternatives to mastic and dammar that have the working properties and appearance desired by conservators, conservation scientists have investigated ways to stabilize these materials. It was discovered that yellowing of the resins could be rapidly induced through artificial thermal aging; light-aging without any thermal aging produced much less yellowing. Of the traditional spirit varnishes, mastic is much less stable than dammar (62). It was demonstrated through accelerated aging trials that eliminating uv light in the environment delayed the onset of yellowing and maintained the solubility of the resin over time. It was also demonstrated that addition of stabilizing compounds resulted in a dramatic improvement in stability, both in terms of aesthetics and removability. Conservation scientists have shown that adding radical scavengers confers vastly improved stability to tree resins varnishes, in particular to dammar when uv light is excluded from the environment. The group of radical scavengers classed as hindered amine light stabilizers have been shown to function as stabilizers of dammar (63). Research has shown that the efficacy of these stabilizers requires that the varnish never be exposed to uv light, which initiates degradation processes that are not inhibited by this class of compounds. A hindered amine light stabilizer, Tinuvin 292, has been determined to be among the most efficient additives to stabilize dammar. Since eliminating uv light is important, uv absorbers may also be added to varnishes to add additional protection against degradation.

Recent work has been undertaken to provide more stable synthetic alternatives to dammar in place of PVA or the acrylates. Related to this, new paints for filling in losses in the original have been developed (64).

Fine Art in Metal and Stone.   Works of art made from silver have been coated to prevent tarnishing that occurs rapidly even in the museum environment. The high gloss of a polished silver surface allows a variety of coatings to be used and the insensitivity of silver to many solvents allows coatings that would unacceptable for paintings to be used. Cellulose nitrate has been shown to be stable and effective for coating objects displayed indoors in the museum environment (65).

Sculpture that is displayed outdoors is coated to protect it from the effects of pollution and to maintain the surface appearance by inhibiting corrosion. Much outdoor sculpture is made from bronze, but many works are made from other metals and other materials. Zinc, Cor-Ten steel, aluminum, and even the reactive metal magnesium, eg, the work "Jarama II, by Frank Stella, (66) have been used for fabricating works of art designed to be exhibited outdoors. Some of these works are painted, others patinated, and others designed to be left to

weathering the environment with the intention that the work will acquire a natural patina, which is, hopefully, a stable, passivating layer of corrosion.

Conservation science has contributed to the development of coatings and protocols for treating and preserving outdoor sculpture (67). Coatings for outdoor sculpture must withstand harsh conditions to protect the works. Hard waxes (eg, carnuaba wax) and Acryloid (paraloid) B-72 have been used.

4.3. Cleaning and Stabilizing Works.   Cleaning works of art was, until ~1800, more the province of artists than professional art restorers. Receipts and accounts from as early as the mid-1400s still exist showing contracts between owners and contemporary artists for the repair and restoration of paintings. Around the beginning of the nineteenth century, specialists began to become more influential. In the absence of a wide choice of solvents that dissolved varnishes, many of which were oil-resin varnishes and lacquers, restorers used methods that today seem harsh or ineffective. Physical methods were employed for removing varnishes; rubbing with mastic tears was cited frequently. Hasher materials, eg, pumice and horsetail (*Equisetum sp*. –scouring rush), a plant with silica crystals in its stem or "pearl ashes," K_2CO_3, were also recommended. Paint films were abraded by these rough materials and in many paintings transparent paint glazes have been thinned or even removed allowing underlying paint to be visible. Today the most common way to remove varnishes is using organic solvents. Lasers are beginning to find application in cleaning works, especially stone and metal sculpture.

Varnish Removal.   Varnishes are often the least stable layer in works of art. They become brittle, discolor, and they can crack; when this occurs they need to be removed and replaced. Organic solvents are the most common way to remove degraded varnishes, but other options are available to conservators including aqueous solutions and laser cleaning.

Organic Solvents.   The swelling, gelling, and solubilizing of old varnishes were studied by conservation scientists early in the maturity of this field (68). The swelling of oil paint in response to solvents was studied and solvents that will cause swelling of the paint film can be predicted by use of the Teas chart. This chart is a triangle plot of three variables that are characteristic of a solvent: Fd, a measure of dispersion forces, Fp, a measure of the permanent dipole in a solvent, a polar force, and Fh, a measure of the hydrogen-bonding ability of a solvent. Conservation scientists have measured the region in this 3D space where oil films will swell and conservators can avoid using solvent mixtures that will cause this to occur (69). Information on solubility parameters as they pertain to cleaning paintings has been compiled (70). Conservators today most often use organic solvents to remove aged and degraded varnishes from works of art, including oil paintings (71). Mixtures of varying proportions of toluene, acetone, and xylene are the frequent choice for removing degraded varnishes from works of art. The effect of solvents on oil paint has been investigated to help conservators in their efforts in the preservation of paintings (72).

Conservation scientists are investigating the methods used to clean contemporary works made using paint formulated with acrylic resin emulsions. Paints made from these obviously behave differently from oil paints and conservators are asking scientists for information on the chemical stability of these

paints and help in devising methods to remove dirt from them. The current state of the approach to treating these works has been reviewed recently (73).

Aqueous Systems for Removing Varnish.   Cleaning painted surfaces using aqueous systems rather than organic solvents has been proposed and investigated from time to time. A recent description of how to clean using aqueous systems and some typical results has been reviewed (74). Traditional soaps, the highly basic sodium and potassium salts of fatty acids, were used for cleaning paintings as were alcoholic solutions, but these have been discarded. While the highly alkaline solvents were effective for removing oil-resin varnishes (now rarer on paintings) they could effect base hydrolysis of oil paints. Enzyme systems for cleaning surfaces and for removing old varnishes have been investigated. "Spit cleaning", using cotton swabs rolled in the mouth, used to be used for removing dirt, including tobacco debris, from paintings before the varnish was removed. This was so useful that there have been attempts to formulate a synthetic saliva. Resin soaps were used in the early twentieth century for removing varnishes, but their use was limited. New work identified resin soaps designed more specific alloy for removing resin varnishes (mastic and dammar), including the salts of deoxycholic and abietic acids, anthracence-9-carboxylic acid and 9-fluorenone-4-carboxylic acid. To formulate solutions for varnish removal, these compounds are mixed with a surfactant, a gelling agent, and triethanolamine. Conservation scientists have investigated the efficacy of these formulations by measuring the rate of removal of varnish from paint surfaces. They have investigated how well the components of the cleaning mixtures are cleared from the surface of paintings and they have made quantitative measurements on how much material is leached from oil paint (75). Despite the recent investigation, this method for removing old varnishes has not yet found wide application in the field. The variability of the chemical nature of old varnishes and lack of experience with the resin soaps hinder their use.

Cleaning formulations based on use of gels and emulsions is under current investigation and development (76). By encapsulating the active component, that is the solvent for an old varnish, within a gel structure or fashioning it into a viscous emulsion, the active ingredient can be kept on a surface for a longer time without its seeping into paint films. This gives time for the solvent action without rubbing.

Lasers.   Laser have been used to clean works of art since the 1970s (77). It has been successfully applied to stone statues and to bronze sculpture (78). It is much more difficult to apply the method to removal of varnish from paintings. As of now, the technique has not found frequent application for this purpose due to the uneven absorption of the laser radiation by the varnish that decreases the control of the process. As with all methods of treatment, skill and experience are important for success.

The Nd:YAG Q-switched laser is most often used by conservators. Its radiation output in the near-ir is strongly absorbed by dirt but only weakly absorbed by stone, terracotta, bone, and other light colored materials. The diameter of the beam can be varied from microns to millimeters. The power can be varied so that layers of soil from 0.1 up to 300 μ can be removed providing good control over the process of removal of dirt.

Works of Art on Paper.   Methods for treatment of works of art on paper have a wide overlap with the methods for preservation of archival material and textiles. Paper made from linen or cotton is very durable, a fact demonstrated by the existence of thousand-year-old textiles made from these fibers. Studies on paper itself suggest very little inherent deterioration; its degradation is induced by added material, inks, pigments, and coatings. Fungi and bacteria are also responsible for degradation of paper. Acidic coatings and contact with wood or wood pulp backings or mats initiate deterioration that leads to discoloration of the wood support. In contrast, the use of the traditional size, gelatin, has been shown to confer stability to paper. The introduction, in the nineteenth century, of paper made from chemically processed wood pulp to papermaking changed the situation dramatically. Wood was processed using chemical and mechanical methods to provide a pulp suitable for papermaking. The kraft and sulfite processes designed to remove lignin were the most common.

Understanding the degradation of paper and how to inhibit it is vital for the preservation of books and archives. A summary of recent work on this was prepared by the Council on Library and Information Resources (79) (http://www.clir.ogr/pubs/reports/pub95/chap2.html).

To extend the longevity of acidic papers, drawings, prints, and even watercolor paintings can be washed to remove soluble acidic compounds. Some colored degradation products are also removed through washing. This leaves the paper prone to becoming acidic again and the process of deterioration continuing. To combat this, papers are "buffered" by washing with water charged with calcium ions. A reservoir of calcium carbonate neutralizes acidic degradation products (80).

Deacidification of the paper of drawings, prints, or watercolors using non-aqueous treatments, eg, magnesium carbonate in ethanol, are not used since they appear to be ineffective over the long term.

Works of art on yellowed paper are sometimes bleached to partially restore the whiter color of the support. Conservators use techniques involving fluorescent lights or natural daylight, called "sun bleaching". Research showed that the dark color of aged paper was due to sugars of the aldose group, particularly xylose and arabinose. These sugars could be produced in paper by artificial thermal aging at high relative humidity, but exposure to light caused little darkening. These sugar products are readily bleached under visible and near-uv light.

5. Degradation Studies

All materials deteriorate and the goal of conservation, of preserving works indefinitely, depends on understanding the degradation processes of materials so that they can be mitigated. Conservation scientists study both artists' materials and conservation materials.

5.1. Degradation of Paintings, Paint, and Varnish.   Paintings are subject to physical and chemical degradation. The common supports for paintings in oil, fabric, and wood, respond more rapidly than paint to changes in relative humidity. Wood panels may crack in response to changes in relative humidity. The unequal response of the paint film and the wood support can

cause delamination of the paint. If a fabric support becomes slack on its stretcher, crack patterns can develop in the paint film. The stress–strain tensions set up in paintings through the paint film/priming layer/support interactions varying over temperature and humidity changes have been modeled (81). Acrylic paint is a polymer–pigment mixture that has a glass transition temperature near room temperature (depending on formulation). At room temperature, the paint can be slightly tacky and dirt can become embedded in its surface. The dirt cannot be removed without affecting the quality of the paint surface. A clean environment is important to avoid this kind of damage. Below the glass transition temperature, acrylic paints become brittle and can be damaged by even a small bump. It may take years for damage from this to become evident. The results of modeling the effects of temperature and RH demonstrate the importance of exhibiting paintings in a stable environment with controlled temperature and relative humidity to safeguard against damage. Artists' paints have been prepared using many classes of organic material. Time has shown that egg yolk, certain mucilages, starch, waxes, and drying oils provide durable paint films.

The degradation of oil paint has been well studied by paint formulators and by conservation scientists. Paint made from a drying oil (eg, tung, linseed oils) or semidrying oils (eg, poppyseed, safflower seed, and walnut oil) cures by oxidation and cross-linking of polyunsaturated fatty acids to form an oligomeric 3D film called linoxyn. Linoxyn degrades over time through oxidation followed by chain scission. Linoxyn films are tough and flexible. The durability of a paint film depends on its drying mode, the pigment/binder ration, and the type of pigment. Paint made from lead white is extremely durable, but others less so. Paint made using linseed oil or other highly unsaturated drying oils yellow over time, sometimes to the extent that pale blue skies acquire a green tint. Paint made from either egg yolk or casein is extremely tough and durable.

The sensitivity of oil paint to solvent cleaning has been examined. It has been found that older paints have higher proportions of azelaic acid, which forms by chain scission and oxidation. Varnishes discolor and become brittle over time. Thermal and photochemical reactions lead to different products.

5.2. Paper. Paper is a polycellulose. It was and is produced from a variety of materials. In Asia, fibers from kozo, mitsumata, or gampi are the most frequently used. In the West, hemp, flax, and cotton were the major sources of cellulosic fibers for papermaking until the nineteenth century, when processes for using wood pulp were developed. Wood pulp papers are notoriously unstable owing to the presence of lignin in the paper; the low pH of these papers, and the use of bleaches in the manufacturing processes has provided papers that are prone to rapid degradation.

Slowing the degradation of paper is important for the preservation of archival documents as well as for the conservation of fine art. There is significant research in this area from scientists working in the field of library science and preservation of archives.

5.3. Glass. All glass is erroneously considered to be a stable material. While some modern formulations of glass do provide an exceptionally stable product, some old glass is inherently unstable; it may become cloudy or crizzled, suffering from so-called glass disease. It is important to identify these glasses,

which may include glazes in ceramics and enamels on metal, and store and exhibit them appropriately. These glasses tend to be a group that has a low proportion of calcium, magnesium, and/or aluminum and lead. Below a certain proportion of these divalent and trivalent ions, mobility of sodium or potassium ions is high enough that the glassy structure in which they are incorporated becomes vulnerable to attack by atmospheric moisture that provides a mechanism for the transport of the alkali metal ions. Sodium or potassium hydroxide can form, which immediately reacts with carbon dioxide to give carbonates. These are hygroscopic and the glass appears to be "weeping" or "sweating". Treatment for this is rapid washing to remove the highly alkaline material followed by drying with alcohols. After treatment it is important to maintain the glass in a dry environment. It has been shown that in some instances, efforts to protect the glass with synthetic coatings were misguided, however, this procedure does provide protection to certain glasses in some instances (82).

Analysis of the composition of glass may be used to identify its provenance. Venetian glass and Dutch façon de venise glassware look very similar. Using electron probe X-ray microanalysis and synchrotron radiation induced X-ray fluorescence, researchers were able to distinguish between them from the relative amounts of the trace elements zirconium and hafnium, which are due to the different sources of the raw materials for glassmaking (83).

5.4. Works of Art Made from Metals and Alloys. Corrosion is a major problem for the preservation of works of art made from metal alloys. Both the stability of a work and its appearence are compromised. The corrosion processes involved are varied and complicated and require a deft analyst to diagnose them and stabilize and restore the work of art (84). Objects buried or submerged in salt water are most rapidly corroded if oxygen is present. On occasion, buried or submerged works of art remain relatively well preserved owing to dryness or to an anaerobic environment. On removing objects from these environments, degradation is mitigated by removal of salts and compacted earths using a variety of techniques. The method for cleaning these objects is chosen to preserve the natural patina on the surface of the objects. Soluble salts are removed by washing, with frequent changes of solutions of sodium sesquicarbonate or distilled water. The process is time-consuming and not always completely successful. It is important to remove all traces of chloride ion from metal objects since residual traces of chloride perpetuate corrosion of copper alloys (bronze, brass, copper) in an autocatalytic cycle. This type of corrosion is called bronze disease. The activity of chloride ions can be reduced by reaction with silver nitrate or freshly precipitated silver oxide to form silver chloride, which has a very high solubility product, and therefore effectively sequesters chloride ions. Artifacts suffering from bronze disease or other active corrosion are difficult to treat and often must undergo stabilization treatments that do alter the appearance of their surface. Though this is always regrettable, it is sometimes necessary for the preservation of the object, which would otherwise become increasingly damaged. Alkaline dithionite has proven to be effective at removing chloride ions. Aqueous benzotriazole (1% v/v) with 5% ethanol (v/v) is used to remove considerable amount of chloride-containing corrosion products on bronzes (85). These treatments might take months to be effective. Objects that have active bronze disease are

exhibited and stored in very low RH environments in order to protect them from recurring corrosion.

XRF can indicate whether different parts of a complicated work are cast from a single casting; late additions and repairs can be found this way. X-Radiography can be very helpful in discovering how sculptures were assembled (86).

Corrosion inhibitors that are useful for clean, polished samples have limited efficacy when used on patinated (naturally or artificially) metal surfaces. Use of benzotriazole, common in technical applications, finds less ready application in conservation of fine art, since it has been shown that a fresh metal surface is required for its best efficacy. Conservators are unable to remove an artist-applied patina in order to obtain the clean surface required for proper application of the compound. The effect of bezotriazole on artist applied and naturally induced patinas has been studied, but is not completely understood. However, the research has shown that while BTA is valuable for treating works of art, their inherent chemical complexity means that BTA may affect the surface appearance and is not as effective on objects with the surface layers as on freshly cleaned copper (87).

While buried or submerged artifacts appear to suffer most corrosion, outdoor sculpture is prone to degradation processes that are accelerated by the environmental conditions such as acid rain, wide temperature swings, and bird guano. Modern outdoor sculpture is made from bronze and from other metals and alloys that corrode, among them cor-ten steel, magnesium, and aluminum. High levels of sulfur and nitrogen oxides in the air and the associated low pH cause severe and ongoing corrosion. The effects can be seen on bronzes as disfiguring blue-green streaks that follow the contours of the sculpture. Reactive metals and the bronzes need to be protected by coatings. Appropriate treatment depends on the material used for fabricating the work, which can be analyzed using any of the techniques already discussed. The corrosion products can be analyzed using XRD and ir. The treatment and repatination of Rodin's "The Thinker" has been described (88). Traditionally, waxes, oils, and resins were used to protect metals; however, their short lifetime in the outdoor environment, their inherent sensitivity to uv radiation and the fact that on degrading, acidic products form has spurred research into synthetic alternatives. Paraloid B-72 has found wide use for this purpose.

Paint on outdoor sculpture is subject to rapid degradation. Conservators working with scientists have found a formulation for black paint that has better longevity than most with the additional benefit of protecting the artwork by decreasing the temperature rise due to exposure to the sun. In these paints the carbon black pigment is encapsulated in alumina that reflects uv radiation (89).

Objects made from lead, eg, portrait medals, and reliefs, can corrode severely with the formation of white whiskery products that obscure the object. The corrosion can be removed by electrolytic methods. The object is made the cathode in an electrolytic cell and stainless steel is chosen as the anode. Sulfuric acid (10%) can be the electrolyte. Following electrolytic dissolution of the corrosion products, very careful washing is required. Basic lead carbonate (hydrocerussite) provides a stable, passivating surface, so a solid, albeit pale, surface should not necessarily be removed or damaged lest further corrosion may be initiated.

A phenomenon called "tin pest' is not a corrosive process. It is rather an allotropic alteration from the alpha to the beta form. Fortunately, few museum objects are found to be undergoing this process since it is unstoppable and irreversible. Worked tin is in a metastable state that becomes unstable when the temperature drops below ∼13 °C. While this is unlikely to occur in the museum environment, it occurred historically in northern Europe.

Inorganic coatings and/or artificial patinas, can be used to passivate the surface of bronzes. In cases where this is insufficient to halt corrosion, organic coatings have been applied to the bronzes. In the past, hard waxes, applied hot, were used to protect the works. There is ongoing work to develop a regime that will provide longer and better protection than wax.

6. Authenticity and Provenience Studies

6.1. Dating. *Dendrochronology.*   This dating technique relies on measuring the width of tree rings. Tree rings form each season as a tree grows; the amount of growth each season depends on several factors. While the exact amount of growth is determined by factors that cannot be estimated, over the long term the ratio of growth from season to season is determined by climatic conditions. It has been possible to establish "master chronologies" for various geographical regions (90). The relative distance between growth rings on a plank of unkown date may be measured and compared to the master chronology and thus its age can be determined. Dendrochronology provides an earliest possible date for the felling of the wood used in the creation of a work of art; this date is useful for discriminating between originals and copies and for detecting forgeries. The caveats of the dating method are uncertainties owing to the indeterminant number of sapwood rings that might have been present on the tree when it was felled, and that while the age of the wood may be known, the date that it was used for making an object is unknown. Oak and fir are among the species amenable to this method of dating. Twenty growth rings are needed for a reasonable estimate of the age of a plank. The wood panel supports of paintings and furniture (and structural timbers of ships and dwellings) may be dated using dendrochronology. Dendrochronology has been applied to works of art for several decades. The method was first applied to the dating of oak panel paintings in 1970 (91). Dendrochronology can be specific enough to show that planks used in the construction of an altarpiece came from the same tree (92,93).

Carbon-14 Dating.   This dating is useful for objects made from organic materials. The long half-life of C-14 makes this dating technique more suitable for archaeological objects rather than those we might call fine art.

Thermoluminescence Dating (TL Dating).   This dating can be used to establish the date of manufacture of ceramics and core materials that contain certain minerals. Quartz, feldspar, diamond, and calcite are among the minerals most amenable to TL dating. Over time, radiation absorbed by these materials allows electrons to move through the crystal lattice until "pinned" at a lattice defect. When the material is heated the electrons are released from these sites and light is emitted. The amount of light emitted depends on the length of

time and the radiation dose received by the material since it was last heated. By estimating the radiation dose the material has received since last heated and measuring the amount of light emitted, the time since heating can be estimated. The range of age that can be estimated using TL dating is 300–10,000 years. For a single sample, the error is $+/-$ 15% so the technique must be carefully applied. TL dating has been used to measure the time since firing of porcelain, terra cotta sculpture, and the core material of cast metal sculptures (bronzes). Owing to the large error, TL dating is better suited to dating or authenticating ancient works of art, however, it has been successfully applied to dating clay core material of Renaissance bronzes.

6.2. Element/Isotope Ratios.   The source of lead used to synthesize the artists' pigment lead white varies. Individual deposits of lead ores have lead isotopes in specific ratios. The ratios of isotopes present in a sample of lead white can be measured and a ratio index of the isotopes then calculated. Data show that until 1800 the ratio index falls in a narrow range that appears to become wider when American sources for lead ores are exploited (94). Comparison of the ratio index of lead white in a painting can indicate if the layers were all painted at the same time. Data suggest that for individual artists the isotope ratio remains stable (suggesting a stable source for their work). Thus, sometimes works can be shown to be unlikely done by the stated artist and later additions can be detected. Outright fakery might be determined using the lead isotope ratio index.

Marble can be provenanced by the calcium/strontium ratios and, as discussed earlier, glass can be provenanced by the ratios of lanthanide and rare earth elements. It has been suggested the ratio of $^{32}S/^{34}S$ could be used to distinguish between naturally occurring and synthetic sulfates (95).

6.3. Detection of Forgeries.   The detection of forgeries has been an integral part of the examination of fine art. Even in the 1500s, authors lamented the problems of the proliferation of forgeries caused collectors. All the analytical and investigative techniques available are brought to bear on establishing or refuting the authenticity of a work of art. Despite the sophistication of modern analysis, the connoisseur's eye is the most important tool. Fakes, forgeries, and imitations (which were never intended to dupe collectors) are distinguished from originals by their materials and their facture. A thorough knowledge of the history of materials, technology, and artists' practices is vital for authentification. Comparison of the casting of a series of bronze (brass) busts of Pope Paul Farneses III with known Renaissance practice, already suspicious on account of their size, demonstrated they are forgeries (96).

X-radiography and ir reflectography can reveal atypical working methods. X-Rays might show no working up of the composition in white paint, when original work would have this. Underdrawing imaged in the ir is sometimes as recognizable as handwriting and can expose a forger's attempt to deceive. Identification of pigments can show a forger's inadvertent use of anachronistic pigments or pigment forms. Thermoluminscence dating has shown that majolica vases once believed to date to the Renaissance are fakes (97) and was used to happily show that a doubted Greek horse sculpture was authentic.

BIBLIOGRAPHY

"Fine Art Examination and Conservation" in *ECT* 3rd ed., Suppl. Vol., pp. 392–442, by L. van Zelst, Museum of Fine Arts, Boston; in *ECT* 4th ed., Vol. 10, pp. 853–900, by Lambertus van Zelst, Conservation Analytical Laboratory, Smithsonian Institution; "Fine Art Examination and Conservation" in *ECT* (online), posting date: December 4, 2000 by Lambertus van Zelst, Conservation Analytical Laboratory, Smithsonian Institution.

CITED PUBLICATION

1. R. L. Feller, *J. Am. Ins. Conservation* **33**, 91 (1994).
2. P. B. Coremans, *L'Agneau mystique au laboratoire: examen et traitement*, De Sikkel N.V., Oostmalle, 1953.
3. M. Hours, *Les Secrets des Chefs-D'Oeuvre*, Denoël/Gonthier, Paris, 1964.
4. M. Faires, in *Scientific examination of early Netherlandish Painting: Applications on art history*, Fibula-Van Dishoeck, Bussum, 1976, p. 89.
5. see, for example, http://www.editech.com/uk/html/servizi-arte-01.html
6. D. Bomford, J. Dunkerton, D. Gordon, A. Roy, and J. Kirby, *Art in the Making: Italian Painting Before 1400*, 1989.
7. A. Burmester and C. Krekel, in A. Roy and P. Smith, eds., *Painting Techniques, History, Materials and Studio Practice*, IIC, London, 1998, p. 101.
8. J. Nadolny, *Rev. Conserv.* **4**, 39 (2003).
9. http://www.iiconservation.org/publications/sic/sicx.php
10. http://aic.stanford.edu/jaic/
11. A. Aldrovandi and M. Picollo, *Metodi di Documentazione e di Indagini Non Invasive sui Dipinti*, il Prato, Padua, 1999.
12. http://arte.ino.it
13. http://www-graphics.stanford.edu/projects/mich/
14. R. S. Berns, J. Krueger, and M. Swicklik, *Studies Conserv.* **47**, 46 (2002).
15. M. Leona and J. Winter, *Studies Conserv.* **46**, 153 (2001).
16. J. R. J. v. Asperen de Boer, *Studies Conserv.* **14**, 96 (1969).
17. E. Walmsley, C. Metzger, C. Fletcher, and J. K. Delaney, *ICOM committee for conservation tenth triennial meeting, Washington, DC 22–27 August, 1993*, ICOM, Washington, D.C., 1993, p. 57.
18. R. Echols, *Ven. Cinq.* **VI**, 93 (1996).
19. C. Baker, in *Application of Science in the Examinaiton of Works of Art: Seminar Proceedings*, 1983, p. 159.
20. M. Bacci and M. Picollo, *Studies Conserv.* **41**, 129 (1996).
21. A. Burroughs, *Art Criticism from a Laboratory*, Little, Brown and Co., Boston, 1938.
22. J. v. Aken, *Studies Conserv.* **48**, 103 (2003).
23. S. Colinart, F. Drilhon, and G. Scherf, *Sculptures en cire de l'ancienne Egypte à l'art abstrait*, Editions de la Réunion des musées nationaux, Paris, 1987.
24. http://www.nga.gov/education/degas-sculp.htm
25. D. S. Barbour and S. G. Sturman, in J. S. Boggs, ed., *Degas at the Races*, Vol. ex. cat., National Gallery of Art, Washington, 1998, p. 180.
26. M. Ainsworth, *Art and Autoradiography: Insight into the Genesis of Paintings by Rembrandt*, Van Dyck and Vermeer, New York, 1982.
27. C. Barry, La Tour and Autoradiography, in P. Conisbee, ed., *Georges de La Tour and His World*, National Gallery of Art, Washington D.C., 1997, pp. 287–310.
28. www.nd.edu/~nsl/Lectures/phys178/pdf/chap2_6.pdf

29. G. D. Smith and R. J. H. Clark, *Rev. Conserv.* **2**, 92 (2001).

30. P. Colomban, *J. Raman Spectrosc.* **34**, 420 (2003).

31. L. Burgio and R. J. H. Clark, *Spectrochim. Acta Part A* **57**, 1491 (2001).

32. M. Mantler and M. Schreiner, *X-Ray Spectrom.* **29**, 3 (2000).

33. C. McCabe and L. D. Glinsman, *Conserv. Res. 1995*, 71 (1995).

34. L. D. Glinsman and L. Hayek, *Archaeometry* **35**, 49 (1993).

35. W. Devos, L. Moens, A. von Bohlen, and R. Klockenkämper, *Studies Conserv.* **40**, 153 (1995).

36. http://webexhibits.org/feast/analysis/paintsamples.html

37. W. McCrone, C., *J. Am. Inst. Conserv.* **33**, 101 (1994).

38. J. S. Mills, *Studies Conserv.* **11**, 92 (1966).

39. J. S. Mills and R. White, *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, London, 1994.

40. S. H. Halpine, *Studies Conserv.* **41**, 76 (1996).

41. J. Kirby and R. White, *Nat. Gallery Tech. Bull.* **17**, 56 (1996).

42. R. Jones, J. H. Townsend, and J. J. Boon, *12th Triennial Meeting ICOM—Committe for Conservation*, James and James, Lyon, 1999, p. 375.

43. N. Wyplosz, *Laser Desorption Mass Spectrometric Studies of Artists' Organic Pigments*, AMOLF-FOM, Amsterdam, The Netherlands, 2004, p. 212.

44. M.-C. Corbeil and K. Helwig, *Studies Conserv.* **40**, 133 (1995).

45. J. van der Weerd, J. J. Boon, M. Geldof, R. M. A. Heeren, and P. Noble, *Kunsttechnol. Konserv.* **16**, 36 (2002).

46. C. Higget, M. Spring, and D. Saunders, *Deterioration of Artists' Paints: Effects and Analysis ICOM-CC Working Groups, Paintings 1 and 2*, London, 2001.

47. A. Roy and B. H. Berrie, in A. Roy and P. Smith, eds., *Painting Techniques: History, Materials and Studio Practice*, IIC, Dublin, 1998, p. 160.

48. G. Thompson, *The Museum Environment*, Butterworth-Heinemann, London, 1986.

49. S. Michalski, *10th Triennial Meeting ICOM Committee for Conservation*, Vol. II, ICOM-CC, Washington, DC, 1993, p. 624.

50. R. H. Brill and S. Moll, *Crizzling—a problem in glass conservation*, IIC, London, 1975, p. 121.

51. R. M. Johnston-Feller, *J. Coatings Technol.* **58**, 32 (1986).

52. S. Staniforth, in *Lighting in Museums, Galleries and Historic House*, UKIC, Bristol, England, 1987.

53. M. F. Mecklenberg, ed., *Art in Transit: Studies in the Transport of Paintings*, National Gallery of Art, Washington, D.C., 1991.

54. W. A. Oddy, *Museums J.* **73**, 27 (1973).

55. L. Robinet and D. Thickett, *Studies Conserv.* **48** (2003).

56. S. Weintraub, *Object Specialty Group Postprints; Am. Inst. Conserv.* **9** (2002).

57. O. Ciferri, *Rev. Conserv.* **3**, 35 (2002).

58. R. J. Koestler, V. R. Koestler, A. E. Charola, and F. E. Nieto-Fernandez, eds., *Art, Biology, and Conservation: Biodeterioration of Works of Art*, The Metropolitan Museum of Art, New York, Yale University Press, New Haven, Conn, 2003.

59. M.-L. E. Florian, *Fungal Facts: Solving Fungal Problems in Heritage Collections*, Archetype, London, 2002.

60. C. V. Horie, *Materials for Conservation*, Butterworths, London, 1987.

61. N. Tennant and J. H. Townsend, *Adhesives and Consolidants*, IIC, Paris, 1984, p. 205.

62. E. R. de la Rie, *Studies Conserv.* **33**, 53 (1988).

63. E. R. de la Rie, *Anal. Chem.* **61**, 1228A (1989).

64. M. Leonard, J. Whitten, R. Gamblin, and E. R. de la Rie, *Tradition and Innovation: Advances in Conservation*, IIC, Melbourne, 2000, p. 111.

65. V. Costa, *Rev. Conserv.* **2**, 18 (2001).

66. http://www.nga.gov/cgi-bin/pinfo?Object=60907+0+none

67. S. Sturman, J. Unruh, and H. Spande, *Maintenance of Outdoor Sculpture: An Annotated Bibliography*, National Institute for the Conservation of Cultural Property, Washington, D.C., 1996.

68. R. L. Feller, E. H. Jones, and N. Stolow, *On Picture Varnishes and their Solvents*, Intermuseum Conservation Association, Oberlin, Ohio, 1959.

69. G. Hedley, *Conservator* **4** (1980).

70. A. Phenix, *Z. Kunsttechnol. Konservier.* **12**, 387 (1998).

71. http://www.buildingconservation.com/articles/solvent/diagrams.htm#3

72. K. Sutherland and N. Shibayama, *Preprints of the 12th Triennial Meeting of the ICOM Conservation Committee*, James and James, Lyon, 1999, White and Roy

73. E. Jablonski, T. Learner, J. Hayes, and M. Golden, *Rev. Conserv.* **4**, 3 (2003).

74. R. Wolbers, *Cleaning Painted Surfaces: Aqueous Methods*, Archetype, London, 2000.

75. D. Erhardt and J. J. Bischoff, *Studies Conserv.* **39**, 3 (1994).

76. L. Dei, E. Carretti, and P. Baglioni, *Proceedings of the 5th World Surfactants Congress - Cesio 2000*, Florence, 2000, p. 517.

77. M. Cooper, *Laser Cleaning in Conservation: An Introduction*, Butterworth-Heinemann, Oxford, 1998.

78. S. Siano, M. L. Nicolai, and S. Porcinai, *Verrocchio's David Restored*, in G. M. Radke, ed., High Museum of Art, Atlanta, 2003, p. 97.

79. Council on Library and Information Resources (http://www.clir.ogr/pubs/reports/pub95/chap2.html).

80. J. Bogaard and P. M. Whitmore, *J. Amer. Inst. Conserv.* **40**, 105 (2001).

81. M. F. Mecklenberg, M. McCormack-Goodhart, and C. S. Tumosa, *J. Am. Inst. Conserv.* **33**, 153 (1994).

82. T. Draymen-Weisser, *J. Am. Inst. Conserv.* **42**, 279 (2003).

83. I. De Raedt, K. Janssens, J. Veeckman, L. Vincze, B. Vekemans, and T. E. Jeffries, *J. Anal. Atomic Spectrom.* **16**, 1012 (2001).

84. D. A. Scott, *Copper and Bronze in Art: Corrosion, Colorants, Conservation*, Getty Publications, Los Angeles, 2002.

85. I. D. MacLeod, *Studies Conserv.* **32**, 25 (1987).

86. L. D. Glinsman and D. Barbour, *J. Metals* **49**, 14 (1997).

87. L. B. Brostoff, *Conservation of Metals*, James and James, Semur en Auxois, France, 1997, p. 242.

88. http://www.philamuseum.org/collections/conservation/works%20of%20art/decorative_arts_rodin2.shtml

89. J. Escarsega, K. Chesonis, D. Crawford, C. Pergantis, A. Mack, and S. Sturman, *Proceedings of the Thirtieth International Waterborne, High-Solids, and Powder Coatings Symposium*, USM Polymer Science Press, New Orleans, L.A, 2003.

90. P. I. Kuniholm, in W. S. Taft and J. W. Mayer, eds., *The Science of Paintings*, Springer, New York, 2000.

91. J. Bauch and D. Eckstein, *Studies Conserv.* **15**, 45 (1970).

92. A. K. Wheelock, *Dutch Paintings of the Seventeenth Century*, National Gallery of Art, Washington, p. 222.

93. P. Klein, *Recent Developments in the Technical Examination of Early Netherlandish Painting: Methodology, Limitations and Perspectives*, in M. Faires and R. Spronk, eds., Harvard University Art Museums and Brepols Publishers, Cambridge and Turnout, Belgium, 2003, p. 65.

94. B. Keisch and R. C. Callahan, *Archaeometry* **18**, 181 (1976).

95. B. Keisch, *Studies Conserv.* **15**, 1 (1970).

96. D. Barbour and L. D. Glinsman, *Conserv. Res. 1995*, 15 (1993).

97. http://www.philamuseum.org/collections/conservation/projects/maiolica/authenticity.shtm

GENERAL REFERENCES

98. *Artists' Pigments: A handbook of their history and characteristics*, Vols. 1–3, National Gallery of Art, Washington, D.C.
99. *National Gallery Technical Bulletin*, Vols. 1–27, National Gallery, London.
100. P. M. Whitmore, Contributions to Conservation Science: A Collection of Robert Feller's Published Studies on Artists' Paints, Paper, and Varnishes, Carnegie Mellon University Press, Pittsburgh, 2002.
101. W. S. Taft, *The Science of Paintings*, Springer-Verlag, New York, 2000.

WEB SITES

www.iiconservation.org
www.iccrom.org
www.webexhibits.org/feast/
www.aic.stanford.edu/jaic

BARBARA H. BERRIE
National Galley of Art, Washington, D.C