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14. Transferable Mass Spectrometry Methods: Examination of Authenticity in Artwork

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ABSTRACT/WEB SUMMARY

This chapter discusses the use of mass spectrometry for the authentication of artwork and its transferability to forensics. The general process for art authentication is first discussed. An overview of the main mass spectrometry techniques that are currently used for art authentication is provided, along with commentary on the associated sample preparation and the data that can be obtained. Five examples of real authentication cases, where mass spectrometry techniques were used, are reported with lessons learnt. Finally, the potential for the use of these analytical techniques during criminal prosecutions involving art is discussed, but the numerous challenges that one may encounter are also highlighted.

14.1 An Introduction to Art Authentication

The general approach to the authentication of art (with particular reference to paintings) generally consists of four steps namely: (i) signature verification, (ii) review of the historical documentation, (iii) collection of new and/or review of existing scientific evidence, and (iv) expert appraisal.

Though signature verification is usually the first step, the practice of the artist signing their work is fairly recent. It started around the 15th century as a signifier of completed work and sometimes a record of time, place and medium were added too. It therefore started out as a practice for artists to keep track of their work. Signature verification is a seemingly simple matter of reference matching using a loupe or microscope and a reference book with known and verified signatures. However, there are some additional aspects that need to match as well. Some artists tend to sign all of their works in the same location, e.g. lower left corner, *cartellino* style, hidden under the frame, on the back of the canvas, etc. Signatures also evolve over time so they could also be used to help date a work or establish a forgery if the painting style does not match the signature for that period. The materials used should ideally also match known references. Signature forgeries tend to fall under two categories: either an entire painting is a counterfeit or the signature of a more famous artist is added to an existing piece in order to increase its value. In the former case, an important feature to examine is the fluidity of the signature as it is surprisingly difficult to sign someone else's signature in one smooth motion. In the latter case, the *craquelure* can also be investigated, because that should have developed after the signing of the painting. In addition, pigments oxidise and fade over time so UV light could be used to check for a notable difference in pigmentation between the signature and the rest of the painting. A floating signature, i.e. one applied on top of the varnish, is also an indication that a forgery, has taken place, although some artists have been known to sign their works in this way. A forged signature does not necessarily mean the intent is criminal either. For example, in the case of *Children in the Breakers* (Jozef Israels, 1877), the signature of Bernard Blommers, one of Israels' students, was supposedly added during

Royal Society of Chemistry – Book Chapter Template

the Second World War in order to hide the fact that the painting was made by a Jewish artist and prevent it from being destroyed.

If no anomalies are discovered during the signature verification, the next step is an investigation of the provenance. Provenance is the record of ownership of a movable piece of art. In essence, the provenance accounts for the whereabouts of a work from the time of its creation to the present day. When buying from a present-day artist, one will normally receive a certificate of authenticity (COA) signed by the artist that will contain physical details of the painting such as style, subject, signature, materials, dimensions, frame, etc. Some artists are known to employ security printing technology for their COAs, similar to those used for banknotes, to prevent forgery. In the case of an older painting, the artists will have been deceased and the buyer will receive a sales receipt from the gallery at which they bought it. Apart from the physical details of the painting, a list of previous owners with supporting documentary proof is expected to be included, as well as any information regarding exhibitions the work might have been displayed at and a bibliography of catalogues it might have featured in. The nearer a work's pedigree approaches an unbroken provenance, the safer the purchase. A truly unbroken provenance is quite rare, but there are works of art that can boast it. One example of that can be the *Ecce Homo*, painted by the Venetian painter Titian, that he personally gifted to King Charles V in 1548. The painting has remained in Spain since then, becoming a part of the Royal Collection of the Prado Museum in Madrid in 1821. Documentary proof of ownership can be very varied in format and again needs to be corroborated.

Section 14.3.3 provides an excellent example of how mass spectrometry can be used for historical document authentication. Examples include bills of sale or sales receipts, auction records, wills or diaries, historic photos, but also documents discussing the work such as inventories or *catalogue raisonné*. In this regard, the back of a painting can also be very informative because it can feature exhibition marks, dealer stamps, gallery labels, shipping labels, etc. The reader can probably guess that there is one period in particular where provenance can be lacking, namely the Nazi era and the Second World War. Looting of course

also happened during many prior wars, but the Nazis did it systematically and on a larger scale than ever before.

After an investigation of the signature and provenance, collection of scientific evidence follows. Analytical techniques such as optical microscopy, various spectroscopy methods, X-ray fluorescence, etc. have all been successfully used for art research and authentication. Section 14.2 provides an overview of the mass spectrometry techniques used in art research along with commentary regarding sample preparation and mode of operation. Every technique will have its own requirements, but the guiding principle is that any technique used needs to be as non-invasive and non-destructive as possible, because of the unique nature of the research specimen. Mass spectrometry is by its very definition destructive, but it delivers molecular information and does not require a lot of sample material. In the case of imaging mass spectrometry, it is also possible to sample small cross-sections of paintings from areas that are unseen, e.g. underneath the frame, or already damaged and destined for modification during a restoration. The decision to use any particular technique will always be made following a cost-benefit analysis and the same applies for mass spectrometry. Section 14.3 consists of a collection of historical examples of the use of mass spectrometry to determine authenticity. In general, forgeries are identified by means of anomalies. When investigating the ingredients of a painting, one can for example identify anachronistic pigments. Section 14.3.4 tells the story of the famous forger Han van Meegeren who sold a fake Vermeer to Hermann Göring and later had to rely on scientific evidence in court to be exonerated of treason. He had used Bakelite, invented in 1907, to speed up the hardening of his paint layers, which, of course, should not be present in a 17th century painting. If the forger were to use the exact same materials as the original artist, a large age difference would be observed, through the absence of degradation products. In general, it would be correct to say that scientific evidence can be used to prove something is not contemporary or that it contains ingredients that the artist was not known to use. The claim that a certain piece of art was made at a time

by a certain artist can be therefore disproved by scientific evidence, but a positive proof can never be given.

Therefore, when all data have been collected, an expert will appraise the painting or artwork by examining the totality of the evidence. It is important that the expert is at least specialised in the style and period or, better yet, in the particular artist. Art authentication is unquestionably a difficult, multidisciplinary process. Ironically, the best forgers can be considered experts in their subject, rendering the authentication process a battle between specialists. Section 14.4 explores the potential relations between art and crime further and lays out the potential and challenges in the context of forensics.

14.2 Mass Spectrometry Techniques and Instrumentation Used to Investigate Authenticity in Artwork

14. 2. 1. Investigated Materials and Related Techniques Specifications

Analytical science is a valuable tool in the authentication process, provided one understands its capabilities and limitations. To derive meaningful information about the original or non-original nature of a piece of art, an in-depth knowledge of the materials used by the artist must be combined with confidently identifying a given material in a complex mixture. The usual analytical uncertainties and the ambivalent results likely to be encountered in complex historical samples can make for a challenging interpretation of the data. The results are later used by conservation experts with varying knowledge levels of analytical science; as such, the analytical information that is disseminated should be as conclusive as possible in order to prevent any misunderstandings when all the evidence is pooled together.

Since the 1950s, conservation science has been increasingly interested in using analytical techniques to obtain reliable information regarding the composition, structure, and evolution over time for various historical materials.^{1,2} These include structural materials including stone, wood, clay, marble, or substrate materials such as paper, canvas and fabrics, also metals,

minerals like pigments or gems, organic dyes, organic materials like oils, resins, egg, glues, wax, used as cohesive binding material, and exogenous pollutants, biological contaminants, pests, and modern variants of these materials. The structure of paintings, one of the most familiar heritage objects, illustrates the diversity of materials employed in artworks. They are built by stacking paint layers, composed of organic binder(s) containing dyes and pigments, over a substrate, e.g. wood and woven canvas made with vegetal fibres, which are then all covered by several resin-based or modern acrylic varnishes.

Due to their invasive nature, the application of analytical techniques to artwork is in fact a rare opportunity. Studies have highlighted good practices and limitations to consider when using analytical techniques to examine artwork, including sample preparation and data treatment. The analysed area should ideally be representative of the whole artwork, but this is seldom possible because of the value of the artwork. Often, submillimetre-sized samples are taken from historical objects of several square metres. Once the object is sampled, a selection of invasive or even destructive analytical techniques can be combined, but the excised sample must be kept as intact as possible to ensure other analyses can still be performed afterwards. If no sample can be taken, for example when the materials are too fragile, too valuable, or when no consent is given by the curator, only non-invasive techniques can be considered. Obtaining prior consent for sampling is very important. This is illustrated by the collections of the crown of Liechtenstein, none of which are allowed to be lent to exhibitions in France after the events occurring in 2016 during an exhibition in Aix-en-Provence (France) and reported in **Section 14.3.1.**

These small samples are often also spatially heterogeneous and composed of both organic and inorganic compounds. Mass spectrometry-based techniques have proved to be a powerful tool to identify and characterise many materials, in particular organic substances as shown in recent literature³. The following subsection describes some of the most frequently used mass spectrometry techniques for the examination of authenticity of artworks, although it is important to remember that these are almost never the sole analytical technique

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employed, as illustrated in **14. 3. 5.** **Table 14.1** compares specifications for these techniques that are relevant for artwork authentication. Reporting times for these techniques applied to heritage samples are difficult to estimate, as they are not standardised and strongly sample-dependent. Each sample is unique and has its own unique issues of limited immediacy; acquiring and processing the data may take years.

14. 2. 2. Separation Methods Coupled with Mass Spectrometry

Separation techniques such as gas or liquid chromatography, coupled with mass spectrometry, can identify multiple organic compounds in complex samples. The analysed compounds are carried by a gas or liquid phase and separated by their relative affinity to a stationary phase, before being identified by mass spectrometry.

Gas chromatography – mass spectrometry (**GC/MS**) and its coupling with pyrolysis (**Py-GC/MS**) stands out as a widely used technique when analysing organic materials in historical artefacts. Its application has yielded a large amount of the knowledge acquired over the last decades regarding chemical composition, chemical structure and behaviour of organics found in art materials.^{2,4,5} Both techniques can identify oils, carbohydrates, waxes, resins, synthetic paint and polymers, dyes, plant material, and even proteins³. These instruments are characterised by high mass resolution, sensitivity, reproducibility, speed and ease of operation. However, GC/MS requires extraction and derivatization steps, while Py-GC/MS allows one to analyse solid samples directly with minimal preparation. Liquid chromatography – mass spectrometry (**LC/MS**) offers similar advantages although controlling the liquid phase parameters adds more complexity. It also requires sample-specific preparation steps to analyse historical proteins, dyes, or plant extracts, and to characterise materials of natural origin.^{6,7}

Because of the limited amount of historical samples available and the variety of mixed compounds, GC/MS and LC/MS sample preparation steps have been specifically optimised to gather comprehensive data about important organic materials for heritage samples. In

particular, to further characterise historical proteins, protocols have been developed for the identification of a selection of proteins of interest in their chemical environment, pigments for instance, while considering their degradation state.^{8,9,10}

[Table 14.1 near here]

In the case of paintings, to access the individual composition of layers of a few tens of micrometres in thickness, these layers must first be mechanically separated. A careful sampling procedure with a blade under a microscope ensures the collection of only the target material without residue from the surrounding layers. In this manner, localised chemical information can be obtained with sensitive techniques.

In addition to the molecular identification of the organic materials, these three techniques (GC/MS, Py-GC/MS and LC/MS) also yield quantitative information, which is relevant when investigating artistic techniques for authenticity research.¹¹ The relative quantity of a specific compound, combined with molecular and structural information, can help to trace back the original materials. Dyes or resins for instance contain molecules in different proportions depending on their nature and geographical origin. In the case of binding media (oils, resin, or glues), GC/MS and LC/MS data have been correlated with preparation processes, ageing and state of degradation.¹² In paintings, these results can be reviewed and compared with historical facts about the alleged artist's working technique, along with the alleged age of the binder and other observations made on the painting surface like the *craquelure* (cracking pattern) induced by the ageing process.

In summary, separation methods coupled with mass spectrometry are routinely used to obtain a good understanding of the organics found in artworks, specifically regarding their nature, state of degradation and relative proportions.

14. 2. 3. Accelerator Mass Spectrometry (AMS): Determining the Age of the Materials

Even with the necessary materials and mastery of the technique to imitate a past artist, hiding anachronism and harmonising the ages of each component found in the structure are difficult issues to tackle when forging an artwork. Therefore, dating techniques are often involved in authenticity investigations. An inconsistency in the ages of materials, supposed to have been prepared at the same date, offer incriminating evidence or clarifying information regarding the artist(s) hand(s). If a part of an artefact has a different look or composition from the rest of it, authenticity is doubted. This also occurs if the whole object has a different look from an expert eye compared to what is expected, given its alleged nature. The dating information helps to distinguish between several possibilities: a modern forgery, if a part is completely anachronistic, or a copy made by another workshop member at the time, or by another painter (or historical forger) much later, the latter's designation as "copy" or "forgery" being debatable.

Materials analysis can identify a specific ingredient that can be delimited in time, or that comes from a specific place.¹³ This indirect way of placing the artwork in historical context is limited to time periods and rely on the known documentation about the use of artistic materials. Moreover, it cannot be excluded that a natural pigment from a specific period is retrieved and used in a forgery.

The age of historical organic material is harder to simulate. Binders in paintings must be applied fresh and then cured. Whether the binder is a triglyceride-rich oil, triterpene resin, or a proteinaceous material, the way these substances harden, dry and then age are complex chemical processes that change their properties, optical behaviour and composition over time, often over centuries. Consequently, a binder applied in the 20th century cannot possibly have been taken from a historical painting and reused. Even if there are suspicions of artificial ageing through observations and chemical composition results, this will not provide the actual date at which the object was created, which is relevant information when investigating the source of a forgery. Radiocarbon ¹⁴C (radiometric) dating can address this question, as it can provide absolute dates, including for objects realised in the 20th century. Calibrations

according to specific conventions have been defined to homogenise the dating results over years.¹⁴

The sampling step is a crucial point, because the method is sensitive to any carbon-containing contaminant. Often for artworks, the underlying support frame has been used for dating purposes because of the large amount of matter needed for radiometric dating. An order of magnitude of grams was required until the 80s. However, even if the artwork support frame has the alleged age, it could still have been taken from non-famous artworks of the correct period and re-used after removing other materials. The support can therefore be older than the art composition on top of it, or younger in the case where a major undocumented restoration (like relining, moving of frescos, reweaving) took place.

Identifying the age of smaller parts of an artwork has been a challenge over the last few decades. A breakthrough in the dating technique occurred around 1980. By separating ^{14}C from more abundant isobaric interferences (^{14}N or $^{12}\text{CH}_2$), thanks to high energy acceleration before mass detection, Accelerator Mass Spectrometry (**AMS**) can detect low ^{14}C concentrations and $^{14}\text{C}/^{12}\text{C}$ ratios down to 10^{-15} .¹⁵ AMS therefore requires much smaller quantities of material than radiometry, down to micrograms, which overcomes the limitation of radiocarbon dating for small samples.^{1,14}

As described in recent literature,^{16,17} sample preparation for AMS is a challenging step to ensure that the measured proportion of ^{14}C is only correlated to the materials of interest. It involves identifying and removing sources of foreign carbon contaminants with different ^{14}C ratios, and then isolating the specific carbon fraction that represents the age of interest in the given sample. This depends on the characteristics of the original environment of creation for each material and on all the history of its storage. In the context of heterogeneous historical samples that enclose several diverse sources of carbon (like carbonates, carbohydrates, wax, varnishes, etc.) sample treatment must be adapted accordingly with selective extractions and

washings. The obtained treated sample is ready for AMS analysis after combustion and/or graphitization.¹⁸

By combining the accuracy of the ^{14}C dating method with the increasingly smaller quantity of the required sample, dating paint layers separately becomes possible.¹⁹ More precise time windows for the age of a painting can thus be obtained, but also for diverse types of artefacts. Nowadays, determining the ages of various binder/pigment mixtures is an active field of research.²⁰

14. 2. 4. MALDI-MS: Characterising Common Biomolecules and Polymers in Artworks

The principle of Matrix-assisted laser desorption/ionisation mass spectrometry (**MALDI MS**) relies on laser generated ions in the gas phase from a sample coated with a matrix, which aids the intact desorption and ionisation of molecules. The main advantage of MALDI-MS is the possibility to produce molecular ions and heavier fingerprint fragments for larger molecules, allowing for the identification of various polymers, triglycerides, phospholipids, carbohydrates, or proteins, all found in artworks. MALDI-MS has been widely used to characterise heritage materials, making it a valuable technique that can access detailed information about proteins and historical or modern polymers.^{21,22}

MALDI-MS requires sample treatment and preparation, as the fraction of interest must be extracted with a procedure depending on its nature and chemical environment. The residue is mixed with a solution of the chosen matrix compound and deposited on an analysis plate where they crystallise together. Matrix molecules will be present in large excess, surrounding the analytes thus protecting them from the direct impact of the laser and preventing fragmentation by absorbing the laser energy. The quality of the spectral information will largely depend on the quality of the matrix-analyte co-crystallisation.

MALDI-MS imaging (MALDI-MSI) is a powerful technique combining the above-mentioned detection/identification possibilities with surface imaging with a spatial resolution of around 10

μm . It is rarely applied on heritage samples, due to the necessary alteration of the matrix deposit and because the spatial resolution is often above the dimensions of interest in art samples, like paint layers. Recent developments push limits of resolution down to $5\ \mu\text{m}$ even with non-flat samples, providing MALDI-MSI with even more assets to analyse heritage samples.²³

14. 2. 5. SIMS: Reaching the Spatial Chemical Information

The microscopic scale impacts the composition and structure of the whole object. When investigating artworks, small samples can be used in combination with GC/MS and AMS to provide somewhat localised data, but mass spectrometry imaging can chemically map a sample surface.

Secondary Ion Mass Spectrometry (**SIMS**) and more specifically Time-of-Flight Secondary Ion Mass Spectrometry (**ToF-SIMS**) has become an increasingly attractive technique to study heritage samples over the last decades. The strengths of this surface imaging technique are the simultaneous detection of both molecular and inorganic compounds, a high sensitivity for all elements, and retention of the spatial information on the surface at the micrometric scale. The surface is impacted by a focussed beam of high energy (e.g. 25 keV) polyatomic primary ions, and the produced secondary ions are identified according to their mass to charge ratio (m/z) in a time-of-flight mass analyser. Spatially resolved data is particularly relevant when analysing sub-millimetric cross sectional samples taken from heritage samples, which are composed of a wide variety of complex heterogeneous materials. Current ToF-SIMS instrumentation also combines high mass resolution with high spatial resolution, thanks to delayed extraction²⁴. The use of ToF-SIMS instrumentation to analyse heritage samples has been exhaustively described in a paper written by authors of this book chapter.²⁵ The limitations, and requirements of its application to historical, heterogeneous, and unique samples are discussed with a special emphasis on instrument parameter optimization.²⁶

Secondary ions produced from large molecules during a ToF-SIMS analysis are fragmented, limiting their unequivocal identification. **MeV-SIMS**, a modern version of the Plasma Desorption Mass Spectrometry (PDMS) technique developed in the 70s and up until the 90s, allows an ionisation with a MeV primary ion beam, along with equivalent secondary ion yield.^{27,28,29} The number of MeV-SIMS applications in the context of artworks characterization has been increasing since a few years.³

The growing shared knowledge about the secondary ions expected for a given material at a given state of degradation enables ToF-SIMS to become a more mainstream analysis technique. Having a dataset that contains the spatial distribution of pigments and associated molecular information about organics is very valuable to better understand how a painting was made, has aged, and has been preserved. In the case of artwork authentication, it offers an extensive overview of each part of the sample's microstructure at once.

ToF-SIMS and MeV-SIMS both have simple sample preparation procedures. The challenge is to obtain a surface that is flat and free from contamination. Several techniques can be applied on heritage samples, depending on the sample characteristics and the question to be addressed. Polishing or microtome cutting are the most used sample preparation techniques. Samples must have small dimensions and be in solid state or be very viscous like a solidifying oil film.

Mass spectrometry Imaging provides a deeper understanding of the identified chemical's distribution on the surface or across the material's bulk, down to the micrometric scale, including the localisation of degradation products, informing about relative states of preservation. In the examination of authenticity in artwork, the spatial resolution, the high sensitivity and mass range, and the possibility to identify inorganic materials make ToF-SIMS imaging a powerful tool to detect, characterise, and localise incriminating impurities trapped inside a sample taken from a questioned artwork. As previously stated, to avoid hasty

conclusions, a thorough examination and evaluation involving multidisciplinary expertise is then needed to define a possible origin for identified compounds.

14.3 Historical Examples of the Use of Mass Spectrometry in Art Investigation

The following section presents examples of authentications and legal cases where the application of mass spectrometry played a role. The interested reader can of course find other cases in the literature.^{30,31} Investigations can take years or decades and are very complex so mass spectrometry sometimes covers only a small part of the investigation as a whole.^{15,32}

14. 3. 1. A Complex Investigation Process: an Instructive Recent Case

Continuing advances in analytical science help tackle authentication problems, but the latest analytical capabilities are unlikely to be applied every time an artwork is exchanged. In parallel, available and routinely used analytical techniques become easier to deceive by educated forgers. Various experts may also deliver outright contradictory results, while analytical investigation can yield inconclusive data. This partly explains why identifying a forgery can take decades in some cases before reaching a formal and final conclusion.

This still-open case, further outlined in a recent book³³, illustrates today's authentication process. It involves a masterpiece attributed to Cranach that has to date been proved to come from a series of alleged forgeries sold by art dealer Giuliano Ruffini. When the painting was first sold, both provenance and signature were sufficient to deliver an authentication certificate, even if some experts noted anomalies and expressed circumspection, suggesting the need for additional dating tests. Therefore, from the beginning of the validation process, there were some doubts concerning authenticity. Earlier, a reputable auction house was presented with the painting but found that it had enough questionable elements to suspect an anomaly and therefore required scientific examination before any transaction took place. The investigation highlighted enough troubling facts to dissuade the house to put it up for sale. At a further stage, imaging studies were suggested to examine the sub-layers and drawings, but these were

never performed. Hence, the painting continued its journey supported by the positive assessment of renowned experts, until it was eventually acquired as part of the Royal Collection of the Crown of Liechtenstein. A second auction house, Sotheby's, eventually analysed the painting and, interestingly, the team stated that if they had not specifically sought to check if the painting was a fake, they would have missed the analytical information. This case shows that the usual approach can prove insufficient, or that, if the artwork is presumed to be genuine, bias causes one to miss what reveals the forgery.

After forgery was suspected, the painting was taken away to be analysed. Multiple analytical techniques were applied by both parties involved during the comprehensive additional investigations, either attempting to prove forgery or authenticity. At one point, GC/MS and FT-IR analysis of the binders from an alleged Brueghel also sold by Ruffini, showed the presence of 20th century materials in several layers, such as polyurethane resin and acrylic paint.³³ One of the key points on which expertise strayed was dating the wooden panel below the painting. Dendrochronology studies led to a set of hypotheses ranging from 1550 to post-1980, keeping in mind that nothing proves a painting has the same age as its support. Because the collection owner prohibited further sampling, ¹⁴C dating was not performed either, which could have allowed discrimination between an authentic past copy and a forgery (see Table 14.2). The disputed investigation so far concluded forgery, stating the alleged Cranach is "*a fake intended to deceive, executed in the manner of Cranach, purposely using materials from the period and treated with artificial ageing*".³³

Amongst the unusual features observed on the painting, lead sulphate protrusions were identified, a phenomenon known to be found in oil painting although in precise conditions yet to be understood. Mass spectrometry has already been applied in the context of genuine painting examination studies aiming at elucidating the composition and structure of similar lead protrusions on paintings, and ToF-SIMS is especially suited to investigate these organic-inorganic features and their distribution in the painting stratigraphy.³⁴ If a link could be established between the facies of these protrusions and their conditions of formation, this

would help in detecting forgeries, in which case SIMS would be a valuable tool in this endeavour, given that microsamples are available.³⁵

This illustrates how an exchange of all examination data between analytical scientists, art experts and authorities is needed for authentication investigations to be conclusive, and likewise, that a difficult exchange both slows and negatively affects the investigation by increasing the expert disagreement on which the fraud relies. Crooks on the art market are aware of how to take advantage of this system. This case also illustrates that analytical techniques like mass spectrometry bring formal results in authentication studies. To that end, fitting the techniques to the constraints of the artwork is mandatory to provide robust data. This case shows the need for developing these techniques as robust tools for routine art authentication.

14. 3. 2. Forgery or Copy? How can Analytical Science Disentangle the Intention of the Executive Hand?

The distinction between a forgery and a copy is discussed in the literature.³¹ The intention defines the fraud of the forgeries, and Table **14.2** classifies some situations. These include a Raphael decreed by the Pope to be given by one ruling family to another, which the former secretly refused and instead sent a copy, commissioned to Andrea del Sarto.³⁶ Hence, today two museums genuinely consider they have an authentic Raphael, while one is a copy made by another Old Master. Fake items found clients in art enthusiasts as early as the 1st century. Nowadays, the buyer is sometimes aware of the fake, for example when artists paint and sell “genuine fakes”,³⁷ copies of masterpieces signed with their name, which are in fact reproductions. It is also important to isolate the case of replica(s) of one painting made in a single workshop at the same period, which had a commercial objective. Conversely, trying to sell an artwork that purposely matches the expectations of scholars eager to find a lost artefact or masterpiece constitutes an intention to deceive. Interestingly, a few famous artists experimented with forgery in their early days, and some, like Michelangelo (1475-1564), even

received further commissions from the duped buyer, who was impressed by his skills. The legal consequences for forgers are equally diverse and rarely very severe, even today. After being exposed in the late 80s, Eric Hebborn edited a few books and appeared in televised programs, as did John Myatt who later even helped the authorities in art fraud investigations.^{37,38} Nowadays, the German forger Beltracchi regularly sets up successful exhibitions under his own name. Some forgers also reached such fame that their exposed forgeries get high prices on the market, so much so that forged forgeries are suspected to exist.

[Table 14.2 near here]

Proving the fraud in judicial cases requires finding and demonstrating who wanted to sell something knowing it was not authentic. Finding who executed the forgery is not enough, because copying something is not illegal if no signature (monogram, watermark, etc.) is forged. In addition, someone else might have added the signature later (see Table 14.2).

Therefore, a careful characterization of signatures is important and benefits from gathering all available knowledge collected throughout the artwork's conservation history. A study related in the National Gallery Technical Bulletin (Vol. 21, 2000) illustrates how long-term expertise combined with analytical science provided decisive information about the genuineness of the signature on a painting.³⁹ *The Madonna with the Iris* (National Gallery, London) was attributed to Albrecht Dürer (1471-1528), with both date "1508" and signature "AD" visible. The signature was not mentioned in a thorough 19th century description in which the date was. The painting also has two sister versions without date or signature. Hence, its attribution has been questioned since 1945. Hypotheses are that either Dürer, or several hands from his workshop with or without his intervention, or a later copyist of Dürer executed it. The latter two options are supported by the many motifs inspired from other Dürer's productions, variable underdrawing details, and the state of preservation depending on the area of the picture.

The “AD” inscription was declared fake in 1958 thanks to visual examination. The paint’s look and texture are unlike the surrounding area and is visibly above a later overpaint applied over scratched paint. In 2000, the analysis techniques that can be applied to paintings had evolved and the wooden support and pigments were proved to be consistent with the 16th century. Microsamples taken around 1958 were still available, and the isolated overpaint layer under the signature could be analysed by both GC/MS and Py-GC/MS. It contains Manila copal, a resin never mentioned in Europe before the second part of the 18th century. Hence, the signature must have been added after 1750, more than two hundred years after Dürer’s death, replacing a scratched signature that is now lost. This was perhaps a deceitful 19th century effort to increase the price of the painting. The hypothesis of other forged parts is excluded, as the paint of the date “1508” contains pigments used before 1750, suggesting authenticity. It was added, likely after the painting was finished, above a slow-drying varnish layer, which is original according to the Py-GC/MS identification. Hence, the artwork must be a genuine production of Dürer’s workshop, executed by several hands at different times over a few years. Only the signature was later forged.

14. 3. 3. Historical Document Authentication with High-Resolution Mass Spectrometry

Forging historical or legal paper documents has been a long-standing practice, motivated by many reasons. Forged documents sometimes had historical implications, like the text entitled *Donation of Constantine*, allegedly from the 4th century and employed until the 15th century to defend the Pope’s influence in Europe, until it was exposed as a forgery of unknown origin by a scholar around 1440.³⁶ The alteration of existing historical records was also illustrated in the context of art history by the tried method of trading forgery by altering archives to establish a false provenance. It is indeed suspicious to try selling a masterpiece by a renowned artist, which has no trace whatsoever in the past. John Drewe, a swindler, applied this to sell the fakes he obtained from an unsuccessful painter named John Myatt, and some of the forged documents he executed and flooded the archives of esteemed museums with many remaining undiscovered today, casting doubt on all that is mentioned.^{36,40}

The motivation can also be direct profit by trading handwritten documents or drawings supposedly from famous artists or historical figures. Eric Hebborn was particularly gifted at this trick, as he sold a significant number of drawings inspired by existing artworks, which he let professional experts misattribute to genuine preparatory drawings by renowned historical artists, when they were all his own work. He eventually was found out because a similar touch (his own) was noticed across the drawings he “discovered” from supposedly different artists. Because he made a point of using historical materials, scientific investigations at the time were unable to reveal the forgeries in the 1970s, perhaps because MS techniques were not yet available for such samples.^{36,38} Paper manuscripts executed with ink, charcoal or watercolour are historical artefacts whose nature complicates the authentication process. This was particularly well illustrated by the case of stolen and forged historical books involving Marino Massimo De Caro, the former director of the Biblioteca dei Girolamini in Naples. Only after he was exposed, it was proven that the manuscript edition of the *Sidereus Nuncius*, a text of major importance for the history of science, in which Galileo Galilei drew the moon for the first time, was a fake, just as it was about to be sold for several million euros.⁴¹

It requires an equally vast expertise to either forge or authenticate paper documents, which highlights the importance of the new analytical advances in the studies related to the actions of Alexander Holland Smith (1859 - 1913), who forged many writings from famous hands, including Robert Burns, the world-renowned Scottish poet (1759 - 1796). This has been known since the end of the 19th century, but most of its work had been dispatched and eluded the scrutiny of experts for more than a century. Found forgeries like those of Smith provide an opportunity to assess the ability of advanced analytical techniques to distinguish fakes from originals. A team from the University of Glasgow recently published an open study presenting an innovative mass spectrometry method efficiently distinguishing original Burns writings from Smith's forgeries.⁴² They used direct infusion mass spectrometry (DIMS) set up, which can work with *in situ* minimally destructive sampling. Liquid extraction was performed in triplicates directly from the manuscript's surface with 2 μ L of solvent using a pipetting tip hovering over

the paper surface. The 8 μL samples were then transferred to a set up equipped with microfluidics chip (Advion Triversa nanomate), allowing analytes to be sent to an Orbitrap mass spectrometer (Thermo Fusion Orbitrap) through direct infusion nanospray with an injection time below 50ms. Quadrupole isolation was used to collect fragmentation data at a HCD collision energy of 60% with a mass resolution of 15,000. This technique combines relatively high mass resolution, and an atmospheric working pressure. Their approach stands out by its simplicity compared to usual ones involving LC/MS or MALDI MS. They were able to isolate a selection of discriminatory peaks expressing significant chemical differences between the manuscripts (ink and paper) of the two writers (Figure 14.1). Specific ions associated with the forger Alexander Smith were identified as a plant metabolite ($\text{C}_{11}\text{H}_{10}\text{O}_4^+$, m/z 207.0654), bis(2-methoxyethyl) phthalate ($\text{C}_{14}\text{H}_{18}\text{O}_6^+$, m/z 283.1178), triphenyl phosphate ($\text{C}_{18}\text{H}_{15}\text{O}_4\text{P}^+$, m/z 327.0782) and $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_5\text{S}^+$, m/z 349.0602. Specific ions associated with Robert Burns were citric acid adduct ($[\text{C}_6\text{H}_8\text{O}_7+\text{K}]^+$, m/z 230.9904), $\text{C}_{11}\text{H}_{10}\text{N}_6\text{O}^+$, m/z 243.0993, $\text{C}_{14}\text{H}_{25}\text{N}_5\text{O}_2\text{S}^+$, m/z 328.1794 and $\text{C}_{21}\text{H}_{24}\text{N}_6\text{O}^+$, m/z 377.2091.

[Figure 14.1 near here]

Most of the peaks associated with Smith's work were linked to the use of infused tea to artificially age the paper, a technique also used by above-mentioned Hebborn,³⁸ and which is likely to be involved in many forged paper cases. According to the authors, their untargeted data analysis to compare both ink and paper opens the path to a wider range of applications in authentication of documents, or even a quick test available for buyer's experts themselves.

Mass spectrometry techniques provide solutions in the field of paper authentication research, where the stakes can be significant. We can also cite the contribution of ToF-SIMS in the characterization of banknote morphology,⁴³ as well as the development of proteomic analysis to further decipher the provenance and authorship of ancient documents and manuscripts through microbial, peptides and protein remains.⁴⁴ This could even help highlight the role of

women in the production of illuminated manuscripts. Advances and perspectives of this proteomic approach have recently been described in the literature.⁴⁵ LC/MS, its coupling with ESI and more recently with ion mobility spectrometry (IMS), are one of the most explored paths, knowing that for ancient materials, nano-LC/MS presents the advantage of allowing a better sensitivity and peak separation than other separation set ups. Thanks to the improved sensitivity of mass spectrometry, minimally invasive sampling methods are developed in parallel, for instance with erasers or gels, to provide sufficient uncontaminated analytes. Approaches relying on MALDI ionisation are also explored for situations requiring limited fragmentation of the analytes.

14. 3. 4. Art Authenticity and Conflicts: Looted Art and Exonerating Forgery

Cultural sites and historical artefacts have highly symbolic value and are among the first targets of war, while art trafficking is a significant resource for armed or criminal groups.³⁶ Artwork authentication thus goes beyond academic debates, as it tackles a challenge of international significance that is tracing artefacts looted from archaeological sites or during wars. In modern history, a vast amount of European art was stolen from personal owners, collectors, or museums by the Nazis during World War II. Such artworks entered the art market without apparent evidence of their criminal provenance. Hence, verifications are routinely carried out when art auction houses intend to sell or buy.⁴⁶ Whenever a looted artwork is found, even unknowingly bought, it must be returned to its rightful owner. For that reason, the investigation focuses not only on the authenticity of the artwork, but also on the documentation supporting its provenance. Beyond conflicts, forging archives is also an effective strategy employed by forgers, as further detailed in section 14.3.3..

The fate of the long career of Dutch forger Han van Meegeren (1889 - 1947) illustrates the importance of losing an artwork regarded as a national treasure. As most art forgers, he was thoroughly trained in old techniques and started out as a genuine painter. In the 1920s, he was no longer popular with the art critics and had to switch to painting restoration for a living,

before eventually turning to forgery. He took advantage of the enthusiasm of scholars for finding referenced yet lost artworks. He executed original work in the manner of Vermeer, for example, using historical materials, then artificially ageing it, and finally having it authenticated by renowned experts who eagerly saw the confirmation of their hypotheses. His works were convincing enough not to be detected by the authentication techniques at the time, of which he had full knowledge. He developed a lucrative and prolific business from a workshop hidden in the basement of his villa. He painted forgeries series, most of them Vermeers, and earned millions from their trade and sale. His success culminated during the Second World War.

In the aftermath of the German occupation in the summer of 1945, his case demonstrates the leniency of public opinion and the justice system towards forgers, who can even gain a positive image based on how their motives are interpreted. When allies found Göring's war treasure in May 1945, "*The woman taken in adultery*" attributed to Vermeer was recovered, and an investigation to find out who sold a Dutch national treasure to the enemy led to Van Meegeren. He had lived a luxurious life during the war (he made about \$2 million with the various sales), and started out rather unpopular with the public, facing trial for treason and risking the death penalty. Even after stating that the painting was exchanged for over a hundred Dutch masterpieces looted by the Nazis, he was still guilty of surrendering a national treasure to the enemy. He had no choice but to reveal his long-kept secret that the painting was his own creation and a fake. Ironically, his work was so convincing that nobody believed him, so he had an idea to prove that he did it that went down in art forgery history. In front of witnesses, he painted a "brand-new" Vermeer in his cell that was convincing enough to motivate a full investigation of the Vermeer paintings he had sold.⁴⁷ He suddenly became the remarkable man who tricked Göring, even if this sale was almost incidental,⁴⁷ and was convicted of mere fraud in 1947 and received a very short prison sentence. He passed away before serving it. The interested reader may find in the literature further discussion about this case and its implications for authenticity research.^{31,36}

Seven international experts in the physical and chemical examination of paintings gave their conclusions in 1947 after a series of invasive and destructive chemical tests performed on about 30 micro-samples taken from more than ten of his paintings, to reconstruct the working technique layer by layer. These trial's experts revealed the use of an anachronistic materials, a 20th century phenol formaldehyde resin called Bakelite, also found in Van Meegeren's workshop, recognized with chemical tests (Schiff reagent for the aldehyde identification ; red colour characteristic for phenolics after potash and diazo-p-nitroaniline addition ; blue colour after addition of 1% vanillin in sulfuric acid).⁴⁷ It has the property, verified by reconstruction made by experts, of hardening the paint when heated in an oven for a few hours, so that its surface exhibits the texture of a properly cured historical paint. Van Meegeren experimented a lot to achieve this result in his "alchemist's workshop",³⁶ drawing on his knowledge of chemistry and paint examination. This proved both that the Vermeer was not authentic, and that he was the forger. Following this case, described as a "*example of science applied in the service of art*", experts insisted on the urgent need of applying physical and chemical sciences where authenticity is in doubt.⁴⁷ In the decades following his death, analytical science applied to the investigation of paintings improved, allowing new analyses (including MS) to be carried out to seek definitive proof that the alleged Vermeers were forgeries, something not easily accepted by some owners who considered the existing analytical evidence insufficiently conclusive. In 1968, a study found that the isotope ratios in lead white pigment from these paintings indicated that they could not date from Vermeer's time, providing solid scientific evidence.⁴⁸

Later analysis conducted in 1975, including pyrolysis gas chromatography, unambiguously identified the resin in the paintings matching samples from six of the "Vermeers" with a sample of the resin found in Van Meegeren's workshop.⁴⁹ The combined studies provide certainty as to which painting was made by Van Meegeren. Today's range of MS techniques would be able to characterise the materials used by the forger in even greater detail, providing

information which was impossible at the time; increasing the knowledge of the materials he used would help to expose others of his forgeries that might still be on the art market.

Currently, there is a growing discussion about the restitution of cultural artefacts stolen or looted from one country in the past or present, which are now being sold or exhibited in another country. Although not easily resolved, these concerns suggest that the nature of provenance is becoming increasingly significant. Regarding this question, mass spectrometry can play an ambivalent role, as discussed in the specific case of ^{14}C AMS dating.⁵⁰ Only artefacts of verified authenticity can be traded, making accurately dated pieces more valuable. AMS dating can even become a tool for looters, to identify archaeological objects granting them the most profitable transaction on the black market, on which authentic items also have great value.⁵⁰ Both examples show that mass spectrometry acts as a tool in art authentication cases, whether to expose forgeries or to trace historical materials to be recovered or sold.

14. 3. 5. Identifying Artwork and Clarifying Provenance with Mass Spectrometry

The methodology to authenticate a lost Picasso painting again illustrates the role of mass spectrometry, this time to prove an artwork is genuine. Unlike the other examples, the painting, entitled *Violon. Céret*, has no signature, which is not a rare thing for Picasso, but it also has an unknown collection history, no conservation history, and no provenance details. It was never studied, never exhibited, and has damage on its surface. Its style, however, matches that of Picasso at its supposed date of execution, 1912. As it was strikingly only documented once, along with a picture in a well-known catalogue of the work of Picasso edited in 1942, the suspicion of it being a forgery of a lost original painting is fairly understandable, considering the previously described cases. The team studying this painting discussed the methodological approach, combining historical, stylistic, scientific, and technical examination to verify its authenticity in a reliable and thorough way, knowing that “*no final outcome is ever wholly conclusive*”.⁵¹ Indeed, when analysing artworks, no formal proof can indicate with certitude its origin, and only clues and the absence of suspicious elements can be confirmed.

A fluid and constructive interaction between disciplines ensures historical and technical relevance. The painting was visually examined before technical and scientific analyses were performed to gather multifaceted knowledge on the artwork and its constituting materials. Imaging VIS/UV/IR, FORS, FTIR, XRF, SEM-EDS, Py-GC/MS, HPLC/MS were performed. The visual examination showed paint damages due to the folding of the canvas and an ill-performed regluing of the original canvas on another support. The elements found in each part of the stratigraphy then made it possible to distinguish the non-original materials from the original. Mass spectrometry played an important role in the study. The material used between canvas was identified using Py-GC coupled to a quadrupole mass spectrometer as a mixture of egg and animal glue, thanks to characteristic ions found in recent literature regarding organic binders **[Figure 14.2 near here]**.⁵²

An original triterpene resin was also identified using Py-GC/MS in the dark regions of the original paint surface.⁵¹ This specific brown substance was available in 1912, and Picasso mentioned a brown pigment he was currently using in a letter to his art dealer when he was in Céret, where the name of the painting comes from as it is suspected to be a part of a series painted there.⁵¹ Hence, an objective clue indicating that Picasso executed the painting was obtained by combining documentation and historical facts with analytical data that could be interpreted as a specific resin.

Authentication research is impacted by historical and modern artefacts. Painting materials underwent a commercial revolution during the 19th century, when tube paint became available to painters, replacing colour merchants or workshop production. In the case of modern paintings, materials are much more diverse, most of them commercially purchased. In this study, HPLC-ESI-Q-ToF helped characterise the lipids found in the binder of the original painting. A series of oxidised triglycerides with unsaturated chains and hydroxyl groups were confidently identified, which match the spectral profile of a highly oxidised linseed oil, a fat especially rich in unsaturated fatty acids. The possibility of it being modern house paint was ruled out thanks to knowledge about their distinctive look and pigment composition. The

information gathered by the approach granted the painting to be officially authenticated as an original Picasso, dated 1912. Regarding the mysterious past of the painting, further studies are awaited.

Another aspect of historical artefact examination in which mass spectrometry plays a valuable role is isotope analysis, for instance using radiocarbon dating, AMS or inductively coupled plasma mass spectrometry (ICP-MS). Depending on the fabrication and conservation of an artwork, or a material in the artwork such as a specific pigment like basic lead carbonate (lead white), the isotope ratios will vary. Background data gathered about the ratios for relevant places, materials, and deposits, a sample can be matched with a given provenance. This provides insightful information regarding provenance of antique or historical artefacts, or raw materials used in later objects, by combining the data with documentation and knowledge about history, the artist's life, trade of raw art materials and geological facts. This can help rectify misattributed artworks or artefacts such as decorated ceramics traded during the 16th century.⁵³

14.4 Potential and Challenges for Forensics Applications

The Art Basel and UBS Global Art Market Report 2023 estimates that the international art and cultural property market generated a staggering \$67.8 billion in 2022, roughly the GDP of Tanzania.⁵⁴ Due to the global art market being somewhat opaque, i.e. subject to many different jurisdictions and under-regulated, and certainly inadequately enforced, it is vulnerable to a host of illegal and lucrative activities. We will focus on crimes where art authentication can play an important role, which we can split into two categories: stolen goods and false goods.

Cultural artefacts are protected by international treaties that states sign and ratify such as the Hague Convention for the Protection of Cultural Property in the Event of Armed Conflict.⁵⁵ In total, 134 states ratified the 1954 Convention for the Protection of Cultural Property in the Event of Armed Conflict. There is also Article 8(2)(b)(ix) of the Rome Statute of the International Criminal Court, which makes it a war crime to deliberately target historic sites or

buildings dedicated to art for destruction or defacement.⁵⁶ There is also the UNESCO 1970 Convention on the Means of Prohibiting and Preventing the Illicit Import, Export and Transfer of Ownership of Cultural Property, which gives member states the right to recover stolen or illegally exported cultural property from other member states and is currently ratified by 142 states.⁵⁷ It also led to the establishment of subsidiary bodies which help implement the treaty and settle disputes. Besides these international treaties, every country has their own national laws governing the sale, import and export of cultural heritage items. Additionally, most countries have laws regarding possession of stolen goods, which would also include cultural objects removed from a country without permission from its legitimate government. In general, the sale of stolen goods does not pass good title so an unsuspecting purchaser down the line would not legally possess the item: "*Nemo dat quod non habet*". If one follows the laws of the country of origin regarding retrieval, transport and sale of archaeological artefacts and cultural heritage, the trade is generally legal. A merchant could prove this by providing a valid export certificate for example.

As mentioned in the introduction, the Nazis looted priceless works of art and antique objects from museums and stole property of the people they murdered. These events were the impetus for the international treaties mentioned, but the reader should not be fooled in thinking this is all a matter of the past. In 2016, the International Criminal Court (ICC) first cultural destruction war crime trial was held at the request of the State of Mali to pass judgement on the destruction of mausoleums in Timbuktu in 2012 and sentenced Ahmad al-Faqi, a member of the Islamist militia Ansar Dine, to nine years' imprisonment.⁵⁸ In August 2015, the Islamic State destroyed the Temple of Bel in Palmyra. They can be tried under Syrian and Iraqi Law, but a body such as the ICC is much less amenable to corruption and intimidation. Unfortunately, neither Syria nor Iraq has accepted the jurisdiction of the ICC, which means it is unlikely the perpetrators will stand trial for their acts of cultural genocide by destroying UNESCO World Heritage sites.⁵⁹ The Islamic State also ransacked historical sites and museums to steal and then sell valuable cultural heritage items in order to help fund their self-

proclaimed government. This reportedly brought in an annual revenue from a few tens of millions up to \$100 million.⁶⁰ Ukraine has accused Russia of violating the 1954 Convention for the Protection of Cultural Property in the Event of Armed Conflict during the ongoing Russian invasion of Ukraine. Ukraine's Ministry of Culture reports that Russia's forces have damaged hundreds of sites and objects important to Ukraine's history and cultural identity.⁶¹ Reports have also surfaced that Ukrainian museums in occupied territory have been looted by Russian troops.⁶² Again, the motivation appears to be both acts of cultural genocide and financial gain.

Other than theft in conflict areas, criminal organisations also target museums, galleries, churches, historic sites and private collectors, attracted by high-value items in not always secure environments. These items then find their way to the market and can fund other criminal activities. Famous works of art might be difficult to traffic and sell, however. There are databases one can consult such as the National Stolen Art File (NSAF), where law enforcement agencies in the U.S. and abroad submit stolen objects, and the Stolen Works of Art Database, where INTERPOL and specific international partner organisations such as UNESCO, and ICOM and ICCROM submit stolen objects.^{63,64} The famous works can be ransomed or used as an alternative currency in the criminal milieu, but it has been suggested these might also be kept as collateral in exchange for reduced sentences once members of these criminal organisations are caught. It is important to bear in mind that some of these thefts could also be crimes of opportunity in which case the thief likely does not know what to do with their stolen goods.

As mentioned, these stolen treasures often end up on art markets and subsequently become part of private or museum collections. The complicity of actors in the art sector is an essential factor to launder these stolen goods, e.g. by providing false export certificates and forging provenance documents. Once introduced to the legal art market, these objects become very difficult to identify, and art galleries and museums are caught having stolen artefacts in their possession with some regularity. The black market for art and antique objects is estimated to generate billions and is known to help fund wars, terrorism and various other activities such

as the illegal arms or drugs trade. It should be clear that there is a role for authentication and specifically the determination of the origin of art objects in the context of forensics.

Art forgeries are another area where authentication could play an important role in forensics. However, most criminal investigations and prosecutions focus on stolen art, because there is clear proof a crime has been committed. Replicating art in and of itself is not a crime. There also needs to be proof of intent to commit larceny or fraud by deceiving another party into thinking the work is original. There are different ways a forger can go about it: one can recreate a lost painting or work of art, forge a hitherto undiscovered piece of art, modify a contemporary piece and/or falsify its provenance to increase its value. These forgers are experts on subject matter experts and often as (or even more) knowledgeable than authentication experts themselves, making it very difficult to identify these falsifications. Forgery is a longer-standing craft than scientific analysis of artwork, and forgers are skilled artisans. They use and develop ways to work materials to create something matching the expected style, age, and technique, and try to make their forgeries pass expert examination. For that, they must be well-informed about the art history, the validation process, the techniques, the lives of the artists and any stylistic evolution. They also must stay up to date with the advances in scientific examination of the art they are forging. For example, Han Van Meegeren was very aware of the latest advances and literature in the field and carefully produced paintings for which he predicted forgery to be undetectable using scientific techniques at the time. Beltracchi even executed a fake painting specifically to ask for it to be analysed by a specialised laboratory to find out what needed to be corrected before trying to sell one. Modern art in particular seems vulnerable to forgery, because its value is not so much derived from its intrinsic quality rather than the identity of the artist. Consequently, while researchers develop increasingly comprehensive analytical approaches, forgers learn about them and try to adapt. This raises the question of the necessity of discretion. In parallel, scientists explore exposed forgeries to develop identification approaches, as shown in part 14.3.3., or apply several analytical techniques on it to highlight how each technique can contribute.⁶⁵

The forged paintings then need to enter the art market, which means the forger needs to have established good connections to agents such as art dealers, auctioneers and art experts. This can be achieved through prior *bona fide* trade and thus building trust, or by seeking out individuals willing to partake in a conspiracy. In addition, things are often not very clear-cut. An art dealer or auction house might be too eager to get their commission of a sale and not do their due diligence. Alternatively, upon identification of a forgery, they may opt to withdraw the item without alerting the authorities in order to avoid damage to their reputation. It is not clear how many forgeries circulate on the art markets, but it likely makes up a larger share of art crime than theft. Even buyers might not want to identify their purchase as a forgery due to the negative impact on their investment. Experts who wrongly authenticated such forgeries might also be reluctant to admit mistakes.

In the event a forgery is identified, criminal prosecution is possible under laws against fraud. In many cases, criminal prosecution does not take place due in part to high evidentiary burdens. There needs to be criminal intent beyond a doubt and many parties involved can claim they were unaware the piece was a forgery. The forger can even play it off as an elaborate joke or hoax. Instead of a criminal prosecution, the matter often ends up as a civil case where plaintiffs are trying to recuperate their losses. A final reason why criminal prosecution might not always take place in the case of forgeries is a lack of expertise. As mentioned, theft is usually clear-cut and law enforcement agencies know how to handle such cases. Nonetheless, there have been numerous successful criminal prosecutions involving art fraud.

14.5 Conclusion

Art authentication has evolved and now regularly relies on scientific evidence in addition to signature verification and provenance review. The evolution of the link between analytical science and art historians is fully discussed in the recent literature.⁶⁶ In the last few decades, mass spectrometry has proven particularly useful in authentication studies with different

objectives and in various contexts as illustrated by the examples in section 14.3. Its capability to obtain molecular information and identify organics along with its sensitivity, which limits the amount of sample needed, are particularly useful for the analysis of complex, precious samples such as art. With mass spectrometry's new developments such as AMS dating and notably advanced imaging capabilities which now allow the microstructure of a cultural heritage sample to be investigated, promising and wider applications can be expected. As the example in part illustrated by Section 14.3.5., a technique alone cannot authenticate an artwork and a multidisciplinary approach will be necessary, including expert appraisal.

Given the large amounts of money involved in the global art trade and the current under-investigation of art forgeries, we believe this to be highly needed transferable expertise. We therefore hope this chapter has provided some insights into the role art authentication using mass spectrometry can play in forensics. It is just important to remember that identifying the forgery itself is not enough for a conviction, as intent also needs to be demonstrated beyond a reasonable doubt. There is probably also a need for added regulation for the art markets as well as international alignment, but that is something for legal experts and lawmakers to determine.

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FIGURE AND TABLE CAPTIONS

Table 14.1: Commonly used MS techniques with their relevant features for artwork analysis

Table 14.2: Short classification of situations in which the artwork was not executed by the person credited for it.

Figure 14. 1. Heatmap of features found between Burns' inks and paper and Smith's inks and paper. Reproduced from Ref. 42, [<https://doi.org/10.1038/s41598-018-28810-2>], under the terms of the CC BY 4.0 licence [<http://creativecommons.org/licenses/by/4.0/>].

Figure 14. 2. Average mass spectra of CAS (casein), EGW (egg white) and GLU (animal glue) obtained in the temperature ranges indicated in Total Ion Thermograms (TITs) as areas A (310-320°C, 300-310°C and 320-330°C, respectively) and B (425-435°C). Reproduced from Ref. 52 with permission from Elsevier, Copyright 2017.

Table 14.1: Commonly used MS techniques with their relevant features for artwork analysis

	GC/MS	Py-GC/MS	LC/MS	AMS	MALDI-MS	SIMS
<i>Sample type</i>	Solid, liquid Microgram	Solid, liquid Microgram	Solid, liquid Microgram	Solid Milligram	Solid, liquid Microgram	Solid > mm
<i>Sample preparation</i>	Extraction Deriva- tization	None	Extraction Deriva- tization	Purification Selective extraction and treatments	Matrix coating Crystallised	Flat clean surface
<i>Analysed compound type</i>	Separated by polarity or T in inert gas	Pyrolysed + separated polarity or T in inert gas	Separated by polarity or T in solvent	¹⁴ C isolated from other isotopes	Desorbed ions protected by a matrix	All ions formed directly on the surface
<i>Adapted for</i>	Light and volatiles compounds	Large range of weights, including natural and synthetic polymers	Large range of weights, soluble compounds, proteins, polymers	Dating small samples of organic materials	Large bio- molecules : proteins, peptides, DNA, carbo- hydrates	Identifying and mapping inorganics and organics
<i>Maximum mass range (Da)</i>	< 1 000	< 1 000	< 2 000	/	< 10 000	< 1 000
<i>Prevalence in the field literature</i>	++	+++	+	-	+	-

Table 14.2: Short classification of situations in which the artwork was not executed by the person credited for it.

Qualification	Intentional act	Signature	Attribution <i>Correct: C ; Mistake: M</i>		Further illustrative references
			Seller	Expertise	
Properly attributed original	None	Lost	none / C	C	Ref. 51
		Original	none / C	C	Ref. 42
Misattributed original		Lost	none / M	M	Ref. 53
Original with past false authentication	<u>Signature swap</u>	<u>Past alteration</u>	none / M	M	Ref. 36 p.29 Ref. 39
Misattributed original workshop copy	Replica	Master only	partial / M	partial	Ref. 36 p.34
Properly attributed copy	None	Copyist	none / C	C	Ref. 37
Misattributed past copy		None	none / M	M	Ref. 36 p.34
Copy knowingly sold as original	<u>Misattribution, artificial ageing</u>	<u>Forged</u>	<u>Falsified</u>	M	Ref. 36 p.34
Past exposed forgery	Forgery	<u>Past alteration</u>	none / C	C	Ref. 36 Ref. 42
Past forgery		<u>Past alteration</u>	none / M	M	/
Exposed forgery		<u>Forged</u>	<u>Falsified</u>	C	Ref. 33 Ref. 38
Forgery		<u>Forged</u>	<u>Falsified</u>	M	/



