Invisible to the Eye: The Scientific Analysis of Decorative and Fine Art

by Jennifer Mass

t has become increasingly common to see chemists working side by side with curators and conservators to gain a more complete assessment of an object of art. Today scientific research departments are found in more than a dozen museums in the United States, including the Metropolitan Museum of Art, the National Gallery of Art, the Art Institute of Chicago, and Winterthur Museum and Country Estate. New technologies are constantly being developed and adapted from the physical, biological, and chemical sciences to increase our comprehension of how works of art are produced and how they modify chemically with age. Through analysis of the composition and physical properties of an object chemists can identify prior restorations, pastiches, reproductions, and occasionally if an object was made intentionally to deceive.

Given the irreplaceable nature of the objects we study at Winterthur's scientific research and analysis laboratory, it is essential to carry out our work nondestructively or in as minimally destructive a manner as possible. Several analysis techniques allow us to obtain chemical information without taking a sample, and none requires a sample larger than a milligram (one thousandth of a gram) — about the size of the period at the end of this sentence.

X-ray fluorescence spectroscopy (XRF) is the nondestructive analysis technique we use to identify the inorganic components of objects such as pigments, metals, glasses, ceramics, and stone. For instance, we can identify early American silver by the presence of certain impurities (indicating production before the advent of electrolytic refining in the mid-nineteenth century) and the absence of



Conservators, historians, and museum scientists discuss sampling Henri Matisse's Joy of Life (1906) at the Barnes Foundation, Merion, Pa.



Winterthur associate scientist Catherine Matsen performing an infrared spectroscopy (FTIR) analysis of an eighteenth-century painted dower chest sample.



adherence to the English Sterling standard (silver content greater than 92.5%). We also use XRF to identify nineteenth- and twentiethcentury porcelains decorated in the manner of eighteenth-century Meissen porcelain. The chemistries of the overglaze enamels and porcelain bodies used by Meissen changed at the beginning of the nineteenth century, so we can use this technique to discriminate eighteenthcentury blanks decorated in the nineteenth century from porcelains wholly prepared in later periods. We are also currently using XRF to identify the yellow pigments in Matisse's *Joy of Life* and to determine the cause of their fading and discoloration.

A greater understanding of an object's origins and state of preservation can be gleaned by looking beyond just identifying the elements present in the object. The analysis tool Raman spectroscopy is a molecular identification technique. It can be used to identify oxide and sulfide-based pigments. A recent Raman examination of red paint from a folk art eagle thought to have been carved and painted by Wilhelm Schimmel (1817–1890) revealed the presence of cadmium red, first sold as an artists' pigment in 1907. This confirmed a growing suspicion in the field that works by later carvers such as Aaron Mountz (1873–1949) were either being genuinely mistaken for works by Schimmel or were being misrepresented as his work. Upon making such a finding it is crucial to consider if the material was from a later restoration or repair; the condition of an object is always carefully examined to take this into account.

A similar detection method is Fourier transform infrared spectroscopy (FTIR), which allows us to determine the molecular composition of artists' pigments. Such identifications can be critical because certain elements such as copper, iron, and cobalt, which appear in some artists' pigments, were available in different time periods. It was recently used at Winterthur to identify phthalocyanine blue a synthetic blue pigment first prepared in 1933—on a Tibetan thangka purporting to be from the eighteenth century. Suspicions were first raised when XRF analysis revealed that what had initially appeared to be appropriate surface soiling/staining of the painting turned out to be a deceptive dusting of a manganese-based pigment.

FTIR can also identify restoration materials such as adhesives and synthetic resins as well as paint binders like gums, natural resins, oils, proteins, and waxes; important components in understanding and authenticating works of art. Gas chromatography-mass spectrometry (GC-MS), a more powerful technique for identifying organic materials, allows us to distinguish a dammar varnish, introduced after 1826, from a sixteenth-century mastic resin varnish, and a twentieth-century alkyd paint from a nineteenth-century oil-based paint. It can also be used to follow the oxidation/decomposition of oils, shellacs, and pine resins as they age-critical in discriminating modern from period materials.

Viewing painted, lacquered, and varnished surfaces in cross section is crucial to our understanding of their evolution and appearance, as these surfaces often undergo multiple campaigns of refinishing over their lifetimes. A range of powerful microscopes image and identify tiny samples: polarized light microscopes are used for pigment identification; reflected light microscopes for viewing paint or finish layers in cross-section, and scanning electron microscopes for ultra-high resolution images. The development of handheld instrumentation for XRF, Raman spectroscopy, and FTIR, has allowed museum scientists to work on site for the first time on large-scale murals/ installations, architectural elements, and archaeological sites.

When we use the techniques discussed here and interpret their data in conjunction with our curatorial and conservation colleagues, we are in an ideal position to obtain an unprecedented understanding of a work of art—a fascinating place to be!

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