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Unmasking Art Forgery. Scientific Approaches

Abstract

Scientific approaches to art forgery provide the rigorous methodology by which claims made about a work can be tested. A plethora of scientific instrumentation is available for the analysis of artwork but data is only useful when assessed against existing secure points of identification. Verifiability of results, therefore, relies on standardised documentation, defined rules of evidence, and ensuring that all processes and findings are reproducible. In building knowledge of what characteristics constitute authentic works, providing effective protocols and rigorous procedures, and bringing together multi-disciplinary knowledge to bear on questions of art forgery, science has become an essential part of good curatorial practice, effective conservation procedure, and art market diligence.

Determining Authenticity

'Unmasking art forgery' sounds like the final chapter in a crime fiction novel where the climatic denouement is revealed, and after the reader has been led through a long, convoluted and gradual process of stripping away of layers of cunningly fabricated artifice that have made the fake a convincing painting. In reality there is more plodding (through process and paperwork) and plotting (of data on seemingly ever expanding graphs and tables) than peremptory revelation, and the complexities of law mean that even if the work is a fake, there may be no denouement. Instead the work may slip quietly back into the hands of its owner and disappear for all time, or resurface at a later stage when the market is less discriminatory, or the work has been reascribed in line with the findings of an art historical or scientific enquiry.

In practical terms, the determination of fraud and forgery is a legal one, and occurs at some distance from the scientific approaches that are involved in the amassing of relevant and useful evidence. In addition, the process of determining whether an artwork is a fake or not is hardly ever linear. Finding the pathway from the proposition that a work is a fake to the evidence-based conclusion that it is indeed a fake requires careful appraisal of the process at each step. Determining authenticity is a process of triangulation that brings together multiple approaches that include: relevant expertise, a number of sources of data including primary documents and relevant research, and various theories and methods of investigation. Nevertheless, it is always the case that any approach to unmasking art forgery must be secured within rigorous scientific methodology, where data that is produced as part of the investigation must be assessable, verifiable, and contestable. This is what differentiates scientific approaches to art attribution from connoisseurship, which is characterised as a method where a recognised expert with specialist knowledge in a particular artist, school or period, brings their expertise and experience to the authentication process. This can be problematic when the conclusions are drawn from individual experience and it is, therefore, difficult to verify the data set used by the connoisseur. In courts of law, where expert connoisseurs were matched against other expert connoisseurs, differing points of view often left the judge and jury to decide an outcome based on an assessment of the expertise of the connoisseur, not on the evidence about the work in question.

There are a number of excellent texts that provide details of scientific techniques available for art attribution and authentication, including Stuart Fleming's *Authenticity in art: the scientific detection of forgery* (1972) and Paul Craddock's edited volume *Scientific Investigation of Copies, Fakes and Forgeries* (2009). The aim of this chapter is broader; to examine scientific approaches

to attribution and authentication. This chapter, therefore, describes the processes and protocols that are required to deliver a sound and scientifically-valid finding as well as discussing some of the widely used techniques.

Scientific Beginnings

The use of science to 'unmask art forgery' has its beginnings in the scientific studies of materials and techniques of artists that were established in the late nineteenth century and early twentieth century. Early pioneers included Friedrich Rathgen at the Royal Museums of Berlin from 1888 (Gilberg, 1987) and Alexander Scott who established the British Museum Research Laboratories in 1920 (Lambert, 2014). In 1928 Director of Harvard University's Fogg Museum, Edward Forbes, opened the Department of Technical Studies to house his extensive pigment collection, and hired chemist Rutherford John Gettens and conservator George Stout to develop programs of scientific investigation for art studies (Torres, 2013). A year later, in New York, Mrs Andrée Lardoux Hahn commenced her case against Lord Duveen over a work purported to be by Leonardo da Vinci, where for the first time connoisseurship and science were called to the service of authentication (Hahn and Benton, 1946; Cohen, 2012). When Dutch forger Hans van Meegeren was convicted of fraud, at the end of the Second World War, forensic science was considered a critical part of rigorous art authentication. Paul Coremans (1949) and the scientific committee assessing the Hans van Meegren fakes provided both the comparative data sets, and the analytical pathways, that enabled evidence to be independently assessed, verified and contested in ways that could be clearly observed and understood by external parties. Scientific analysis, therefore, became an important third platform for art authentication, joining art historical knowledge and provenance as the modus operandi for understanding where a work of art might fit within an understanding of an artist and their oeuvre.

At this point the distinction between scientific approaches and scientific analysis should be noted. The former describes a method of building data using a correct process to ensure verifiability; the latter describes particular investigative techniques that may be used within this method. This chapter deals with both. Before examining specific methods of analysis it is, however, useful to examine the intellectual traditions of connoisseurship and forensic science, which inform scientific approaches to attribution and art authentication; and the two historical figures who loom large in these traditions, Giovanni Morelli (1819-1891) and Edmond Locard (1877-1966).

Gionvanni Morelli

Giovanni Morelli was an Italian art historian, collector and politician. He brought an evidence-based approach to the study of art history and in particular to collection assessment and attribution. His methodological approach was based on his training in medicine and comparative anatomy (Anderson, n.d.). He proposed that, when provenance is insecure, a thorough examination and subsequent comparison of detail was the best way to determine the authorship of a painting. This theory gained him an influential reputation as a connoisseur. Art historian Edgar Wind described Morelli as 'a clear headed amateur', explaining how Morelli had

> ... worked out a well-defined method ... which he claimed ... transformed attributions from inspired guesses into verifiable propositions ... adopted by Frizzoni, Berenson, Friedländer and others, and now in use in all the schools of art history, Morelli's method rests on a meticulous technique of visual dissociation (Wind, 1960, p. 2).

He went on to characterise the Morellian method as 'an extreme case of the kind of detachment' (Wind, 1960, p. 2). Art historian Max Friedlander ridiculed Morelli's claims of objectivity,

arguing that Morelli was simply validating intuition rather than applying rigorous process (Spencer, 2004, p. 34). Analytical studies of Morelli's technique, however, have reached a different conclusion. Tocchini-Valentini & Tocchini-Valentini (2012), examining the links between Morellian methodology and Bayesian methods for determining statistical likelihood (devised by the Reverend Thomas Bayes and published three years after his death in 1764), concluded that Morelli was using Bayes' method of probability. They demonstrated statistical validity in Morelli's deductive methodology, based on the Bayesian process of determining the conclusion from the probability of a hypothesis being correct. According to Tocchini-Valentini & Tocchini-Valentini (2012, p.4) this probability is determined, in turn by:

- 1) prior belief about E or the probability P(E) and
- 2) likelihood, probability of observing the evidence given that the hypothesis is true.

Or as they more succinctly describe:

$$P(H/E) = \frac{P(E/H)\,P(H)}{P(E)}$$

Today, probability, which identifies the degree to which the evidence supports a theory of a work being by an artist or conversely not being by the artist, is a significant part of the scientific methods used in attribution.

In practice, Morelli's working proposition was 'that a painting should not be judged by forms that could be easily imitated' such as composition, subject matter, colour, and form but rather by 'the kinds of forms that were not influenced by school or tradition' (Vakkari, 2011, p. 46). Morelli's method assumed that a forger is less likely to be interested in, or able to reproduce the characteristics of brushstrokes, nuance in paint application, variations in tone, application of paint and the like, in areas that cannot be dealt with generically. Subject matter, composition and palette, on the other hand, can all be easily reproduced, and are therefore of little use in assessments of attribution. The Morellian method, therefore, relies on examining the minutiae of a painting rather than the overall impression: the lace in a painting by Rembrandt, or the ear lobe in a work by Raphael for example. His books on attribution contain, '... illustrations of fingers and ears, careful records of the characteristic trifles by which an artist gives himself away' (Wind, 1960, p. 5).].

Morelli's assertion that 'the starting point for identification of the fundamental forms must be an authenticated work of art which provides a source of comparison' (Vakkari, 2001, p. 47) is a keystone of contemporary attribution studies, the existence of the secured record from which to draw comparison. Without a secure body of works with direct, validated and verifiable links to the artist, it is impossible to determine where a work of unknown provenance may fit. Conversely, if works that do not have validated and verifiable links to the artist are allowed to corrupt an artist's oeuvre then it becomes increasingly difficult to find secure points of verification. A result of this is that scholarship relating to an artist's oeuvre and their place in art history may be compromised. Morelli was also a regular visitor to Guiseppe Molteni's restoration studio where great works were restored and sometimes attributed or reattributed prior to their export to places such as the National Gallery of London (Anderson, n.d.). His familiarity with the process of restorative intervention led him to also stress the need to understand the condition of a work and ascertain the extent of previous restoration prior to ascribing authorship.

Morelli's methodology produced extraordinary results. In the Dresden Gallery a work that was catalogued as copy of a lost Titian by Sassoferrato was reascribed to Giorgione. The work in question is Giorgione's masterpiece 'Sleeping Venus'. After Morelli completed his examination of the Dresden Collection over 45 works had been reascribed (Wind, 1960, p.4).

Edmond Locard

The second intellectual pioneer in establishing scientific approaches to attribution and authentication was Edmond Locard. Like Morelli, Locard had studied medicine but he also studied law. In 1910, he founded a laboratory for the study of criminalistics under the auspices of the Lyon Police Department, and in 1931 he published his groundbreaking treatise *Traité de Criminalistique; Les Empreintes et les Traces dans l'Enquete Criminelle* (*Treatise on Criminalistics, Prints and Traces in Crime Investigation*). Locard's criminological aphorisms are frequently quoted including 'Le temoignage est un fait vu a travers un temperament' (Testimony is a fact seen through a temperament) and 'Le temps qui passe c'est la verite qui s'enfuit' (As time passes truth flees) (Giovenelli, 1932, p. 448). The most significant quotation ascribed to him, however, is what has become known as the Locard Principle- 'Every contact leaves a trace'.

The Morellian method demonstrated that the entire artwork is capable of being presented as the trace of a set of activities relevant to an attribution or authentication investigation. This means that the work can be 'interrogated' from the aspect of its materials and techniques, its stylistic attributions, its method of construction, and many other aspects that can be verifiably matched to a point of production. This assumption forms the methodology for the scientific analysis of artwork, where the aim is to determine the link between the work and a particular artist, and indicates again the necessity for a comparative set of securely provenanced works.

In his review of the first two volumes of Edmond Locard's seven volume *Treatise on Criminalistics* Heinrich (1932. p. 939) claimed:

"It is a basic principle in criminal investigation that active movements of persons, animals and things always result in disturbances to locale which are recorded or evidenced by scattering of dust and minute debris, by scars, scratches, imprints, odors, color phenomena sound phenomena etc. in greatest variety. They traces are physical. They are concrete. They are facts ... they are always indicative of their source and the kind of action that produced them. Singly or in combination these traces reveal the drama of action.
These physical facts are the foundation of circumstantial evidence".

In his review of Locard's second two volumes Heinrich (1934) argues that Locard demonstrates:

It is more useful and unerring for him [the police] to know the exact color of the eye than its expression; the true shape of a certain facial features than their complex play in emotional mimicry; and so on. (1934, p. 993)

He goes on to explain how in Vol. IV Locard

... deals with scars and markings; observable veins such as those in the hands and forehead; the utilization of photographs; habitual actions and mannerisms; anthropometric measurements and reference tables; and certain applications of intelligence tests. (1934, p. 994)

Scientific approaches to determining forgery seek to ascertain whether a work is what it was purported to be, not what the intention of the artist may have been, and while the purposeful construction of a work to appear to be other than what it is constitutes forgery, and profiting from the sale of what is known to be a forgery is the crime of art fraud, proof of intentional deception that results in profit is required to substantiate fraud. Whereas evidence of how this deception was manufactured can often be clarified by the scientific analysis of artwork, and while this

might be sufficient to determine that the work should not be in the marketplace, it is not sufficient to determine art fraud. Artworks can be misattributed by mistake rather than intention, but art fraud requires an intention to enable the van Meegeren to trade as a Vermeer, the Hebborn as a da Vinci, the Myatt as a Matisse and so on.

Scientific Theory: Falsification and Points of Identification

Both Morelli and Locard established comparative methodologies, but the ability to compare data requires having valid data sets that can provide points of identification from a known set of data (works by Vincent van Gogh) to a propositional set of data (a work claimed to be by Vincent van Gogh). The security of comparative data sets is, therefore, important, so that the data that might be provided by fake works does not corrupt the evidential data used for comparative purposes. This is why study collections, such as that which was established at the Fogg Museum (now the Strauss Centre for Conservation and Technical Studies) and securely provenanced works in public institutions are important. There are also standard spectral atlases available, such as those used for Raman infrared reflectography or mass spectrographic instrumentation such as gas chromatography mass spectrometry (GC-MS), that provide comparative data. In some cases there is no comparative data and a set of standards need to be developed. Peer-review journal articles or expert research reports such as those published in the National Gallery of London's *Technical Bulletin* also provide useful information about artists' materials and techniques as well as information on methods of technical analysis.

An initial step in unmasking art forgery, then, is to determine what data can be verified in an authentic work by the artist in question, so that comparisons between secure data and data in the work under investigation are possible. As positive results for all the questions below are likely to be the same for thousands of works, such results are not sufficient to confirm a theory of authorship. One adverse finding, however, may be sufficient:

Did the artist use lead white and does this work indicate the use of lead white? Yes.
Did the artist use cadmium yellow and does this work indicate the use of cadmium yellow? Yes.
Did the artist use bone black and does this work indicate the use of bone black? Yes.
Did the artist use Prussian Blue and does this work indicate the use of Prussian Blue? Yes.
Did the artist use Cobalt Green and does this work indicate the use of Cobalt Green? Yes.
And so on through an encyclopedia of possible pigments, or alternatively;
Did the artist use titanium white and does this work indicate the use of Titanium White? No. The artist painted before titanium white was produced as a pigment. Yes, this work is painted using titanium white.

It is necessary, therefore, to establish which points of identification are going to be most useful. Scientific analysis may demonstrate an anomaly, for example finding of a twentieth century pigment in a painting purported to be from the nineteenth century. If, however, further investigation shows that the work had been heavily restored in the twentieth century then the indication of a twentieth century pigment may not be anomalous. If, however, a painting purported to be from the fifteenth century is executed on a canvas containing polyester, which was first commercially produced in 1941, then this is evidence against its authenticity. Falsifiability enables a theory to be contested, and finding an anomaly in the investigation of art fraud is critical.

Determining evidence

The Morellian method determined the requirements for good comparative data sets. The Locard Principle demonstrated the need for rigorous analytical testing. Both require secure

documentation, and in art attribution the Condition Report is the key document. It includes identificatory details about the work: the title, the artist to whom the work is attributed, its method of construction and media, any indications of change in condition, and other relevant information, and a high definition image. It provides a strict framework for recording information about the work, and forms the basis for all subsequent documentation for the work. Importantly, it verifies that the work in question is the work that has been examined, securing the evidential link between the work under investigation, the evidence provided during the investigation and the assertions drawn from that evidence. The Condition Report provides the points of identification that set out the authentication process for that particular work. For example, the Condition Report might show that there are parts of the artwork that appear to be heavily restored, and therefore the twentieth century pigment titanium dioxide found in the work is not evidence of forgery but of restoration. In a Condition Report that indicates no evidence of restoration then the presence of titanium dioxide would support the hypothesis that the work may be a fake, or at least misattributed.

The Condition Report also informs decisions about the analytical pathway that will be chosen for the work in question, based on the general principle that examination and analysis proceed from the most basic visual analysis through more lab-based techniques to high-end analytical techniques. As decisions relating to the analytical pathway rely on what information is required from the examination, there is not one defined analytical pathway that suits every attribution investigation. The following provides an overview of the kinds of questions that science can assist with, but always with the proviso that a set of standards exists, usually consisting either of securely provenanced works by the artists or a set of scientific standards against which to compare the work in question.

The following outlines areas that are most likely to form the basis for data-collection when assessing whether a work is likely to be a forgery.

Material characteristics:

- Material type; for example it may be important to know whether the paint may be oil paint or acrylic paint, or to be able to identify other materials that may have modified a paint's behavior and appearance.
- Material constituents (in some cases examining trace elements at parts per million); which may help to identify, for example, the source of a pigment such as a particular form of ochre or additives that indicate a particular manufacturing process.
- Qualitative and quantitative; what kind or how much of particular materials occur in the artwork?
- Age; does the paint surface exhibit cracking and what kind (mechanical, drying or environmental?)
- Environment; is there evidence that matches the history of the work? For example, if it is argued that the work was displayed in a men's club in London in the nineteenth century is there evidence of carbon deposits (London smog) or nicotine staining. If it was produced in the Australian desert is there evidence of red dust?

Materials manufacture:

- Grinding method; morphology and size can help determine whether a pigment was ground by hand or by machine and assist in assessing a possible date or place of production.
- Additives; these be found at different periods and for different manufacturers, and may include driers, extenders, and other forms of modifiers
- Recipes, batches; in some cases it is possible to identify particular recipes, patents or

production batches
- Carrier, binder, medium; materials analysis will assist in determining what kind of material binds the pigment, including oil paint, acrylic, or egg tempera

Object manufacture:
- Layers of application; for example what kind of ground was applied, is there is underdrawing, what layers exist and how are these constructed, are there glazes present?
- Artist's choices made during manufacturer; these may include changes to the composition.
- Later additions, restorations; for example the application of a new support such as a new canvas adhered to the back of the work.
- Artist's preferred materials; some artists have a set of preferred materials, often obtained from one manufacturer, that can be identified in archives such as letters and invoices.

Materials behaviour:
- Ageing characteristics; with time materials change due to inherent degradation or external influences with characteristic and measurable chemical and visual changes.
- Mechanically-induced changes; for example embrittlement, cracking, and dimensional changes.
- Environmentally-induced changes; light, pollution, temperature fluctuations all affect materials and the subsequent appearance of the object
- Inherent vice; different materials, or different modifications to materials, have characteristic ageing mechanisms that produce deterioration such as the discolouration of papers or canvas through oxidation, or the drying cracks in paint

Once the work has been examined a determination needs to be made about what evidence will be collected. It is important that the process for collection is systematic so that it the link between the proposition (premise) and decision as to attribution (conclusion) is verifiable. For these reasons investigations generally proceed from macro-investigation to micro-investigation in the following stages.

<u>The Initial Examination and Documentation</u>
An initial examination assesses the work, which is then accessioned and receipted and the more comprehensive Condition Report is completed. At this point a proposition can be formed based on the data that has been collected. During this process the context for the inquiry will be developed and a framework for identification established. An assessment of primary sources and secondary sources that relate to the artist or the object is usually completed, and securely provenanced works by the artist in question are assessed. Such investigations confirm what points of identification might best be considered, for example the palette, ageing characteristics, use of underdrawing, or specific materials. Based on this assessment the most relevant analytical pathways will be determined.

<u>Macro-investigation</u>
A hierarchy of examination techniques is employed in the analysis of artwork, generally proceeding from non-invasive, low-tech examination, to precision instrumental analysis. Non-invasive visual examination employs a range of advanced light sources to enhance the investigator's visual acuity, thus extending the ability of the naked eye to detect information that might be of interest to the investigation. This visual enhancement is done in three ways:

1. By using visible light in a variety of ways to extend the ways in which the object can be examined.
2. By using light at ends of the spectrum that is in the UV or infrared range.
3. By employing a combination of these tools with magnification.

The light spectrum can be understood as a continuum of electromagnetic waves with extremely short wavelengths at one end of the spectrum to long wavelengths at the other; the shorter the wavelength the higher the energy of the light at that point in the spectrum.

Light is measured in nanometers (nm) or micrometers (μm). A thousand nanometers make one micrometer. Visible light (0.7μm – 0.4μm) sits in the middle of this wavelength band. Ultraviolet (UV) light (0.3 μm – 3 nm) sits at the shorter end of the spectrum (next to the wavelength for violet in the visible spectrum) and infrared (IR) light (300μm – 0.4μm) at the longer end of the spectrum (next to the wavelength for red in the visible spectrum). Microwaves occur at the far end of the infrared spectrum. Radio waves (with wavelengths from 1 mm to 100 kilometres), comprising the longest wavelengths in the electromagnetic spectrum, are at the furthest end of the spectrum. X-rays (3nm – 0.03 nm) occur at the end of the extreme UV band and, beyond this band sit gamma rays (0.03nm – 0.003 nm) that provide the highest energy wavelengths in the electromagnetic spectrum.

Visible light
Visible light is used to enhance the examination of an object by the naked eye, with both the brightness of the light and its hue (colour temperature, measured as Kelvin or K) being important. If the light source is producing light at 6500K then some colours will take on a blue or 'cool' cast, whereas at 3000K the cast will tend to orange or 'warm'. As this may make some parts of a painting more difficult to see, it is important to use a light source that simulates the spectra for daylight, thus providing illumination over the entire visible spectrum.

The angle of light is also important. A light source located at 90 degrees to the surface is useful in overall examination. Raking light, with the light source placed to the side of the object (at 45 degree or less), will throw the morphology of the work into sharp relief. This is useful when looking for the characteristics of brush strokes, for damage that has occurred or has been restored, or for anomalies across the surface. Transmitted light, shone through from the back the work, may provide information on the thickness or structure of the support or paint and may help identify inconsistencies within the painting, such as identifying heavier reworked areas or determining whether the work has been relined.

Infrared light
Infrared light produces heat. It is used in a range of instrumentation but for macro-examination it is most commonly used to examine underdrawing or changes that sit below the paint surface, or to enhance inscriptions on works. IR light passes through some materials rather than being scattered or reflected at the surface, heating up reactive materials such as carbon that are lying beneath the surface. These materials absorb and then reflect IR light and the resultant image can then be captured on imaging software or viewed on a screen to investigate these areas lying below the surface.

Ultraviolet light
Ultraviolet light, having a shorter wavelength than visible light, is invisible to the human eye. Some materials respond to UV light by fluorescing, while others appear darker in contrast to the

surrounding surfaces. Pigments with distinctive UV fluorescence include madder, with a characteristic bright orange fluorescence, and zinc white with a distinctive yellow fluorescence. Different varnishes also have different responses to UV light, with many synthetic varnishes appearing milky and lighter, and aged natural varnishes such as dammar having a green hue. As more recent paint is less transparent to UV light than older paint more recent additions, such as signatures that have been applied to 'strengthen' the attribution of a painting, will appear darker under UV. Characteristic UV fluorescence is also useful in identifying other types of materials, for example distinguishing between ivory and a synthetic substitute, or aged and recently manufactured marble. Evidence of mold on paper, or areas where bleaching has been used to remove mold, may be invisible to the naked eye, but clearly evident under UV light.

X radiography

X-ray images work through absorption. Denser materials absorb more X-rays than less dense material, which is why X-rays are used to examine damages in bone structure. As X-radiography is a comparative method it will only be effective where there is a difference in the density of the materials. X-rays are passed through the object to a photographic plate beneath which then produces an image of the layers. Dense materials resist the transmission of the X-ray and register as lighter areas on the image. Less dense materials allow more penetration of the X-ray to the photographic plate resulting in darker areas in the image. In the examination of artwork X-radiography is particularly useful in determining the internal structure and condition of objects.

Spot Tests

Spot tests are another form of macro-investigation for materials characterization that are relatively quick, easy, cheap, and provide indicative results that can, if necessary, be tested further with more complex instrumentation. Some spot tests, such a using a magnet to test whether an object is made of iron, are readily available. Others require chemical reagents that give specific results for particular materials. Spot tests for metals may involve delivering low voltage to the object against which a small piece of blotting paper dipped in an acid is held. This is then introduced to the relevant reagent and indicative colour change recorded. Testing lead, for example, involves soaking filter paper in nitric acid and then adding potassium iodide to the paper, with a yellow colour change indicating lead. Metallic cations and anions associated with corrosion products can be tested in this way (Organ, 1969; Odegaard et al, 2000). Commercial Merck test strips are available for cations and anions for copper, iron, nickel, zinc, and silver cations and for chloride, or chromium oxide anions, and others. Other materials such as starch can similarly be identified using specific reagents.

There are drawbacks associated with some spot tests. Reagents can stain materials, and the introduction of additional chemicals to a surface may affect later analysis. Results may be affected by interference from other ions on the test surface. Sometimes the change is not clear enough and the results are not well enough delineated to use as evidence.

<u>Micro-investigation</u>

Cross sections

A useful technique for scientific analysis is cross sectioning, where a small section, usually the size of a full stop in standard print, is taken from an artwork. These small sections can be examined without further preparation, or they may be embedded in polyester resin and polished to give a smooth surface, or microtomed to produce thin sections suitable for transmitted light examination. Cross sections provide information on the stratigraphy of the layers that comprise the object. Cross sections are also useful in differentiating natural ageing or 'tricked up' layers that simulate ageing. In the analysis of metals, sectioning may indicate the depth of corrosion. In

a silver alloy evidence of copper precipitation running in line with the grain boundaries is characteristically evidence of a long process of chemical interaction in a burial environment and is not easily reproduced with modern alloys (Bennett, 1990, p. 180).

Basic Microscopy

Basic microscopy is an essential tool with which to undertake detailed examination of artworks. Microscopic examination provides information about the physical nature or structure of the work, useful when assessing brush strokes, tool marks, inclusion, grain size, patination, varnish and so on. It is critical in the initial examination of cross sections and samples.

There is an extensive range of microscopes, each having a particular function in the investigation of artwork. Stereomicroscopes give good depth of field and enable the topography of a surface to be carefully examined. This is useful when analyzing a brush stroke or examining layers of dirt or dust on a surface. Compound microscopes provide high levels of magnification and are useful in examining a particular part of the layer of a cross-section. Polarised light microscopy (PLM) uses light that has been polarised, so that the vibration of the light occurs in a single direction, to investigate materials that have exhibit particular polarising characteristics. This is the case with a range of anisotropic pigments, viewed as cross-sections or simply as powdered fragments, where morphology, colour, and refractive index are enhanced under polarised light. UV fluorescence microscopy utilises the characteristics of some materials to emit fluorescence under UV light. It is used to examine paint layers and is useful in determining a range of materials including pigments with specific fluorescence characteristics such as rose madder or zinc white or varnish layers that may occur as a top coating, as a glaze or as an isolating layer between pigment layers.

Nano and instrumental techniques

When enough contextual information has been collected by non-invasive and low-tech methods an investigation will often move to more specific analytical equipment, using instrumental analysis that may provide nanotechnology capability, to identify the materials used in the artwork. Such analysis may provide evidence of trace elements, or contaminants or answer a particular question, such as what form of titanium white, anastase or rutile, is indicated in the artwork. This in turn may help with questions of dating, manufacture or authorship. For example the anatase form of titanium dioxide pigment came into production in its pure form in the 1920s; however, rutile was not produced commercially until late 1938. Both these compounds have the same chemical composition, but different crystal structures. Different techniques have different capabilities and it is important that the research question is clearly formulated before specific instrumental analysis is employed in an art fraud investigation.

Scanning Electron Microscopy (SEM)

SEM or frequently SEM/EDX (Energy Dispersive XRay) scans a beam of electrons over the sample sitting in a vacuum chamber to provide both high-resolution micro-images, and qualitative and quantitative data. SEM provide high photomicrograph magnification so it is a favoured instrument for high level visual examination. For example SEM provides information on morphology, and assessing the size and shape of pigments to determine whether a particular pigment has been ground by hand or by machine, may help determine the level of technology involved and indicate whether the pigment was naturally occurring or manufactured (Haswell et al, 2011, p. 368). SEM can be used to identify pigments, binders, fillers, grounds and other materials (Keune et al, 2011); useful when clarifying the sequence of materials within a cross-section in order to describe the various components in composite layers. SEM analysis can be constrained by the inability to detect light elements such as hydrogen (H), lithium (Li) or others below sodium (Na) on the periodic table.

X-Ray Diffraction XRD

X-ray diffraction employs incident X-ray waves to elicit characteristic patterns based on the diffraction caused by particular crystalline atomic and molecular structures. It is particularly useful for determining differences in crystalline structures for minerals and metals, and thus for differentiating various forms of a pigment. For example, it is useful in identifying the rutile or anastase forms of titanium dioxide, or differentiating between the two European forms of lead tin yellow produced between the 13th and 18th centuries, the later type I (Pb_2SnO_4) and the earlier type II ($PbSn0_3$). X-ray diffraction is also useful in identifying changes in the colour of pigments, such as the red lead (minium Pb_3O_4) which, when it alters its state to litharge (PbO), takes on a pale cream colour.

Particle-induced X-ray emission - PIXE

PIXE is a highly specialised form of analysis. With high levels of sensitivity to parts per million and very short data acquisition times (generally 1-2 minutes), and excellent multi-elemental and quantitative characteristics, it is useful for evaluating relatively low concentrations of trace elements or contaminants. It is generally non-destructive so the sample is available for further testing. PIXE uses a focused beam of protons to excite atoms near the surface to emit x-rays. The graph of the resultant peaks indicates specific chemical bond energies and from this it is possible to determine the chemical structure of the sample. It is limited in use because it is a very expensive to operate (Andaló et al, 2001, p. 280). PIXE lacks portability, and does not identify elements lighter than sodium, so it is not sensitive to organic compounds (Andaló et al, 2001, p. 281).

Raman spectroscopy

Raman microscopy uses near infrared spectra to provide a non-invasive and through air technique using the conventional microscope to focus the Raman beam on the area to be analyzed. This means an artwork or sample can be placed on the microscope stage and focused visually and then analyzed using the Raman infrared capability. Raman provides high chemical selectivity, high spatial resolution to one micron (1 μm) and high spectral (1 cm-1) resolution (Best et al, 1992, Mathieson and Nugent, 1992, p.4). It provides results for both organic and inorganic compounds and can assess crystalline structures, thus being able to differentiate between pigments with the same formula but different crystalline structures such as rutile and anastase (Best et al, 1992, p. 69). Raman provides rapid spectrum collection time, but unless the appropriate filters are in places Raman may burn out certain pigments such as vermillion, albeit at micron level. Fluorescence of some pigments under Raman may also impede effective data collection (Mathieson and Nugent, 1992, p.7).

Fourier transform infrared spectroscopy (FTIR)

FTIR is a useful instrument capable of identifying organic, polymeric, and some inorganic materials, from relatively small sample sizes. It can therefore provide data on inorganic, organic, natural and synthetic pigments, binders and fillers and polymers. As FTIR can operate in situ, and non-destructively it useful for tasks such as analysing plastics, gums and varnishes (Burgio and Clark 2001, p.1499; Spring et al 2008), or characterising patina on bronze. (Burgio and Clark 2001, p. 1519). Some disadvantages associated with FTIR include the fact that mixtures may be difficult to analyze, and as water is a strong absorber of infra-red, it may be hard to get spatial resolution lower than 10 micron in samples with high water content, resulting in poorly defined spectre.

X-ray fluorescence (XRF)

In X-ray fluorescence X-rays are used to displace electrons from the innermost shells of atoms, which are replaced by electrons from secondary shells, releasing fluorescent X-rays that provide indicative spectra of the elemental atomic weights of the material. Portable XRF provides elemental analysis without the need to remove a sample from the object. Although a useful tool there are some limitations to the conclusions that can be drawn from XRF; X-rays only penetrate the surface to a depth of approximately fifty micrometers so any surface leaching or surface enrichment may be misread as being representative of the object (Bennett, 1990, p.181), and it is difficult to measure light elements with atomic numbers below sodim (Na) (Schreiner et al, 2004, p. 8).

Gas chromatography-mass spectrometry (GC-MS) and pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)

GC-MS is used to identify organic materials. It involves vapourising a sample in gas or liquid form, which is analyzed while being conveyed along a chromatographic column. The detectors within the column are specific for different classes of materials. Solvent extraction, outgassing (desorption) or pyrolysis is used for the analysis of solids. Pyrolysis (Py-GC-MS) uses heat to break down the sample for GC-MS analysis. Py-GC-MS is a relatively quick technique, it does not require pre-treatment of the sample losses, contamination is minimised and the process overcomes some of the issues with materials that are difficult to run through GC-MS directly (Bonaduce et al, 2004, p. 298). The appendix to this paper describes some case studies where GC-MS and Py-GC-MS have been used in attribution and authentication studies.

Dating techniques

Radiocarbon dating

Radiocarbon dating is used for ascertaining the age of organic material. Its effectiveness as a dating technique is based on the fact that a living organism takes up carbon 12 and carbon 14 during its lifetime. The half-life of carbon 14 is 5,730 years and when the organism dies the carbon 14 in its system begins to break down, while the more robust carbon 12 is retained. The ratio of these two can be determined and on the basis of this predictions of age are possible. While radiocarbon has a range of uses in archaeological enquiry, radiocarbon dates are dependent on the amount of background carbon 12 to which the sample may have been subjected, such as bushfires or volcanic activity, and the results of radiocarbon need to take account of potential errors which may be in the order of several hundred years (Bennett, 1990, p. 181).

Thermoluminescence

Thermoluminescence (TL) is useful in dating ceramics and glass, and is based on the process that occurs when materials with crystalline structures release electrons when heated. Materials that behave in this manner include feldspar and quartz, which absorb radioactivity from a naturally occurring source such as uranium. Heated beyond a certain temperature, the sample from the object release electrons as light, and an equation using the total TL emission and the annual radiation dose is employed to determine the likely age of the artefact. Thermoluninescence is not always reliable; refiring an object may reset radioactive take up by the material and an original low firing temperature may not have been enough to alter the original radiation levels. In wet environments the isotopic level may be lower than in drier environments for objects of the same age (Bennett, 1990, p. 181).

There are many more techniques that could be discussed here, with new ones constantly coming into use. Reviewing literature in peer-review journals is, therefore, a necessary part of the scientific approach to art attribution and forgery investigation.

Conclusion

Scientific approaches to art forgery employ sets of verifiable evidence that are relevant in proving, or disproving, the hypothesis that an artwork is a forgery. While different types of scientific instrumentation may be used for analysis, adhering to scientific principles and protocols is critical. Examining the colours used in constructing the image in order to determine the palette, measuring the width of brush strokes to identify brushes that were used, comparisons with characteristic techniques found in authentic works by the artist in question such as scumbling (dragging the brush over the surface), sgraffito (scratching the surface), or the particular use of glazes or methods of varnishing, all constitute a scientific approach to the examination of the artwork. On the other hand, scientific approaches to art fraud may include complex analytical instrumentation and a team of scientists working to determine a particular trace element, to parts per million, in a paint sample. In all cases, what is necessary for an enquiry to claim scientific validity is that strict protocols are in place when data is collected, processes are documented, evidence is analyzed, and the finding recorded, to ensure reproducibility, verifiability and testability of the approach.

Identifying art forgery requires a complex and carefully constructed chain of evidence. Attribution, which attempts to locate a work within an artist's oeuvre, must similarly ensure that works can be verifiably linked to the purported source. When this evidential chain has been in place from the time the work was created, through diligent record keeping by the artist, their family or dealer, and subsequent owners, this provides a secure provenance, and questions are unlikely to be raised about the work. Scientific investigation is useful in analysing these securely provenanced works in order to provide data sets for comparative purposes, and against which to assess questionable works. In the majority of cases, however, provenance is rarely complete and evidence must be collected after the work has been called into question. In both cases the answer to the question, what constitutes an authentic artwork, relies on the findings of sets of data that are collected according to scientific methods, thus ensuring that the conclusion is sound and based on the evidence. If new evidence is uncovered then the conclusion is reviewed, and may need to be revised. It is the legal context, not the scientific analysis, that will determine whether the issue is one of art fraud or not.

Scientific analysis cannot operate independently of art historical and provenance studies in approaches to unmasking art forgery. Scientific approaches, however, provide the methodology that builds a context in which claims made about a work can be tested. Developing a hypothesis, then testing this by a rigorous process of contestation, is as important in the investigation of art forgery as in any other form of scientific research. Standardised and rigorous documentation, agreed methods of verification, assessing competing hypotheses, and ensuring that all findings and analysis are reproducible, are all important protocols in the investigation of art forgery. In helping to build knowledge of what characteristics constitute authentic works, in providing effective protocols and rigorous procedures, and in bringing together multi-disciplinary intelligence to bear on questions of art forgery, scientific approaches to art forgery have become an essential part of good curatorial practice, effective conservation procedure, and art market diligence. As attested to by the outcomes of a number of recent major art fraud scandals, there would be many more highly problematic works masquerading as originals if it were not for the effective use of science in unmasking art forgery.

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Appendix. Selected case studies of the use of scientific equipment in pigment analysis for attribution studies.

Raman spectroscopy is a useful technique for art authentication studies as it can provide analysis of both organic and inorganic compounds, as well as elemental analysis, and can be completely non-invasive. Raman's high spatial resolution and high spectral resolution makes it suitable for extremely small samples, and when trying to determine the difference between pigments with the same formula but different crystalline structures (Best, 1992, 69) such as the two forms of titanium white, with anatase (first produced in the early 1920s) and rutile (from the late 1930s) (MFA, 2016).

Researchers at the Harvard Art Museums used raman spectroscopy, SEM-EDX, and LDI-MS (laser desorption ionization time-of-flight mass spectrometry) to analyze pigments in three paintings from a group of thirty-two that were attributed to Jackson Pollock (1912-1956). The analysis indicated a number of pigments that are expected to be found in paintings from the nineteenth and twentieth centuries, such as synthetic ultramarine, cadmium red, and rutile titanium white, but also a number of pigments that were produced in the second half of the twentieth century including a benzimidazolone pigment only available since 1971 (Khandekar et al, 2010, 207) and 'a diketopyrrolopyrrole (DPP) pigment that was first reported by Farnum in 1974 and was subsequently developed by Ciba-Geigy in the early 1980s, coming onto the market in 1986' (207-208). As the works were subjected to conservation in 2002 (204) it was important to determine the sequence of the pigments but the conclusion of the study was that: 'Some of the pigments identified in this study raised questions about the proposed date of creation, 1946-1949, of the three works analyzed.' (210) These included a red paint 'containing PR 112, which as of 1992 had only been marketed for 'a few decades".

> Dark orange paint on MBJPl 4 and red paint on MBJP29 were found to contain PO 43, which was not industrially produced before 1953. MBJPl4 contained a pigment, PY 151, in the orange paint that was not available until 1971. The red pigment, PR 254, included in the brown paint from MBJP29 was discovered in 1974 and came onto the market in 1986. Some media raised similar questions. MBJP09 and MBJPl4 contained media that were most likely not available until the mid-1960s or 1963, respectively. (Khandekar et al, 2010, 210)

GC-MS and in particular Py-GC-MS, which can both provide good results for organic materials, are particularly useful instruments for investigating materials that cannot be readily identified by other techniques, or that require complimentary techniques. In the case of a work in the National Gallery London purported to be by Albrecht Dürer (1471-1528), now known as Workshop of Dürer *Virgin and Child* (NG 5592), GC-MS coupled with FTIR was used to identify two different types of varnish on the work. Analysis revealed that the earliest varnish on the painting contained sandarac, a material that was common in the sixteenth century, and that the layer under the signature contained what was probably 'Kauri copal from New Zealand, produced by *Agathis australis*' (Ackroyd, 2010, 40) and available from the end of the 18th century. An earlier form of copal, manila copal, has not been identified by the National Gallery in paintings before the eighteenth century (42), indicating a later date for the addition of the monogram, and supporting the hypothesis that the claims of the work being by Dürer were not correct. The GC-MS results,

combined with other forensic investigation, indicated that the panel is likely to be by a number of hands, perhaps from the Dürer workshop, and later strengthened with a Dürer monogram after the late 18th century.

Another series of works produced in the Netherlands are the Van Meegeren fakes, sold as Vermeers, in the middle of the twentieth century. In 1975, results were published on the use of pyrolysis gas chromatography to verify Van Meegeren's account of how the hard paint layer, which simulated centuries old oil paint, was produced. The analysis of material from the Van Meegeren studio, and from works purported to have been faked by Van Meegeren, 'confirmed irrevocably that the binding medium in these samples is identical to the synthetic resin Van Meegeren stated he had used' and demonstrated that this material was a polymerized phenol formaldehyde synthetic resin (Breek & Froentjes, 1975, 188).

Some of the most difficult art materials to analyze are the large number of contemporary paints that are manufactured using organic dyes and pigments that are bound in organic media. Many of these colourants are strong tinting agents, but have small particle sizes and are often found in low concentrations. They are therefore difficult to identify with many standard techniques including optical microscopy. In addition, new technology is continually producing new colourants and media (Russell et al, 2011, 1473). These issues make GC-MS a useful instrument for analysis of contemporary artworks, and Py-GC-MS particularly useful. In a 2011 study Russell et al used the technique to examine paints used by Francis Bacon (1900-1920). The researchers were able to simultaneously identify synthetic organic pigments and synthetic binding media in five securely provenanced samples and one from a work attributed to Bacon. In order to have a set of reference samples they collected over 70 synthetic organic pigments from a range of sources, including the Tate. These included azo pigments the first of which was in production in late nineteenth century; diketo-pyrrolo-pyrrole pigments which from the 1980s; the commonly used phthalocyanine pigments first introduced in 1935; isoindolinone pigments dating from the 1960s; and perylene pigments produced as artists' pigments in the 1950s. Samples of around 0.5mm in diameter were analyzed using Py-GC-MS, with SEM-EDX, FTIR and polarised light microscopy also used to identify the pigments. Paint flakes collected from works by Francis Bacon (at around 0.2mm in diameter) were also analyzed. What this studied demonstrated is that for a range of otherwise difficult to analyze organic materials found in contemporary works 'pigments found on works of art can be matched with pigments in paints from the artist's studio, or other known works by the artist, using ... Py-GC–MS' (1490).

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