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The Bond between Chemistry and Art

The chemical sciences play an increasing role in today's world. As the number of applications increases, there is a growing demand for chemists and chemical engineers to adopt a more interdisciplinary role toward extending applications to a broader society. The successful collaboration between chemistry and art is a response to society's wish to preserve and authenticate historical and contemporary artwork. As a result, modern chemical-analytic techniques are now extensively used for detection of fraudulent art and for determining the age and composition of a painting or sculpture.

Art authentication has posed a great challenge in the art world for many years. A skilled forger is capable of mimicking the style and composition of an original artwork with techniques that can artificially age the art or introduce colors used long ago by a particular artist. Thus museum curators and art historians must rely on chemical science to provide scientific evidence for stylistic mistakes in forgeries that often cannot be detected by the naked eye.

History

Forgery is as old as the history of art, from imitations of Greek classical sculpture that spread throughout the Roman Empire, to the proliferation of Neolithic art, a period referred to as the New Stone Age for its early development of metal tools. Today we have numerous potential forgeries of Neolithic art, facilitated by the artwork's simplicity of technique and media.

A hundred or more years ago, the techniques to determine fakes were not efficient, but they certainly leave us with a great appreciation for the devoted efforts of previous scientists who worked without modern technology. Chemical examination was key in the 1932 trial of Otto Wacker, who was charged with forging Van Gogh's paintings. X-ray photographs proved pivotal to the case because they depicted Van Gogh's technique of modelling the surface with bold strokes over a heavy foundation of impasto, the thick application of paint that indicates the texture of the painting. Wacker's paintings lacked impasto. Wacker’s trial thus signified a revolution in authentication: by examining the physical and chemical properties of the originals, applied chemistry could now be used to reveal inconsistencies in an artistic product.

Techniques used for analysis of paintings

Modern chemical-analytic techniques are essential for art verification. Microscopy, spectroscopy, and chromatography are extensively used to reveal chemical composition. The various techniques can indicate the presence or absence of craquelure, a pattern of cracks formed on old paintings that are difficult to copy in forgeries. The high-power optical microscope, used to study aging effects, can also be used to investigate metal corrosion. Surface corrosion, called patination, traces the effects of long-term exposure of the metal to the atmosphere or to moisture from the soil. Over time, impurities present in the metal, such as tin, may oxidize to give a silvery sheen and thus distinguish genuine metal from a replica. Ultraviolet light is used to examine the surface of paintings while X-rays or infrared excitation analyze the sub-surface of paintings to detect pentimenti, that is, subdrawings that reveal the changes in composition that the artist made while painting. The underlying image serves as proof of an original draft made by the artist and displays earlier images and brush strokes. Dendochronology, the analysis of tree-ring growth patterns, aids in age determination because it is possible to determine the date of oak panels, used in early European paintings, by counting the number of tree rings. Radiocarbon measurements are also used to date organic materials by measuring the radioactive decay of carbon atoms in samples ranging from parchment paper to cast iron.

The Heller Trial

A more recent trial showed that science is indispensable to art identification. In 2000, James Heller was convicted of producing and selling fake paintings of the 19^{th}-century artist William Walker, known for his Civil War paintings. Prior to the trial, a materials scientist used Fourier transform infrared (FTIR) spectroscopy to detect small organic binders; he thus identified a yellow pigment (PY3) in Heller's painting that was not in use during Walker's life. To verify the authenticity of other suspected Walker fakes, chemists used a stereomicroscope to examine the surface structure of the painting and found organic pigments that were present only on the suspected fakes. Scanning electron microscopy and X-ray energy dispersive spectrometry revealed the presence of a zinc white pigment that was not used by Walker in his paintings. Fundamental lab techniques were thus used to identify features of Heller's paintings that did not correlate with Walker's original paintings.

Van Meegeren or Vermeer?

Another notorious forger was Han van Meegeren, a Dutch artist who, about 70 years ago, produced some now infamous forgeries of Johannes Vermeer's paintings. Vermeer, a 17^{th} century Dutch painter, depicted domestic scenes that were renowned for their use of light. Van Meegeren utilized techniques and materials that were common to Vermeer, which is what made his thoroughly researched forgeries so well executed. Van

Meegeren's paintings were remarkably true to the original work, and the authentication methods of the time could not distinguish his forgeries from Vermeer's original paintings. After finally called to trial in 1947, van Meegeren was charged with forgery. To exonerate himself, van Meegeren painted a Vermeer from his jail cell. A thorough chemical investigation lasting two years unveiled the chemical composition of the pigments van Meegeren used and found a mixture of white lead and phenol formaldehyde resin in the forgeries, both products of the 20th century and thus not used by Vermeer. The trial confirmed the importance of chemistry in identifying the most exquisite forgeries.

Methods

Preserving the purity of an artwork is achieved by utilizing non-destructive analytical techniques. Scientists first obtain a cross section of the layers of paint by either using a scalpel carefully to cut a sample at a region of paint loss or by pricking with a hypodermic needle, thus ensuring that paint layers are distributed on a cylindrical section. The pigment is placed in solution and individual droplets of the pigment can then be extracted to analyze and identify particular compounds, such as lead nitrate. Once positively identified, the pigment is analyzed via X-ray diffraction which yields a crystal structure whose pattern on photographic film yields spacings and intensities that reveal composition and chemical structure. X-ray techniques are consequently used to look for anachronisms, for example, whether a pigment in the suspected forgery was available at the time the original picture was produced.

Chemical Analysis of Ceramics

Chemical analysis is not limited to authentification of paintings. Ceramics were a common medium for ancient artists; to determine the authenticity of ceramics, chemical tools are of fundamental importance. Thermo-luminescence is the primary technique used for detection of ceramic forgeries; the method provides critical information the age of the ceramic. Thermoluminescence pottery dating uses a high-temperature method for archaeological dating of 500 to 30,000 years and is based on the assumption that the burial environment of the ceramic sample contains crystalline compounds, such as quartz or calcite. These mineral deposits exhibit natural radioactivity (for example uranium, thorium) that can be measured. The mineral deposit is exposed to a radiation dose, termed pre-dose, from ultraviolet or other ionizing radiation and is then heated to 500° C. Heat causes radioactive energy from the sample to be released in the form of light, and the amount of light given off is proportional to the dose of radiation received. Therefore, the radiation levels measure the age of the ceramic by measuring the accumulated dose of radiation during its archaeological burial. An older ceramic would release more energy from its crystals in the form of light, thus luminescing more.

Chemical Analysis of Metal Composition

Silver, gold and bronze are widespread media for art, jewelry, and coins. The love of money has particularly fueled forgeries, for example, using mould cavities to mimic the surface of a genuine coin. X-ray fluorescence is the most common technique used to detect forged metals. It is often called ‘The Curator’s Dream Instrument’ because it is non-destructive and can readily detect the chemical composition of a coin or a piece of jewelry. A material is bombarded with high-energy gamma rays that displace electrons and emit fluorescent X-rays from the metal sample. This radiation is then used to sort the energies of the photons that correspond to the percentage of a particular element in a sample. Scientists have used neutron activation analysis to study coinage from the Sassanian Empire, a prosperous period of the Second Persian Empire that existed from AD 224-641. Neutron activation analysis determines concentrations of elements in materials by bombarding the metal sample with neutrons, yielding radioactive isotopes. Comparison with the radioactive emissions of these isotopes to known values for each element reveals the concentration of metals in the sample. The Sassanian coins contain 80% silver but they also contain fractions of gold, about 0.5-1%. Modern forgeries are easily detected due to their high silver purity; some forgeries have a gold content less than 0.001%.

Preservation

Fundamental to the preservation of artwork has been the development of natural resins. Historically, paintings were coated with a natural resin varnish meant to darken the painting and make colors appear more saturated. However, over time the varnish deteriorated and, due to photo-oxidation, it became insoluble and thus difficult to remove with hydrocarbon solvents. Chemical research on synthetic varnishes showed that a better varnish would be one that is low in molecular weight and viscosity. Today this has led to the use of hydrogenated hydrocarbon and aldehyde resins, which mimic the optical properties of natural resins while maintaining color saturation and gloss.

Finding a balance

While chemical science provides powerful analytic tools for revealing differences between genuine and forged art, should we completely erase the profound knowledge and experience of art historians and connoisseurs in judging an artwork? Should we only look at chemical data that present objective results? Where does an artist's instinct play a role?

A remarkable example, the Kouros mystery, demonstrates the need for a more cooperative relationship between the humanities and experimental science.

In 1983, The Getty Museum in Los Angeles acquired a statue that was believed to be a kouros, a male nude statue that was stylistically prominent in the Archaic period of Greek sculpture, 6th century B.C To confirm its authenticity, scientific investigations lasting 14 months studied the statue with a high-resolution microscope, electron microscope, electron microprobe, mass spectrometry, X-ray diffraction, and X-ray fluorescence. All the tests confirmed that the statue was authentic and probably dated thousands of years back. But one look at the statue by prominent art historians discredited all scientific experiments. Their experience and knowledge of the style of the kouros and what it should look like after it is excavated, resulted in a feeling of "intuitive repulsion." Italian art historian Federico Zeri had only to look at the fingernail to know that the statue was a fake. It is still unknown whether or not the statue is a fake but new information such as misleading certificates of authenticity and also the possibility that the statue was exposed to potato molding to make its surface appear older has led many art historians to question its authenticity.

The Kouros mystery provides an important lesson for both the sciences and humanities, because it showed that one cannot function without the other. We rely on tests to give us verified data, but just because we cannot quantify our own perceptions and instincts, does not mean that our qualitative knowledge should be disregarded, particularly in the arts.

Collaboration between the applied sciences and humanities is the only way to keep checks and balances on both. Scientific investigation is indispensable to the authentification and preservation of art. At the same time, art introduces a dimension of beauty in the often arid scientific environment. And one wonders whether the two worlds are fundamentally different. Is an artist's studio, with its bottles of paint, so unlike the chemist's laboratory? Both artists and scientists aim to illuminate and to enrich human existence.