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Proof Positive: Applications of Chemical Analysis Techniques in Art Forgery Detection

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**State University of New York
College at Buffalo
Department of History and Social Studies Education**

Proof Positive: Applications of Chemical Analysis Techniques in Art Forgery Detection

**By
Joseph Fryc**

**An Abstract of a Thesis
in
Museum Studies**

**Submitted in Partial Fulfillment
of the Requirements
for the Degree of
Master of Arts
December 2021**

**SUNY Buffalo State
Department of History and Social Studies Education
Museum Studies Program**

Abstract

In response to the subjective nature of older forgery detection techniques, modern forgery detection methods rely heavily on chemical analysis of the materials utilized in a given piece of work in order to make authenticity determinations. Chemical methods of detection at their core provide an objective determination of facts regarding the composition of materials utilized in contested pieces and provide a relative date of production for those materials. In this way, chemical analysis helps service the field of modern forgery detection as a direct compliment to traditional stylistic analysis, by providing extra data on the piece that can often be much harder to refute.

In this paper, the author will provide an overview of the modern techniques being applied to forgery detection based heavily in the field of chemistry. Additionally, the author will present case studies in which the methods discussed have been applied to success in determination of authenticity, or have been proven effective for future use in authenticity determination. Finally, the author will touch on the direction in which the field of forgery detection is heading into the future.

**State University of New York
College at Buffalo
Department of History and Social Studies Education**

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A Thesis in Museum Studies

**by
Joseph Fryc**

**Submitted in Partial Fulfillment
of the Requirements
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**Master of Arts
December 2021**

Approved by:

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Chapter One

Introduction

The field of art forgery detection has long been seen, at least from the outside, as stylistic experts observing the brush strokes, color choices, mediums, and general overarching style of an artwork. Likewise, some might imagine investigators carefully examining the artist signature, if any were present, through handwriting analysis. Still others might picture the discovery of a warehouse of identical works of art, clearly depicting forgery at play. Though, in modern times this is often not the case, and determining the authenticity of artwork has become more refined and much more technical. Chemical methods of detection at their core provide an objective determination of facts regarding the composition of materials utilized in contested pieces and provide a relative date of production for those materials. In this way, chemical analysis helps service the field of modern forgery detection as a direct compliment to traditional stylistic analysis, by providing extra data on the piece that can often be much harder to refute.

It is important first and foremost to have an understanding of what constitutes a forgery, why forgeries are made, and the philosophical debate over them. Forgery is defined as any work, be it literature, sculpture, painting, or any variety of other medium, which represents itself to be the work of someone other than its true maker. This can range from the production of original work misrepresented as that of someone else, or the outright counterfeiting of an established work. However, it is important to distinguish copies produced with no intent to deceive, i.e., a pupil replicating their teachers' style as a means of practice (Bonner & Noble, 2020). Copying has long been a fundamental element

in training aspiring artists and the practice has been popular as far back as the Renaissance. Similarly, it was not uncommon for masters to sell the practice work of their pupils as their own, as many studios achieved stylistic similarity through copying. As a result, significant confusion has ensued in the years to come in the attribution of works to the true artist. This confusion, as expected, is further exacerbated when one considers that pupils would often utilize the same materials as their masters making distinction incredibly difficult (Jones et al. 41)

As one could imagine, acquiring or already possessing a forgery can pose a number of challenges for museums and collecting institutions. The inherent duplicitous nature of forgeries makes them difficult to immediately identify, and it follows that an institution may unknowingly acquire a forgery and represent it as genuine. Subsequently, when it is revealed or discovered that the work was indeed a forgery it can call into question the credibility and intentions of the institution. In essence, a forgery represents a misrepresentation of an artist, time period, culture, etc. In this way, many forgeries can be seen as a perversion of the truth based in modern perceptions of the aforementioned subjects, and could potentially mislead those hoping to learn more (Bonner & Noble, 2020).

The most common motivation for forgery, as would be expected, is monetary gain. Particularly, when there is a scarcity of works in a certain style or from a specific artist the market value for those pieces rises. As such, unscrupulous artists, and even art dealers, are incentivized to “find” rare pieces and underrepresented styles in order to fulfill the market demand. Forgers are also often motivated by a desire to gain recognition for their own skill level, or even perhaps the enjoyment of deceiving those who had previously panned their

original artwork. Many forgers begin as legitimate artists in their own right, but a lack of success or critical reception can cause them to seek validation for their skills by successfully representing their work as that of an already revered artist (Bonner & Noble, 2020).

In terms of philosophy questions have been raised regarding the artistic merit of forgeries. In particular, Nelson Goodman asks in his essay “Art and Authenticity”, whether in the absence of any way to distinguish the two pieces, whether there is an aesthetic difference between an original and forged artwork. He argues that to the casual observer, whom lacks the level of familiarity exemplified by an expert, an original and a forgery appear identical. As such, he asserts that an aesthetic difference only arises for a casual observer once they are informed that one is fake. He argues that the viewer’s perception is informed by the information they have been given, and only then can they begin to observe a difference, even if one is not obviously apparent. Goodman goes on to question whether a forged piece of artwork has inherently any less aesthetic value than the original. He offers a comparison to musical compositions as a framework for thought. He questions why subsequent performances of a classical composition are not forgeries if they have not been performed by the original composer. Goodman also questions whether a performance of a classical composition is “forged” if is misattributed, i.e., is a performance of Mozart any less a performance of Mozart if the musician claims that it is Haydn. Similarly, he questions whether an incorrect performance of a piece of music should be considered forgery, i.e., does the musician’s lackluster performance of Mozart make it no longer Mozart (Goodman, 1976). Michael Wreen provided a critique of Goodman’s essay several years later in which he argues that while Goodman’s essay emphasized the importance of

production history in a way no other publication had, he disagreed with many of the points he felt Goodman was trying to make. Specifically, Wreen argues that much of Goodman's arguments on aesthetics hinge on the notion that the observer is aware that the given work is a forgery. As such, Wreen argues that in order to constitute a forgery there must be misrepresentation and intention to deceive, which would be made null in Goodman's given example therefore shifting the focus onto the causal history of the objects. Wreen goes on to argue that any two given objects have a different causal history, and thus by that logic would have an inherent aesthetic difference (Wreen, 1983). At the crux of much discussion around forgeries from a philosophical standpoint is the discussion is the inherent "worth" of forgeries. Many forgeries may in their own right be stunning works of art, however once revealed our perception immediately skews. In essence, the object has not changed in any physical way to alter its aesthetic value, but rather it is our view of the object that has changed for the worse now knowing that it is not legitimate.

The stylistic methods of detection that one outside the field might imagine are still utilized to great success to this day. Some of the most common stylistic analyses are performed by art historians. These experts are well-versed in an artist's style and can identify the unique idiosyncrasies indicative of their style. This might entail examination of the brush strokes, the color palette, and overall composition of the work. These experts are well-versed in the evolution of any artist's style, and thus are able to place a piece in a relative timeline of the artist's career on the basis of some of the aforementioned criteria. It may be helpful for some to think of an artist's style as something akin to handwriting. An expert might also examine the iconography of an artwork, looking for any inconsistencies that might appear from forgers with less scholarly backgrounds. Similarly, many objects

can be examined on basis of their usage. In the case of ancient clay pots, for example, there are areas in which the object would have logically worn from continued use. Many forgers attempt to obscure their deception further by manufacturing false documentation. In most cases some minor digging, and a few phone calls to the correct people can reveal the falsehood of the documentation (Bonner & Noble, 2020). Other factors that might rule out any given piece might include inconsistencies in the signature, and incorrect support materials. While the stylistic methods of forgery detection hold a lot of merit, have been used to success in uncovering forgeries, and are highly respected by professionals within the field, they are also often viewed by those outside the field in some ways as being a bit subjective. After all, no one is infallible and thus there is always room for any given expert to be incorrect. In essence, there is often a glimmer of reasonable doubt remaining, i.e., the artist may have injured their hand and that is why the signature is incorrect. This is compounded in some ways by highly publicized cases of experts misattributing a piece of work to a famous artist, after which public perception of these experts can turn.

It is possible that those outside the field might get the impression the stylistic approaches are all that art forgery detection researchers have at their disposal. However, these interpretations belie the innovations that have been made in forgery detection, that have vastly improved the field. Modern forgery detection is now highly dependent on chemical analysis techniques in order to provide concrete determinations of authenticity. In this way, the field has grown in leaps and bounds, and continues to improve to this day. Modern forgery detection techniques are now in line with investigative techniques utilized in a variety of other forensic scenarios. As such, in this paper the author will explore a variety of cases studies outlining the usage of modern forgery detection techniques. The

author will also provide context for the scientific basis of the discussed techniques in order to fully understand the factors at play, as well as further illustrate the highly technical nature of modern forgery detection.

For the purposes of this paper, the author has opted to utilize a number of contemporary case studies in order to paint a picture of the technical nature of modern forgery detection. The case studies presented display successful applications of chemical analysis in the field of forgery detection. The cases selected cover a range of modern chemical analysis techniques and provide context into the wide array of tools at the disposal of modern forgery detection professionals. These cases were selected in order to illustrate not only successful applications of the techniques discussed but also the further refinement of the techniques in order to better serve the field. In some of the cases discussed, the aim of researchers was to test the efficacy of a new application for an already proven technique in order to solve vexing issues in detection. In others, researchers hoped to apply techniques already proven in the field of chemistry to the field of forgery detection in order to provide yet another tool for future researchers to utilize. These cases may be of particular interest to those within the field for a number of reasons. In several of the cases presented, decades long questions on the authenticity of highly contested objects were finally definitively answered. In others, claims of attribution to famous artists were quashed for pieces that, to the casual observer, may have seemed legitimate. In the vast majority of cases presented, the questions of validity for the contested pieces were raised on the basis of stylistic analysis, or in many cases lofty claims of provenance. These cases illustrate the need for interplay between stylistic approaches and technical approaches to detection in order to paint a full picture of the contested work, i.e., stylistic approaches

provide the catalyst and framework for study and chemical analysis seeks to provide the hard evidence rooted in science. Similarly, these cases may be of interest to those looking to learn more about the field, or perhaps even casual fans of forensic detection. In many of the cases presented, determinations of authenticity often hinged on a single thread or paint chip that revealed an undeniable inconsistency in the proposed provenance of the work.

Chapter Two

Literature Review

The case studies discussed provide a fascinating window into the field of forensic art forgery detection. Particularly, these studies highlight the need for chemical analysis in forgery detection, as it plays a critical role in authenticity determinations. Several of the studies discussed involved highly contested historic objects and artworks, which in the absence of chemical analysis whose provenance would have remained a mystery.

Forgeries and Museum Exhibitions

Widely considered to be a classic in the field, *Fake? The Art of Deception* by Jones et al 1990, is an exhibit catalog created by the British Museum. For the purposes of the exhibit, the museum unearthed a vast array of pieces both from their own collection as well those from other collections that had been shown to be forgeries or misrepresented, many of which that had been previously hidden in storage. The catalog goes into detail on many of these pieces outlining the variety of ways in which the forgeries were discovered. Among the methodologies discussed are x-radiography, dendrochronology, radio-carbon dating, thermoluminescence, amongst a variety of other scientific analysis techniques. Similarly, the catalog discusses on a case-by-case basis, a variety of other observational evidence for forgeries. In one example, a piece was revealed to be a forgery when it was discovered that it had shrunk during its time in storage providing evidence that it was not produced during the proposed time period, but rather sometime later.

Similarly, the catalog goes into detail on a number of techniques that would have been utilized in the production of the forgeries. One interesting example is the process of pointing, in which a sculpture is replicated through the use of precise points taken from the surface of the work. Those points are subsequently transferred to a stone block, and then holes are drilled in the corresponding areas. The sculptor, or often an assistant, would need only chisel in the drilled areas, and then complete some simple polishing and refining and a near identical copy could be created. There is historical precedence for this technique being utilized by students learning to replicate their master's work. Another fascinating example is the production of collotype facsimiles. Dating back to the 1860s, collotype facsimiles are created by applying a thin bichromated film of gelatine to a piece of glass. A photographic negative of the desired piece is projected onto the glass, and the gelatine hardens in correspondence with the amount of light. The remaining "soft" parts are subsequently washed away and thus a duplicate is created. The practice became quite popular for reproducing chalk and pencil drawings due to its ability to replicate the soft lines.

The catalog also touches on some of the motivations behind forgeries, the philosophy of what may or may not constitute a forgery, and a general discussion of what can be considered fake, among a host of other pieces of historical context and discussions of the limits of expertise. The exhibition and catalog are quite extensive, and are widely considered to be among the most comprehensive resources in the field of forgery detection. The catalog discusses pieces spanning thousands of years of history dating back as far as Ancient Egypt and Rome, and as recent as the 20th century. Similarly, the catalog discusses pieces from all over the globe spanning nearly every continent. The pieces discussed also range from the seemingly mundane to highly publicized cases such as the Flora Bust, the

Tiara of Saitapharnes, the Turin Shroud, as well as pieces from infamous forgers like Van Meegeren.

Fake? The Art of Deception is considered a cornerstone in the field for good reason, and in the time since its production, a number of similar exhibits have been curated with a similar goal in mind. Exhibits like “Treasure on Trial” at the Winterthur Museum in Delaware sought to reveal the truth behind forgeries in the Winterthur collection, and provide a peek behind the curtain of forgery detection. Pieces at the Winterthur included forgeries previously believed to have been authentic works of artists like Matisse, Tiffany, and Coco Chanel, among others (Fine Books & Collections, 2017). Similarly, exhibits like “Intent to Deceive” at the Springfield Museum in Massachusetts provide an interesting take on forgeries by presenting known forgeries alongside authenticated works. In this way the viewer can note the distinct similarities, and gain insight into the cunning mind the forgers whom often go to great lengths to produce deceptive works that resemble the genuine article. As part of the exhibition authenticated pieces from artists such as Matisse, Picasso, and Signac are presented alongside pieces from infamous forgers (International Arts & Artists, n.d.). These kinds of exhibits display a trend of museums coming to terms with the uncomfortable reality that their collections contain forgeries, and embracing that truth as an opportunity to educate the public on the fascinating world of art forgery.

Individual Case Studies Sources

The study of the painting attributed to the Russian avant-garde artist Natalia Goncharova, by Chaplin et al, 2014, relied heavily on Raman Spectroscopy to determine the chemical composition of the pigments utilized. Identification of pigments became

critical due in part to the nature of Goncharova's work. Many of the works created by Goncharova lacked a signature, and those that did exhibited a signature that was relatively simple and easy to replicate. Likewise, pieces were rarely dated causing difficulty in determining the age. However, in this particular case the usual lack of signature and date was what flagged initial suspicion, although that evidence alone would have been largely insufficient for determining the authenticity. Further complicating matters, Goncharova had two major periods of time in which she could have made the piece, based on the rayist style, although the latter period in the 1950's would have been much sparser. In the end, researchers found the presence of pigments that would have been unable to be sourced during the proposed year of production. The pigments however could feasibly have been used during the Goncharova's 1950's rayist period, although it would be highly unlikely for Goncharova to have backdated the painting, let alone include a date at all.

From the study of medieval alabaster, conducted by Kloppmann et al, 2017, the efficacy of utilizing isotope ratio mass spectrometry for determination of material sourcing was established. Although no forgeries were identified or tested, the research had far-reaching implications for the further investigation of possible forgeries. During the study, researchers traced the source location of nearly 60 exemplars of medieval alabaster through the use of isotope "fingerprints" present in the works. Beside the forgery detection potential, the process held potential for further study of medieval trade routes and the sourcing habits of medieval artists. In regards to forgery detection however, utilizing IRMS in order to ascertain isotopic finger prints is quite exciting. One can only imagine cases in which iron or bronze sculptures could be traced back to the foundry in which the metal was

poured, and thus any discrepancy between the artists preferred foundry and the foundry identified through IRMS could be evidence of a forgery.

In the study of the forged artwork by Robert Lawrence Trotter, conducted by Hendriks et al, 2019, the efficacy of utilizing radio-carbon dating was proven for both the supports of the piece and the binder present in the paint. Interestingly, through radio-carbon dating, the canvas of the piece in question was determined to indicate a production date during a period spanning from the late 17th century all the way through the early 20th century. In the event that the team had stopped there the piece could have, under normal circumstances, continued to be considered legitimate. The practice of utilizing correctly aged support materials in forgeries has become increasingly common, and thus the team noted that any modern studies of provenance for suspected forgeries would need to go further than simply testing the support material. As such, the team also tested the binder present in the lowest level of the painting. This feat could not have been possible previously and was credited to vast improvements in the development of carbon-dating procedures. Upon investigation of the binder, it was found that the binder utilized by Trotter in the forgery would not have been available at the time he alleged the painting was made. This case study was unique in its use of an already known forgery. In this way, the efficacy of radio-carbon dating could properly be demonstrated as the team was simply confirming information that was already established and exhibiting how carbon-14 dating could also have accomplished the task. This study highlighted the need for multiple testing sites on a given work in the application of any technique, as simply testing one site could paint an incorrect picture of the authenticity.

For the purposes of the mural studies, conducted by Beck et al, 2020, researchers hoped to further confirm the effectiveness of radio-carbon dating on pigments, while simultaneously attempting to expand the possible applications of the method to a wider selection of pigments used in mural painting. A group of unique challenges in carbon-dating murals were noted, including an inability to test the support material, which in many cases would have already been quite old at the time of painting. Many pigments utilized in mural painting are inorganic and thus contain very little carbon if any. Further complications in the process would include the difficulty of extracting the carbon present in the selected samples, meaning that researcher would need to employ methodologies that had not yet been proven effective. Keeping this in mind, researchers conducted testing on samples of the desired pigments utilizing the yet unproven method, and compared the results to those taken from easier to test samples from the same works. This case once again demonstrated further development of chemical analysis techniques in detecting forgeries, in lieu of discovering a forgery. However, the researchers were clever in their application of radio-carbon dating by comparing their proposed methodology to one that was already established. By utilizing art works whose relative dates had already been determined, researchers created a set of goal posts they would need to hit in order to claim their proposed process was sound for proper identification of mural pigments. Ultimately, researchers felt confident that the way in which they sourced the samples for carbon-dating could be applied effectively to other murals and works depicted on non-organic materials.

The case study on the Flora bust, a wax sculpture, conducted by Reiche et al, 2021, provided further evidence that only stylistic judgements of questionable pieces were insufficient for proper attribution, and that hard scientific evidence is needed to provide a

sound conclusion. The Flora bust, was a highly contested piece of artwork that, despite mounting evidence to the contrary, was believed to have been carved by Leonardo da Vinci. In spite of previous early scientific analysis, historical documentation, and historical precedence, supporters still believed the piece to have been from the Renaissance. Recognizing this, researchers sought to put the matter to rest utilizing modern science in order to provide definitive results. In the end, researchers would use a battery of chemical testing techniques in order to establish the composition of the wax utilized in the pieces, as well as establish the relative date at which the wax could have been obtained. This case was particularly interesting due to its contentious nature. It was eye-opening to see the resistance by supporters of a da Vinci attribution in the face of already convincing evidence prior to the current study. This case highlighted the stark difference in reliability of stylistic judgments in comparison to scientific evidence.

The case of the Vinland Map, outlined in the articles by Cummings and Cascone as well as the study by Brown & Clark, culminated in the decades old mystery surrounding the highly contested document finally being solved. In essence, questions of the validity of the Vinland map started immediately after it was first donated to Yale. The discovery was thought to be almost too good to be true, as the map exemplified the most complete depiction of the area of any document from the alleged time period. Preliminary testing conducted in the 1970's would discover evidence pointing in the direction of creation by a modern forger, however the technology of the time could not provide sufficient evidence to convince those in support of the maps alleged Viking origins (Cascone, 2021). Keeping this in mind, more modern research initiatives sought to provide further concrete proof of the document's modern origins.

By focusing their efforts on the possibility of other anachronisms in the materials utilized, modern researchers hoped to identify yet another hole in the claims of the document's origins. Through their efforts researchers identified age discrepancies between the Vinland map and its associated document the Tartar Relation. In this way, further evidence was provided of deliberate deception (Brown & Clark, 2002). Finally, Yale University itself finally sought to put an end to the controversy by allowing university researchers unprecedented access to the Vinland map, the Tartar Relation, and the *Speculum Historiale*. Yale researchers would employ a multi-faceted approach reliant on chemical analysis in order to put the final nail in the coffin of the Vinland Map. For their efforts, researchers would find a number of chemicals present that could not have possibly been used during the time of Vikings. Analysis of writing on the Tartar Relation would reveal further evidence of deliberate deception in order to further obscure the true origins of the map. Research culminated in Yale University officially declaring the Vinland map a fake and subsequently putting the decades long controversy to rest (Cummings, 2021). The on-going controversy regarding the Vinland map is incredibly fascinating, although perhaps more fascinating is the discovery of evidence pointing to alterations made to the Tartar Relation in order to obscure the forger's deception. This case presents solid evidence of a need for a multifaceted investigative approach that employs not only scientific analysis, but also condition assessment, stylistic assessment, and historical evidence as investigative tools. Namely, despite not being able to identify a forger, the collection of research conducted was able to paint a decent picture of how the deception was achieved, and the lengths to which the forger went in order to convince observers of the map's legitimacy.

In the case of the “Oldest Persian silk knotted-pile carpet”, conducted by Smith et al, 2021, a battery of chemical testing was conducted in order to determine the relative age of an intricate carpet fragment from the Cleveland Art Museum. The fragment in question had been obtained by CMA in the late 1980’s, and had been the matter of much debate. Questions arose regarding its provenance almost immediately, with definitive history on the fragment only going as far back as 1928. At that time, experts provided a stylistic assessment and asserted that the fragment could be among the oldest, if not the oldest, exemplar of Persian carpet making techniques. Keeping the controversy in mind, many desired a clear answer on the relative age of the fragment. By 2018, requests for carbon-dating were made, however researchers felt the process would prove too invasive on the small multicolored fragment. As such, they employed a battery of other tests, which in the end would find evidence of several modern pigments utilized in the manufacturing process. Thus, the carpet was deemed to be of modern origin dating back to only the late 19th century at best. The Persian carpet case was quite interesting, as researchers had to conduct quite a bit of testing in order to definitively provide evidence of the carpets true age. It was encouraging to see that the group of researchers, which included a CMA conservator, opted for less invasive processes in order to preserve the fragment in spite of the difficulties they encountered. This case provides further evidence that utilizing a variety of chemical testing techniques can prove beneficial when investigating artwork, as each step revealed critical information in regards to provenance. Equally as interesting, the study does not list any provenance claims prior to those asserted in the 1928 writing by Raymond Koechlin and Gaston Migeon. As such, the case could be one of mistaken identity rather than deliberate forgery, as the provenance prior to 1928 is largely unknown. It should be noted that the

CMA website does not specifically acknowledge the fragment as a forgery, however it does state that the provenance is unknown prior to 1928 and includes a note that research into the object is still on going. It seems likely that CMA acknowledges that the fragment is of more modern origin but has not found sufficient evidence to point to a specific manufacturer.

The case study of the three alleged Jackson Pollock paintings, conducted by Khandekar et al, 2010, utilized a wide array of chemical testing techniques in order to provide concrete proof of their illegitimacy. The pieces in question, found in a New Jersey warehouse, were part of a lot of 32 attributed to Pollock on the basis of style and the presence of his name on the wrapping. Selections from the lot even went on to be exhibited at the McMullen Museum of Art, however many questioned the authenticity of the pieces. Researchers would go on to employ a variety of chemical testing techniques to identify pigments utilized in the paintings, and to attempt to detect the presence of “bomb” carbon in the supports. Upon completion of their study, researchers would find evidence of pigments not available until after Pollock’s death, and thus provide evidence that the works were indeed not attributable to the late artist. Jackson Pollock is colloquially said to be the most forged artist in American history. This study alone helped cast aspersions on nearly 32 alleged works by the late artist, that likely represent only a fraction of the pieces that have been attempted to be attributed to Pollock. This case was unique in that several other studies were also being conducted contemporaneously, and that researchers would have to contend with claims that one of the pieces had been restored, potentially contaminating the results. The battery of tests utilized by the researchers was vast, and thus was able to identify several key pigments that unraveled claims of attribution to Pollock in spite of any

challenges in obtaining proper samples. This case should be noted as an example of researchers completely foregoing certain tests on a piece in order to avoid irreparably damaging it.

Finally, in the case study of the Armenian manuscripts, conducted by Maybury et al, 2018 researchers hoped to determine the efficacy of utilizing an already widely employed chemical analysis technique in order to examine cultural works. For their purposes, researchers would compare results returned from the new application of this technique to the already established technique of Raman spectroscopy. Through the analysis of several centuries' old Armenian manuscripts, researchers would identify the specific strengths and weakness when applying hyperspectral imaging to cultural documents. Upon completion of their study, researchers would find that, at least for the time being, the hyperspectral imaging was best utilized in conjunction with other chemical analysis technique in order to examine artwork and cultural documents. This study is notable in that it examined the application of an established analysis technique on cultural objects. Similarly, it highlighted the need for multifaceted investigations in order to cover for inherent weakness in certain methodologies. Likewise, it is indicative of a new wave of techniques that hope to expedite the process of investigation in order to significantly reduce the time needed to analyze cultural works.

Chapter Three

Overview of Scientific Methods

In this section, the author presents a non-exhaustive review of a variety of scientific techniques that have been utilized in the detection of art forgery. The modern techniques presented were developed primarily in the field of chemistry first, as modern forgery detection has, by and large, exhibited an increased focus on assessing the materials used in the production of a piece in lieu of stylistic and other observational assessments. Stylistic judgements can be quite useful, but lack the ironclad proof needed to convince some skeptics. There is always the distinct possibility that those assessing the work may be swayed by personal interest or a desire to indicate a specific outcome. These kinds of assessments are not likely to be deliberate, as they are rooted in the individual's expertise, however inherent bias may lead some to missed critical details that refute their assessment. The inherent subjective nature of many older forgery detection methods leaves some room for doubt from those wishing to call the assessments into question. Expert forgers often go to great lengths in order to create convincing forgeries. This may include obtaining period accurate materials or artificially aging works, among other methods. By placing scrutiny on age of the materials utilized, proof of relative production date can be obtained, and by placing scrutiny on a variety of aspects of a given work, modern research initiatives can circumvent forger's attempts to obscure their trickery. Advancements in the techniques presented have eliminated the vast majority of previous concern regarding the invasive nature of chemical testing, as nearly all modern techniques have become minimally invasive to the artwork. However, each methodology does have its own set of disadvantages.

Radiocarbon(^{14}C) Dating

Radiocarbon(^{14}C) dating, otherwise known as Carbon-14 Dating, was first developed by physicist Willard F. Libby circa 1946, and has been proven to be a versatile technique in dating fossils and archaeological specimens dating from 500 to as far back as 50,000 years ago. Widely used by geologists, anthropologists and archaeologists, the method relies on the observing the degradation of radiocarbon (carbon-14) (Editors of the Encyclopedia Britannica, 2020). Since 1939, it had been known that carbon-14 is continuously produced in nature through the interaction of neutrons, produced by cosmic rays interacting with earth's atmosphere, with the nitrogen-14 present therein. Libby concluded that if the aforementioned was true, that carbon-14 should always be present in atmospheric carbon. As such, the carbon-14 present in atmospheric carbon-dioxide enters the carbon cycle first through plants. Once the carbon dioxide is absorbed from the air by green plants, it is eventually passed on to animals through the food chain. As time goes on, the carbon-14 levels in any living organism will be continuously replenished through this process. However, when that organism dies, they will cease the absorption of carbon-14, and thus we can begin observing its decay (Kauffman, 2021).

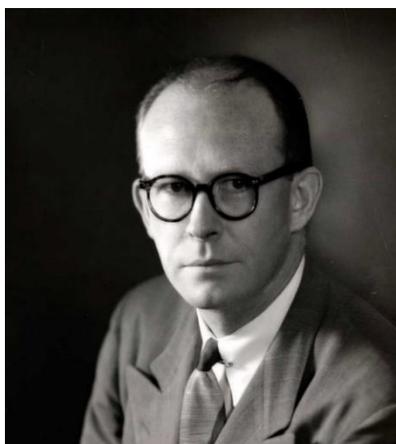


Figure 1 : Willard F. Libby, professor of Chemistry in the department of Chemistry and Institute for Nuclear Studies (Enrico Fermi Institute) at the University of Chicago, and recipient of the 1960 Nobel Prize in Chemistry.

Carbon-14 decays at a constant rate, with a half-life of $5,730 \pm 40$ years. In other words, half of the radio isotope present upon the organism's death will undergo disintegration over the next 5,730 years. As such, this allows those hoping to determine the date of an organism's death to measure the amount of radiocarbon remaining in the specimen, and subsequently produce a rough estimate of the specimen's age (Editors of the Encyclopedia Britannica, 2020).

Libby first verified his method of dating by applying it to a number of samples and artifacts whose relative ages had already been determined, including samples of redwood and fir trees, as well as wood from the funerary boat of Pharaoh Sesotris III. After obtaining the first age-determination using his carbon-14 technique, in collaboration with his students, Libby went on to identify a variety of artifacts. Among these artifacts were linen wrappings from the Dead Sea Scrolls, bread buried by the eruption of Vesuvius in Pompeii, and charcoal from a campsite at Stonehenge. In most controversial application of his technique, Libby's carbon-14 dating determined the relative age of the Shroud of Turin to fall between 1260 and 1390, falling short of the original proposed age. In addition, Libby dated a number of corncobs found in a cave in New Mexico and found evidence that refuted the previously held belief that the Ice Age in North America had ended 25,000 years prior instead revealing that the date was only 10,000 years prior (Kauffman, 2021). Since then, the technique has been utilized in perpetuity for a variety of applications. More contemporary applications have also benefited from an admittedly tumultuous and regrettable period of human history. Namely, objects made after 1963 hold a significantly higher level of carbon-14 due to the nuclear bomb tests of the mid-20th century releasing an

excess of the isotope into the atmosphere. In this way, researchers are able to create a distinction between paintings made before and after World War II (Solly, 2019).

Carbon-14 dating does however present a few challenges that limit and complicate its usage. First, carbon-14 dating cannot be utilized on inorganic materials, as they of course do not contain active carbon. This means that in the case of inorganic pigments, binder, or other materials, researchers are quite restricted in their ability to test the piece in question. Second, samples can often be contaminated by carbon from other materials close to them, i.e., the glue from a label may contain carbon of a different age than the frame and thus contaminate a sample taken near the label. This means that researchers could obtain a false positive (or negative) on the basis of a contaminated sample. Third, the method lacks reliability in objects older than 40,000 years of age, and is completely unusable for objects older than 60,000 years of age as the carbon present has degraded so far that any traces would not be able to be detected. Additionally, the effect of human activity on the atmosphere, as well as natural occurrences, has changed the radio-carbon levels on several occasions, and thus the standards for calibration for carbon-14 dating have changed as well (Blakemore, 2021). In fact, a new calibration curve for carbon-14 was adopted as recently as 2020, following much anticipation from those in the field. The new curve, dubbed IntCal20, utilized nearly twice the data in comparison to the previous update in 2013, drawing from nearly 13,000 raw measurements (Gannon, 2020). The implications of this update could have far-reaching effects, as previous determinations have potential to be updated. As the precision of methods such as carbon-14 dating are refined, there is the chance that previous data could be disproven when utilizing the new curve.

Isotope-ratio Mass Spectrometry (IRMS)

Isotope-ratio mass spectrometry involves the measurement of minute difference in the presence of isotopes such as hydrogen, carbon, nitrogen, and oxygen, among others. By passing samples through an electron beam, the ions of the sample are accelerated. The accelerated ions are then passed through a magnetic field, creating a trajectory for the ions en-route to the detector. At the detector the ions are collected and a chromatogram is produced. The method allows for the use of both liquid and solid samples, which are subsequently converted to gas through combustion or thermal conversion. Variations in isotopic profiles are found in a wide range of materials, meaning that the isotopic profile is unique to the origin of the substance. As such, IRMS is widely applicable to a variety of fields including forensics, archaeology, biology, as well as determining the authenticity of food, among other application (Pico et al, 2020). In the framework of art forgery detection, IRMS could prove vital in identifying the source of a variety of materials used in forgeries, and thus help identify discrepancies in the authenticity of art work. However, IRMS does pose a few issues when it comes to positively identifying forgeries. IRMS is quite good at painting a picture of the source of a material, but does not denote how that material was obtained. In this, way we can only say where the material obtained, and there is room for doubt on whether the material could have a been obtained by the proposed artist. It follows that skeptics could question whether or not it was really feasible for the proposed creator or artist to obtain such materials. As such, IRMS is likely best used in conjunction with other methodology, in order to paint a more comprehensive picture, rather than a standalone method for authenticity determination.

Raman Spectroscopy

In order to understand Raman Spectroscopy, one must first understand the Raman Effect. The Raman Effect was first discovered by Nobel-prize winning physicist Sir Chandrasekhara Venkata Raman in 1928. The Raman Effect is the observed change in wavelength of the light when a beam is deflected by other molecules. In essence, when passing through a dust free and transparent sample of a chemical compound, a fraction of the light beam emerges in a direction other than that of the incoming beam. The vast majority of this scattered light remains at the same original wavelength; however, a small part emerges at a different wavelength and its existence is a result of the Raman Effect. Conceptualizing the Raman Effect may be easier if one pictures the particles or photons present in the light beam. When the photons strike the molecules of the sample, most bounce off with no energy transfer. However, a small amount of the photons may gain or lose energy to the molecules as a result the collision. As such, the frequency of those photons changes thus effecting their wavelength. Though the effect is minute, the pattern of Raman lines produced is directly proportional to the number of molecules obstructing the

path of the light, and as such Raman spectra are viable for both qualitative and quantitative analysis (Editors of the Encyclopedia Britannica, 2021).



Figure 2: https://en.wikipedia.org/wiki/C._V._Raman#/media/File:Sir_CV_Raman.JPG

It follows that in Raman spectroscopy, a measurement is taken in order to determine the amount to which a given substance induces the Raman Effect. A beam of photons, usually within the visible spectrum, is fired from a pulsed laser and impacts a surface. The molecule contained in the sample subsequently scatter the photons and in turn some photons lose energy corresponding to the vibrational levels within the sample's molecules. The scattered photons are then analyzed by a spectrometer to detect the energy lost which is characteristic of the molecules with which the photons interacted (Hercules & Hercules, 2018). As with all techniques, Raman spectroscopy comes with its own set of disadvantages. For example, samples which exhibit weak Raman signals often result in long acquisition times, thus slowing down the process. Similarly, the longer acquisition

time runs the risk of destroying the sample due to extended exposure to the laser. In addition, the data revealed through Raman Spectroscopy often requires extensive data analysis in order to be interpreted (Eberhardt et. al, 11-12). Among the other issues present with Raman spectroscopy, is it's inability to be used on materials lacking a crystalline structure. Likewise, darker colored materials, especially black materials, are almost impossible to identify using Raman spectroscopy as they absorb most light, as thus often do not reflect enough to get an accurate reading (Allen, 2019). In general, the main challenge to be combatted with Raman spectroscopy is identifying samples that exhibit sufficient reflective properties in order to be tested.

Chromatography

Chromatography is a technique in which the components(solutes) of a mixture are separated on the basis of the relative amounts of the solute distributed between the stationary and mobile phases of the mixture. The mobile phase of a mixture could be either a gas or a liquid, while the stationary phases could be a liquid or a solid. In the mobile phase, the solution moves through the chosen substrate and distributes. In the stationary phase, the components settle in their separated state and can be observed. The history of chromatography can be traced as far back as the 19th century or perhaps earlier. In some of the first applications, dye chemists dipped string or filter paper into their dye vats. As the dye traveled up the inserted material through capillary action, the various components would produce dye bands of different colors. In fact during the early 19th century, German scientists carried out several deliberate experiments in order to observe the phenomenon. In one documented case, a treatise was published by Freidrich Goppelsroder describing a

method of dropping solutions of inorganic compounds upon the center of a piece of filter paper. As the compounds absorbed, they produced concentric rings of color. Goppelsroder would dub the process “capillary analysis.

Despite these early experiments, the official discovery of chromatography is credited to Mikhail Tsvet in 1901. Tsvet not only observed the phenomenon, but also applied it in a rational way in order to separate carotenoid and chlorophylls plant pigments. Through his experiment, Tsvet outlined a process not dissimilar to some modern applications. Tsvet filled a vertical glass column with a variety of materials that exhibited absorptive properties including powdered sugar, alumina, and silica. He then poured the solution of plant pigments into the tube and aided their distribution by adding an organic solvent to wash the pigments down. The pigments subsequently separated into a series of colored bands, each separated by a noticeable region devoid of pigment. Over time the method would garner the attention of a variety of other scientist who would further refine and develop the technique in order to improve its efficacy.

Modern chromatography methods can be classified on the basis of four criteria: Geometry of the system, mode of operation, retention mechanism, and phases involved. The two major geometric classifications of chromatography are column and planar chromatography. In column chromatography thin tubes that can be made of a variety of materials are packed with materials that support the stationary phase, while the mobile phase moves throughout the interstitial space between. In planar chromatography, a thin two-dimensional sheet, of either paper or a film of bound particles, is utilized to support the stationary phase. The sheet is then dipped into the mobile phase, and the solutes are absorbed through capillary action. In terms of modes of operation, chromatography can be

separated into either development chromatography or elution chromatography. In development chromatography, the mobile phase is stopped before reaching the bed of the stationary phase. Elution chromatography, used only for columns, entails the process of allowing solutes to completely pass through the entire system. As the solutes emerge, they fall on a detector that registers an impulse that is then recorded. Classifying retention mechanisms can be defined as approximate at best, as retention is generally a mixture of mechanisms combines. Finally, chromatography can be separated in to two main phases, gas chromatography and liquid chromatography.

Chromatography has long been employed in the fields of biology and chemistry, being widely used in biochemical research in order to separate and identify the chemical compounds of biological samples. Chromatography yields a distinct advantage over older separation techniques such as distillation or crystallization in that it is capable of separating out all of the components in a mixture without the need for prior knowledge of relative amount and relative identity of substances present. Similarly, some forms of chromatography can detect the presence of substances in a concentration down to an atto-gram (10^{-18} gram). In this way, the process is also often used in forensic investigation including that of art forgery. Chromatography does however have its own set of shortcomings. For example, when using liquid chromatography there is the chance for “dead-bands” in which the small changes in the amount of solute cause indistinguishable regions. Similarly, there are a vast array of considerations to be made when selecting the correct type of chromatography to utilize. In this was some previous knowledge of the sample’s composition may be necessary in order to properly select the correct combination of methodologies (Keller & Giddings, 2020).

Fourier Transform Infrared Spectrometry (FTIR)

Infrared spectroscopy has been a staple technique for materials analysis in laboratories for over 70 years. Infrared spectrum absorption peaks correspond to the frequencies of vibration between the bonds of the atoms in a given sample. In this way, an infrared spectrum can serve as a “fingerprint” for a sample, as any given material will have its own unique spectrum based on the arrangement of the atoms, and thus a positive identification is possible for most materials. Additionally, the size of the absorption peaks directly corresponds to the amount of material present, meaning the concentration of the material can also be determined.

In the past, infrared instruments were classified as dispersive. These early instruments separated the individual frequencies of the energy emitted, usually through the use of a prism or grating. After separation, a detector measures the energy emitted at each frequency which has passed through the sample. The results are called a spectrum, and plot the relationship between intensity and frequency. While the early dispersive forms of infrared spectroscopy were used for many years, Fourier Transform Infrared (FTIR) spectrometry was developed in order to overcome some of the shortcomings present in earlier methods.

The primary challenge of early methods was the slow scanning speed, and a solution came in the development of the interferometer, which produces a unique signal that has all of the infrared frequencies encoded within it. This meant samples might only take a few seconds to be processed, rather than the several minutes needed in the past. In addition to the speed advantages allowed by FTIR, often referred to as the Fellgett Advantage, there are

a number of other advantages noted by scientists. First, the sensors employed in FTIR are markedly more sensitive than the past. Second, as there is only one moving part required in FTIR, the likelihood of mechanical breakdown is quite low. Finally, FTIR is self-calibrating through the use of an internal wavelength calibration standard, often called the Connes Advantage, (ThermoNicolet, 2001).

FTIR does however have limitations that restrict its application. Namely, the chamber utilized to house the sample is somewhat small, and thus restricts the process to only small samples. Similarly, this means that only small objects can be tested without needing to obtain remove a sample from the object, something that is not always feasible when trying to preserve the object. Likewise, there are a host of materials that absorb infrared radiation, and thus are not feasible for testing with FTIR (Allen, 2019).

Matrix-Assisted Laser Desorption/Ionization (MALDI) Mass Spectrometry

The term matrix-assisted laser desorption ionization was first coined by Franz Hillenkamp and Michael Karas in 1985. The pair discovered that the amino acid alanine could would ionize much easier if it was first mixed with the amino acid tryptophan and then irradiated using a pulsed 266 nm laser. Due to the widespread availability of small, inexpensive nitrogen lasers operating at a wavelength of 337 nm, and the introduction of commercial instruments in the 1990's led to the widespread adoption of MALDI by many researchers.

Due to its versatile nature, MALDI is utilized in order to analyze labile molecules, peptides, oligonucleotides, lipids, proteins, and synthetic polymers. As part of the process,

the sample is mixed with matrix and subsequently dried on a target plate. The plate is then loaded into a mass spectrometer and irradiated by a laser. The irradiation excites the particles in the sample, and the excited ions are accelerated down a flight tube. At the end of the tube, a detector records the intensity of the ion current and the time that the ions spent in flight. Among the common uses of MALDI is the characterization of synthetic materials and natural products (Duncan et al, 2014).

Hyperspectral Imaging (HSI)

Hyperspectral imaging (HSI) is a reflectance technique in which each pixel of an image produces a reflectance spectrum for the wavelength detected. Among the advantages of hyperspectral imaging is the ability to scan large areas of objects quickly, holding the potential for large scale pigment analysis. The spectra produced through HSI are typically used in order to characterize the materials present of the surface of the image and produce a map of their layout. However, hyperspectral imaging has also been used to uncover hidden messages and text on objects, due to its ability to detect reflectance at a wide array of wavelengths, even those outside the visible spectrum. In the past, HSI has been widely applied to the fields of astrophysics, medical imaging, and in various military applications. However, more recently hyperspectral imaging has been applied to the investigation of cultural heritage works, including The Declaration of Independence in which text alterations were revealed, and “The Scream” in which the pigments used were characterized and mapped. Generally speaking, most applications of HSI to the analysis of artwork involve the use of HSI as a primary analysis, with other techniques utilized to

provide more accurate results after a general map of materials is created. The identification of these materials using hyperspectral imaging is achieved by comparing the returned reflectance spectra to a reference database. HSI does however come with its own set of shortcomings. The reliance of HSI on databases means that often times, testing utilizing other methodology may be required in order to identify the proper database. Additionally, processing the information requires the utilization of a number of algorithms, which means that researchers must test an array of algorithms in order to accomplish proper analysis (Maybury et al, 2018).

Chapter Four

Applications of Modern Techniques in Forgery Detection

This chapter is an overview, in which the author will present a collection of case studies that the aforementioned techniques, along with several more experimental methods, were applied to the field of forgery detection. In most cases, the method utilized have already been proved effective for the specified purpose. However, in several cases, researchers embarked on initiatives in order to prove the efficacy of the presented method, and thereby aid in establishing a precedent for their use in forgery detection.

Across the studies, evidence is presented confirming the likelihood of forgery through a variety of applied chemical analysis techniques. These technique range in level of invasiveness, however all techniques are considered to be minimally invasive, and in some cases requiring no physical samples to be collected. In all cases, researchers carefully curated the application of methodology in order to ensure that the pieces remained in their initial condition.

In cases that required physical sampling, areas of pre-existing damage were selected in order to avoid further degradation. In those cases that no significant damage was present, techniques and sampling locations were selected in order to minimize damage to the works. And when necessary, select pieces from the larger sampling groups were omitted if no feasible methods of sampling could be identified without damaging the work.

Investigation of alleged Goncharova painting with Raman Spectroscopy

In 2014, a team of researchers in England sought to apply Raman Spectroscopy to a piece of abstract artwork allegedly painted by famed Russian avant-garde painter Natalia Goncharova. As researchers noted, the scientific study of Russian painters' palettes had at the time been quite limited. As such, researchers selected an untitled work in the rayist style, signed "N. Gontcharova" and dated 1913, from a private collector for study.

Researchers were drawn to the piece for a number of reasons. Natalia Goncharova (1881-1962) was best known for her colorful technique and wide array of styles including impressionism, neo-primitivism, cubism, and futurism. In 1913, Goncharova, alongside her lifelong companion Mikhail Larionov, pioneered a new style dubbed rayism. Rayism found its inspiration in the depiction of light rays emanating from a variety of objects and their intersection therein. However, the early rayism period was reportedly quite short-lived only lasting from 1912-1924. During this time Goncharova's set and costume design work took precedence, as well as the development of the neo-primitive and cubo-futurism styles. However, in the mid-1950's Goncharova returned to rayism in order to produce a limited number of pieces for a Galerie de l'Institut exhibit in 1956. It has also been noted that Goncharova rarely signed or dated her paintings upon completion. Of the few signed pieces, her signature ranged from simple initials to several variations on her last name including "N. Goncharova" and "N. Gontcharova". As such, there was reason to doubt the validity of the piece (Chaplin et al. 1322-1323).

Due to the wide array of colors utilized, the piece was an ideal candidate for Raman Spectroscopy, and no evidence of restoration overpainting was found. For their purposes,

researchers collected 6-10 Raman spectra from 6-10 of each of the major color areas of the painting in order to identify the pigments. In all, 9 pigments were identified with nearly half being pigments produced after 1930. Two pigments, carbon black and iron oxide, were identified from the black and red areas respectively, and could be traced back to antiquity and thus could feasibly been used at the alleged date of creation. Likewise, barium white and zinc white, used in the vast majority of the white areas could both be traced to the early 19th century meaning they too could have feasibly been used in 1913. However, from the blue and green areas respectively, phthalocyanine blue and phthalocyanine green were identified, two pigments which would not have been commercially available until the mid to late 1930's. Likewise, disazo pigment was identified from the yellow, brown, and orange areas, and can only be traced back to the 1930's as well (Chaplin et al. 1324-1325).

Researchers noted that the most interesting findings can in the discovery of titanium white and polycyclic pigment in the work. Titanium white, identified from the edges of the painting, would not have been utilized until 1947. Similarly, the polycyclic pigment found in the purple areas would not have become commercially available until 1952. Researchers also noted that upon further analysis of a sample of red pigment the presence of an oil binder was discovered. Oil pastels in general would not have become widely available until the 1930's, and would have been difficult for artists to obtain during World War II, only becoming easier when a fine art version was developed in 1949. As such, researchers took the presence of oil as further evidence the piece was likely not created until after 1950 (Chaplin et al. 1324-1325).

Keeping all this in mind, researchers concluded that it would be highly unlikely that the piece was a genuine Goncharova. Researchers noted that while Goncharova did produce

a few rayist pieces in the 1950's, she was also quite afflicted by arthritis at the time. Additionally, the clear disagreement between the date adorning the piece and the time frame in which the piece could have been created was quite damning. In the end, researchers felt confident that the piece was not genuine and that the study highlighted the need for more reliable dating procedures like Raman spectroscopy (Chaplin et al. 1325).

IRMS proven effective for tracing origin of Medieval alabaster

In response to a noted lack in written resources detailing medieval trade routes, a group of researchers set out in 2017 to utilize IRMS testing in order to determine the efficacy in pinpointing the origins of medieval alabaster. Contrary to common belief, alabaster was not simply a substitute for marble, but rather one of the preferred materials of Renaissance era sculptors. The lustrous whiteness and ease with which the material could be carved made it ideal for numerous applications, the homogenous nature of alabaster sourced from different regions made for a predictable experience while carving. However, the similarity in characteristics of alabaster from different regions of the world poses a unique challenge when it comes to identifying the source region by conventional methods such as minerology, chemistry, or texture (Kloppmann et al. 11856).

For their purposes, the researchers focused on “true” alabaster, gypsum or anhydrite, which was widely used throughout medieval Europe. Among the well-documented major distributors of alabaster of time were sites in the Midlands of England and northern Spain. However, there is a wide distribution of alabaster deposits all across continental Europe, and regrettably little is known about distribution from these sites.

Through IRMS, the researchers hoped to identify isotopes such as sulfur, oxygen, strontium in order to tie a variety of alabaster artifacts to the region from which they were sourced. In total, researchers tested 66 artifacts provided from institutions including the Louvre, the Petit-Palais Museum, the Cleveland Museum of Art, and a variety of smaller institutions, churches, and collections from America, Sweden, France, and England (Kloppmann et al. 11856-11857).

Upon the conclusion of the study, three main regions were identified and the corresponding artifacts were linked. Researchers found evidence of significant deviation in isotope levels between regions to the extent that a piece with a matching isotope “fingerprint” could be reasonably attributed to a region. Of the 66 total pieces, fifteen were identified as alabaster sourced from the English midlands, ranging from the 1400’s through the 1700’s. Evidence was also shown of heavy English exportation of alabaster to France and northern Europe post 1550. Twenty-two pieces were tied to northern Spain, and evidence was shown of clear favor towards southern Europe and the Mediterranean region of France. Researchers noted that their most interesting finding indicated that nearly all of the late 14th century and early 15th century tested that related to the popes of Avignon came from a very small grouping in the Alpine region of France. The remaining artifacts were tied to a variety of smaller source locations spanning Europe. By in large, researchers felt that the study successfully demonstrated the efficacy of utilizing IRMS to identify “fingerprints” on alabaster that can be used to positively identify a source region. Researchers also noted the further reaching implications of the research in the authentication of a variety of artistic mediums, and thus providing another tool to detect forgeries (Kloppmann et al, 11857-11860).

Radio-carbon dating proven through analysis of Trotter Forgery

In 2019, researchers in Zurich, Switzerland embarked on an initiative to prove the efficacy of utilizing carbon-14 dating on individual paint layers in order to detect possible forgery. In the vast majority of cases, carbon-14 dating can be utilized to determine the relative age of a variety of materials utilized in the construction of the canvas on which the painting has been made. Some examples might include the wood used in the frame, or the canvas on which the painting was completed. In this way, researchers can generally determine whether a piece falls significantly outside of the likely range of production date, by estimating the period of time in which the raw materials were harvested. Generally speaking, sampling materials in this way can yield a time lag of roughly 2-5 years, thus setting an acceptable deviation range. However, sampling these materials can prove unreliable and inconclusive if the potential forger reuses materials contemporaneous with the correct time period. Famously, Han Van Meegeren, notorious for his forgeries of Vermeer paintings, would scrape the paint from old paintings in order to replicate the appearance of a correctly aged painting. Similarly, forgers such as Wolfgang Beltracchi would purchase period accurate frames from antique markets in order to obscure their deception (Hendriks et al. 13210).



Figure 3: <https://www.google.com/amp/s/news.artnet.com/art-world/nuclear-tests-identify-art-forges-1566637/amp-page>

In the past, radiocarbon dating required the use of larger amounts of material (possibly tens of grams), and as such would prove quite invasive to any given piece of artwork. However, with advances in technology such as accelerator mass spectrometry (AMS) and the continued development of gas ion sources (GIS) for AMS, the required sample size has significantly decreased allowing researchers to utilize micrograms of material for testing. Previously, even with the creation of AMS sample as large as 100 mg would have been necessary in order to properly utilize the carbon-14 method, which would have simply been an infeasible sample to be taken from any given piece of art. However, by utilizing GIS-AMS, viable sample sizes have been reduced to micrograms (μg) making the process far more accessible. By utilizing an elemental analyzer in conjunction with GIS-AMS, samples can be combusted and converted to carbon dioxide, allowing for as little as $10\mu\text{g}$ to be utilized (Hendriks et al. 13210).

Additionally, in cases like those of Van Meegeren's forgeries, the pigment utilized may indeed be period accurate. However, in many cases there would still be a need to utilize a modern binder in order to complete the work. As such, in the absence of any other anachronisms in the pigments, degradation products, or the support products utilized, being able to date the binders in the paint layer is vital to determining authenticity, something that was now possible to accomplish in a minimally invasive way (Hendriks et al, 13210).

For their study, researchers utilized a piece from known forger Robert Trotter, who admitted to selling 52 of his forgeries between the years of 1981 and 1988. The piece in question dated "May 5, 1866 AD" and signed "Sarah Honn" replicates the style of a primitive American Folk-art piece entitled *Village Scene with Horse and Honn & Company Factory*, and was seized by the FBI as part of the case against Trotter. Likewise, the piece in question already had flaking damage making it an ideal candidate for testing, without causing noticeable damage to the artwork, allowing for a small sample of white paint to be extracted (Hendriks et al. 13211).

During the study, a sample was taken of both a canvas fiber and a paint chip, and both were tested utilizing the carbon-14 method. The hairlike fiber, measuring less than a few millimeters was tested first and as expected, proved inconclusive, returning results indicating a wide range of dates from the late 17th century all the way up to the early 20th. This not only allowed for the provided date of 1866 to be viable, but also did not discount the possibility of an earlier or later creation date. As such, testing the canvas alone would have proved useless in the long run. However, when researchers tested the binding medium present in the paint chips an anachronism was revealed. The oil utilized as a binder was extracted from seeds that were shown to have been harvested between 1958-1961 or 1983-

1989. In both scenarios, the results indicated a production date after 1950, thus contradicting the alleged date of production. Keeping this in mind, the researchers believed that carbon-14 dating on micro-samples could prove to be a viable method of forgery detection (Hendriks et al, 13211-13214).

Radio-Carbon Dating proven effective for use on Pigments

Not long after the study in Zurich, a similar study was conducted by researchers from France and Switzerland into the efficacy of utilizing carbon-14 dating on lead white and verdigris paints utilized in mural painting. In case of mural paintings, a few key challenges arise when attempting to utilize the carbon-14 method to identify a forgery. First, there is no organic supports available for testing, as the paint is directly applied to the rock, mineral wall, or dry or wet plaster (secco or fresco respectively). In the case of fresco there is no organic binder present for testing, as the pigments are mixed directly with water. As such, the only option is to test the pigment itself, which proves difficult as many common pigments contain no carbon for dating. One exception is carbon black, whose main ingredient is charcoal, and as such contains viable carbon-14 for testing. This is due to the fact the charcoal has long been produced by burning fresh cut trees. Up until the trees are felled, they continue to absorb carbon-14, and upon cutting the decay can begin. In this way, most charcoal used in even the oldest paintings still contains carbon-14 viable for dating. As such, carbon black had been previously utilized for the carbon-14 method. A few other key exceptions come in the form of lead white and calcium carbonate. Researchers felt that these were important, as finding another viable pigment could prove

key in properly identify pieces of art that lack binders or supports that were viable for testing. Calcium carbonate however poses a few issues, due to the way in which it is manufactured. As the name suggests, the pigment is made from calcium carbonate harvested from quarries. However, the calcium carbonate extracted was formed several million years ago from a variety of micro-organism. As such, any carbon-14 that was once present in the calcium carbonate has long since decayed to near indistinguishably minute levels. Keeping this in mind lead white, a pigment used by house painters and masters (such as Da Vinci and Vermeer) alike, arose as a key contender. Lead white, in contrast to calcium carbonate, has been artificially synthesized as far back as the 16th century. The process involves corroding metallic lead using other materials like vinegar, horse manure, and tan bark, among others (Beck et al. 1-2)

A unique challenge arises however when attempting to separate the carbon present in lead white, as the conventional approach of hydrolysis runs the risk of contamination from any calcium carbonate pigments present in the sample. Researchers solved this issue, through an innovative thermal separation process. Through precise control of carbon dioxide release, researchers were able to separate the organic carbon remaining in lead white, from the dead carbon present in calcium carbonate as well as from any other pigments (Beck et al. 2)

For the purposes of the study, two sets of data were collected from paintings at two historic sites based upon their known historical context and chemical composition. The first set was comprised of samples from the decorative painting adorning the walls of Margaret of Bavaria's dressing room at the Chateau de Germolles in Burgundy, France, dated between 1388 and 1390. The second set was comprised of 9 fragments that were obtained

from the remains of the decorations that once adorned the damaged rood screen of the Church of the Cordeliers in Fribourg, Switzerland, from these remains, two paintings were recovered. The first was determined to be the main painting and was dated between 1500-1510 by a stylistic analysis, while the second was far less accurate with a proposed period between 1340-1700. This uncertainty meant that the researchers would need to compare 6 samples of lead white to 3 samples of carbon black from the same pieces in order to determine the efficacy of process as carbon black had already been shown to be effective for carbon-14 dating (Beck et al. 3).

Upon completion of the process, the researchers were pleased to find that in both cases the separation of carbon-14 from lead white was successful and resulting samples proved accurate for utilizing the carbon-14 dating process. Samples taken from the Chateau de Germolles returned a date range of 1380-1400 when combined and balanced, placing the relative date firmly within an acceptable range of known dates of production. When compared to the samples of carbon black, samples of lead white from the Church of the Cordeliers returned a combined and balanced date range of 1426-1460, while the carbon black returned a range of 1420-1478, placing both solidly in a comfortably similar range, and both falling closely within the suspected range of production dates. Researchers did note however that the pieces in question were allegedly all attributed to painter Hans Fries, who was present in Fribourg between 1490-1510. They believe the explanation for the nearly 50-year discrepancy lies in the methods of trade in the 16th century, during which time lead white was mass produced and subsequently stored for extended periods of time. As such, it would not be infeasible that Hans Fries to have utilized paint that was several decades old. The researchers also noted that there more important finding at the Church of

the Cordliers was the agreement in dates between the carbon black and the lead white .

Upon conclusion of the study, researchers determined that carbon-14 dating of lead white paint was not only possible but effective in providing reasonably accurate dates, opening up the possibility for further application of the process (Beck et al. 4-7).

Radiocarbon dating suggests 19th century origin of Flora Bust

Since 1909, the Flora Bust has been the subject of much scrutiny regarding to whom attribution of the piece could be given. Within two years of its acquisition, by Wilhelm Bode for the Berlin Royal Museum, more than 730 articles had been written arguing for and against an attribution to Leonardo da Vinci. At the crux of the argument, is the usage of wax as a medium as wax sculptures would have been highly unusual for the Renaissance. To date, no other renaissance wax sculptures were known, however Bode insisted the piece had been sculpted by da Vinci. In opposition, a museum director from Hamburg, Gustav Pauli, suggested the possibility of 19th century sculptor Richard Cockle

Lucas as the true artist. Lucas was known to have created a vast number of wax sculptures modeled after ancient models (Reiche et al. 1).



Figure 4: [https://commons.m.wikimedia.org/wiki/File:Bust_of_Flora_by_Richard_Cockle_Lucas_\(1800-1883\),_wax_-_Bode-Museum_-_DSC02998.JPG#mw-jump-to-license](https://commons.m.wikimedia.org/wiki/File:Bust_of_Flora_by_Richard_Cockle_Lucas_(1800-1883),_wax_-_Bode-Museum_-_DSC02998.JPG#mw-jump-to-license)

Since then, arguments for and against a da Vinci attribution have relied heavily on the chemical composition of the piece, as well as historical documentation. As a primary point of contention, the presence of spermaceti in the bust's wax, as confirmed by chemists. Spermaceti would have been incredibly rare during the Renaissance, but quite common by the 19th century when it was used for candle wax and in the creation of sculptures from 2-dimensional models. As early as the 1980's, a sample of the wax was also carbon-dated and results indicated that the wax would not have been from the Renaissance. In addition, a statutory declaration was presented by the son of Richard Lucas asserting that his father had created the Flora bust in 1846, accompanied by a watercolor painting of the bust created by the son. Similarly, evaluations conducted regarding the

casting method further supported a 19th century creation date. Namely, upon opening the back of the bust it was found to contain wooden fragments, newspapers, and a variety of other materials from the 19th century. Researchers noted however that the possibility the bust was simply modified after its initial creation was also possible. Finally, it was also well known that no other Renaissance wax models existed. For their part, supporters of a da Vinci attribution also presented evidence. Initial analyses of the wax in the 1900's proved inconclusive, however an expert analyzing the surface noted cracks they felt were indicative of significant aging. Likewise, from a stylistic standpoint, experts suggested that the polychromy was applied using Renaissance era techniques and the face closely resembled other figures created by da Vinci. Finally, supporters pointed out that while spermaceti was incredibly expensive and rare during the Renaissance, it was still in use. The current researchers felt however, that while these analyses held merit, the art-historical interpretation of the bust was likely highly influenced by a desire to have uncovered a rare work from da Vinci (Reiche et al. 2-3).

Keeping the controversy in mind, researchers in 2021 sought to put the matter of the Flora busts provenance to rest. For the purposes of the current study, researchers obtained a variety of small samples from the Flora bust taken from both the inside and the outside of the bust, in order to exclude the possibility that samples from the surface could be qualitatively different in compositions from the original state of the bust. For the purposes of comparison, samples of wax were taken from two reliefs sculpted by Richard Lucas, namely "Leda and the Swan" and "Woman and Winged Woman." A battery of tests was employed, centering around the common goal of accurately and definitively carbon-dating the bust. Among the tests utilized were microproton induced x-ray emission (micro-PIXE),

Fourier transform infrared spectroscopy (FTIR), gas-chromatography mass spectrometry (GC-MS), and accelerated mass spectrometry for the carbon-14 dating (Reiche et al. 3).

Upon investigation of the wax, researchers discovered evidence in line with previous testing. Across all samples tested, the presence of both beeswax and spermaceti was detected. Specifically, all samples exhibited a high level of spermaceti with a relatively small concentration of beeswax. Promisingly, the results also indicated a high level of similarity in the compositions of the waxes utilized in both the Flora bust and the two 1850's reliefs from Richard Lucas (Reiche et al. 4).

The process of carbon-dating the samples was made more complicated due to the nature of materials tested. Namely, carbon-dating on the samples required curving in order to properly adjust for the variety of source locations. On objects such as the wood fragments and the newspaper found inside the Flora bust, a terrestrial curve was utilized as these objects would have been sourced on land. However, in order to properly date the wax a terrestrial curve and a marine curve were necessary. The inclusion of a marine curve was made necessary, as spermaceti is sourced from whales, and thus the absorption of carbon-14 would be dissimilar to that of land-based creatures. Moreover, because the wax was comprised mostly of spermaceti, with lower amounts of beeswax, careful consideration was given on how to apply the curves. Due to the similarities in composition, the same curve structure was applied to all samples of wax. In the end, results showed that all tested materials from the Flora bust could be dated to the 18-19th century, thus further disproving the claim that da Vinci was the artist. Upon completion of the study, researchers made special note of the need to carefully take the heterogeneity and diversity of objects into

account when carbon-dating, as some may contain uncommon materials that require special testing (Reiche et al. 7)

Multi-faceted approach puts Vinland Map Mystery to rest

For decades the Vinland Map has been the subject of much research and controversy. Yale first acquired the map as a gift from Paul Mellon in the mid-1960's, and unveiled it not long after in 1965 to much excitement. From quite early on, the map was hailed as further proof corroborating archeological evidence that the Vikings had landed in North America many years before the historic voyage of Christopher Columbus. However, from the very start questions arose regarding the legitimacy of the map.

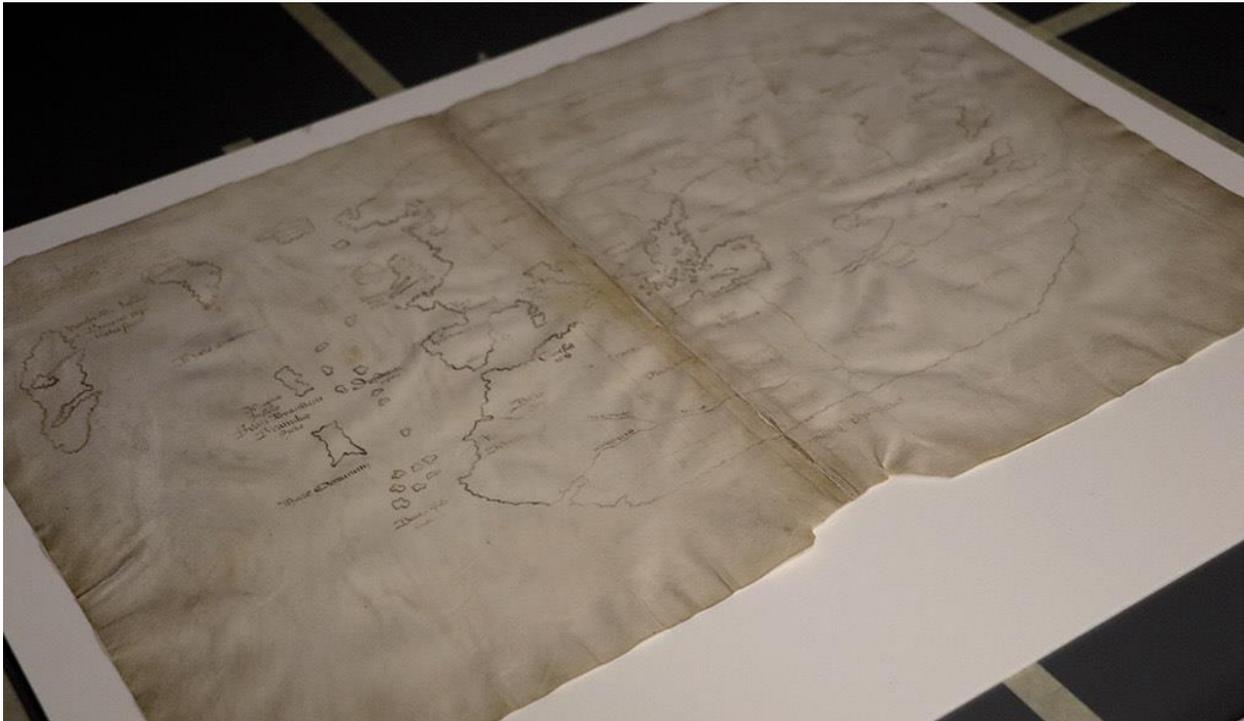


Figure 5: <https://news.yale.edu/2018/02/28/yale-putting-high-tech-tests-its-controversial-vinland-map>

Early matters of suspicion included the lack of ornamentation typical of medieval cartography. The map was quite unusual in that it was surprisingly accurate considering the

proposed time period, namely the depiction of Greenland as an island. Laurence C. Witten III, the dealer who sold the manuscript to Mellon, also refused to disclose from where he had obtained the work. Witten would later admit to purchasing the map from Ferrajoli de Ry, a well-known manuscript thief, without asking for any information regarding the work's provenance.

By 1973, the McCrone Research Institute of Chicago was granted access in order to conduct initial testing on the document. Through their initial findings, the institute uncovered evidence that the map may indeed have been falsified. Specifically, testing revealed the presence of anatase, a form of titanium dioxide, which would not have been available until its first use in commercial inks in the 1920's. Despite this evidence, experts still contended that the map could be legitimate, refuting the validity of the findings. As a result, conflicting reports continued for decades, going back and forth arguing for and against the authenticity of the map (Cascone, 2021). However, in recent decades several research initiatives have been undertaken in order to conclusively determine once and for all the validity of the highly contested Vinland Map.

In 2002, a team of researchers embarked on an initiative to test not only the Vinland Map, but also the Tartar Relation, for their legitimacy utilizing Raman microprobe spectroscopy. Previous research initiatives had focused on the use of anatase on the map, as well as carbon-dating of the parchment. Likewise, at the time of publishing, researchers could not find any research conducted on the black pigment, though several possibilities had already been considered. As such, researchers aimed to utilize Raman microprobe spectroscopy in order to identify the pigments utilized. Raman spectroscopy was selected specifically for its ability to detect pigments in subnanogram quantities. Researchers

selected several areas of study on the documents on the basis of pigment density, as well as other features of interest not listed (Brown & Clark. 3658).

Upon completion of their study, researchers uncovered new evidence on the date of production for the Vinland Map, as well as new information regarding the Tartar Relation. The Tartar Relation seemed to utilize a vermilion red ink, as well as black. As part the results, it was found that the inks utilized in the Tartar Relation were vermilion based red, and iron gallotannate black ink, both of which would have been feasible for use during the given time period. Given this info, researchers saw no need to question the validity of the Tartar Relation (Brown & Clark. 3659-3660).

Researchers noted that the ink lines of the Vinland Map appeared to be mainly composed of two distinct pigment lines. The first, was a yellowish line that closely adhered to the parchment, and the second a black line that overlaid the yellow which had been, in some cases, almost entirely lost. As part of the results, researchers determined that the yellow ink present contained traces of anatase. Researchers discounted the possibility of anatase contamination from an outside source by noting that traces were only found in and around the yellow ink lines. The spectra taken from the yellow ink areas was also peculiarly florescent, suggesting organic materials, such as gelatin, in agreement with previous testing by the McCrone Institute. It was also discovered that the black ink present was neither iron gallotannate or ilmenite as previously suspected by those in support of the document's validity. Instead, the ink was identified as being carbon-based. This fact became important for a few key reasons, specifically indicating that the document may have been made to appear artificially older than it really may have been. Researchers noted that prior to the development of the printing press, both iron gallotannate ink and carbon-

based inks would have been used. The most common way of differentiating between the two, prior to scientific analysis, was by observing the yellowing caused to the paper by iron ions leaching from the iron gallotannate ink into the surrounding area. This trait however would not occur from a carbon-based ink. As such, the presence of a yellow line covered by a carbon-based black ink suggests that the creator of the document sought to artificially replicate the degradation that would have come from iron gallotannate ink. Keeping this in mind, as well as the presence of anatase throughout the map, researchers concluded that the map was likely a 20th century fake (Brown & Clark. 3660-3661).

More recently, Yale itself concluded to finally put the matter of the Vinland's Map legitimacy to rest. During this most recent analysis, Yale's scientists were given unprecedented access to the document, along with the *Speculum Historiale* and the *Tartar Relation*. Yale's scientists concluded through their initiative's what they consider to be their final verdict on the Vinland Map, as well as evidence that may clear up the relation between the three texts.

As mentioned previously, the unprecedented access granted to researchers allowed them to analyze the Vinland Map alongside the two documents with which it is believed to have been once bound. The first was *Speculum Historiale*, a well-known medieval encyclopedia by Vincent de Beauvais. While the second was the *Tartar relation*, or the *Hystoria Tartorum*, an account of two Polish clerics' journey into the territory of Genghis Khan in the mid-1200's. Specifically, the evidence provided in favor of the documents once being bound together come in the presence of matching wormhole patterns. Researchers felt that this indicated that the Vinland Map was likely originally located in the front of the *Speculum Historiale* and was more than likely drawn upon one of the end

sheets. Researchers believe that at an indeterminate time, the map was then removed and bound using modern binding inside the Tartar Relation. Similarly, when the radiocarbon dating was performed on the manuscripts a date range of 1400-1460 was returned. The recent discovery of a complete version of the *Speculum Historiale*, revealed a copy of the Tartar Revelation bound within the final volume also led Researchers to note a historical precedent for the manuscripts being combined (Cummings, 2021).

At the crux of the new research, Yale utilized X-ray fluorescence spectroscopy (XRF) in order to identify the distribution of elements throughout the map. Previously, XRF was restricted to analyzing specific points on an object, however with new innovations macro-XRF allows researchers to analyze entire 2-dimensional objects at once. Researchers noted that through macro-XRF they could create a one-to-one scale elemental map of the document, and thus allowed them to share a dataset that covered the whole map rather than select points. It has been noted that medieval scribes typically wrote with iron gall ink, which is comprised of iron sulphate, powdered gall nuts, and some form of binder. Upon XRF analysis of the map, results showed little to no presence of iron, sulfur, or copper. However, the scan showed the presence of titanium throughout the ink. Upon scanning the “Vinlanda Insula” portion of the map, which made the map famous, high levels of titanium were identified, as well as small amounts of barium, pointing in the direction that modern titanium-white pigment was utilized. Similarly, after completion of the full XRF scan, Raman microscopy was utilized in order to confirm that the titanium dioxide present was in the form of anatase (Cummings, 2021).

In order to further confirm their findings, researchers also analyzed 50 manuscript fragments, from the Beinecke Library, produced during the 15th century in Central Europe.

As expected, the fragments contained high levels of iron, and low levels of titanium. It had also been discovered that text on the Vinland Map and Tartar Relation had been altered. The original Latin text written in iron gall ink translates to “second part of the third part of the Speculum’ and was suspected to be a bookbinder’s note. However, the text had been overwritten, with what researchers suspected to be modern ink, to include the map now reading “drawing first-part, second-part of the third part of the Speculum.” (Cummings, 2021). As such researchers conducted field emission scanning electron microscopy on samples of ink from the previously discovered altered text on the Tartar Relation and the Vinland Map in order to confirm that the anatase present wasn’t naturally occurring but rather of modern origin. The FE-SEM process produced highly magnified images of ink components, which revealed anatase particles consistent with pigment commercially produced in 1923. Having determined the composition of the ink and taking the overwriting into account, researchers deemed that the alteration of the text with modern ink was clear evidence of motive to deceive, and more over further evidence that the map was a forgery (Cummings, 2021).

Ultimately, researchers and Yale officials agreed that the Vinland Map was indeed a fake. However, at least for the time being, the map will remain at the Beinecke with the other manuscripts. In the opinion of the Beinecke early books and manuscript curator Raymond Clemens, despite that fact that the map is a fake, it has become a historical object in and of itself demonstrating a great example of a forgery that had a broad international impact (Cummings, 2021).

Oldest Persian Carpet Disputed using Multi-faceted Scientific Approach

In 1988, the Cleveland Museum of Art acquired a carpet fragment (1988.243) which was believed to be, on stylistic grounds to be representative of the oldest Persian silk knotted-pile carpet, possibly dating back to the 15th century. The provenance however could only be traced back to 1928, leading some to consider the claims of 15th century manufacture to be dubious (Smith et al. 2).



Figure 6: <https://www.clevelandart.org/art/1988.243>

The carpet fragment first emerged, already in its fragmented state, when it was described by Raymond Koechlin and Gaston Migeon for *Oriental Art: Ceramics, Fabrics, Carpets* in 1928. Koechlin, president of the French Council of National Museums, and Migeon, a French art historian and former curator at the Louvre, described the fragment thus:

“We have however the good fortune to be able to illustrate here a piece of silk carpet decorated with conventionalized animals so unique in its archaic style (whether

original or survival) that we feel justified in offering it as the oldest known example of a carpet containing living figures though we are unable to claim Persia or Egypt as its origin, rather than Sicily or Spain. Persia is however the most probable.” (Smith et al. 2)

A colored photograph was included with the description featuring a caption that further claimed that the fragment was “Without a doubt the oldest specimen of carpet known with the exception of the small piece with Cufic inscriptions from the excavations at Fostat.” The fragment would be acquired not long after by George Hewitt Myers, founder of The Textile Museum in Washington, DC, from a Parisian dealer named Paul Mallon in 1928. The piece would serve as an addition to the roughly 275 carpets in his personal collection. However, by 1947, Myers would be influenced by Maurice Sven Dimand, curator of Near Eastern Art at the Metropolitan Museum of Art, to request a refund from Mallon upon Dimand’s assertion that the carpet was fake. The whereabouts of the fragment would then remain unknown for nearly 40 years until 1988 when Mallon’s step-son, Milton Girod-Mallon, gave the fragment to CMA following Paul Mallon’s death in 1975. The true provenance remained a mystery until 2018, when a London-based carpet expert and dealer requested that CMA carbon date the fragment in order to finally put the mystery to rest. However, Robin Hansen, CMA conservator, recognizing the intrusive nature of carbon dating, developed a battery of other tests in conjunction with her fellow researchers (Smith et al. 2-3).

For the purposes of their testing, researchers first employed stereo, bright field, fluorescence, and polarized microscopy in order to verify the pile was natural silk. Next three small sample bundles were taken, without compromising the structural integrity of the fragment, of the red, green, and blue dyed areas. These bundles were then subdivided

into two parts, one to be used for the study, and the other to be saved for further study if necessary. Likewise, authentic reference dye samples were acquired from a variety of suppliers for comparison during testing. The battery of tests included X-ray fluorescence spectroscopy (XRF), Raman microspectroscopy, and liquid chromatography – diode array detector – mass spectrometry (LC-DAD-MS) (Smith et al. 2-5).

From the XRF analysis, researchers discovered the presence of aluminum, sulfur, calcium, potassium, and iron in all three bundles. Researchers noted that this would suggest the use of alum, cream of tartar, and/or ferrous sulfate as a mordant to treat the silk threads. In order to utilize many historic dyes, the fiber must first be treated with a mordant prior to submersion in the dyebath. The mordant binds to both the dye and the fiber in order to create an insoluble complex, and can in some cases also affect the final color of the fiber as a certain dye can change hue when interacting with certain mordants. Researchers determined that each possible mordant was consistent with the standard of the period, and the results were qualitatively similar to a contemporaneous study in which particle induced x-ray emission (PIXE) testing identified widespread use of Al and Fe mordants in Safavid Period (1499-1722) Persian wool rugs. Researchers further noted that all the elements present in the samples could have been naturally been introduced through dust accumulation, from hard water in the dyeing process, and from the use of the object in its past life. Thus, researchers concluded that XRF analysis provided results that could potentially be consistent with a 15th century silk textile (Smith et al. 5).

For the purposes of the research, Raman microspectroscopy was utilized in order to pre-screen the fibers for their dye content. When the red fibers were tested, the Raman scattering returned was very weak and thus yielded an unidentifiable Raman Spectrum.

However, when the blue and green fibers were tested the scattering was far stronger and thus yielded results. The spectra returned for the blue and green fibers were consistent with the Raman spectrum for both natural and synthetic indigo. Notably, the green fibers returned a weaker spectrum, indicating the likelihood that they were comprised of indigo mixed with an unidentified yellow dye that could not yield a strong enough Raman spectral profile. Researchers noted that it has been shown that discriminating between natural and synthetic indigo is possible through their dispersive Raman spectra in a previous study by Vandenaabeele and Moen. However, this approach could not be applied to the current study as they lacked an appropriate quantity of authentic indigo standards, and likewise the process had not been proven to be effective for dyed fibers or extracts of historic fiber samples. Thus, the Raman microspectroscopy analysis also could not provide definitive evidence of age (Smith et al. 6)

By in large, the LC-DAD-MS analysis provided the most conclusive evidence, definitively clearing up the question of the carpets relative age. From the analysis, indigotin was identified as the major chromatographic peak. Indigotin is the main colorant in both natural and synthetic indigo, consistent with the data from the Raman testing. The indigotin was found in both the blue and green fibers, though the green contained a much lower concentration. Additionally, a small amount of isatin was detected in the blue fibers, though its presence would not be unexpected as it is not only used in the synthesis of indigo but also a product of degradation in natural indigo. Noticeably absent from the samples however was the presence of other indigoids including the red isomer of indigotin, indirubin. The lack of indirubin could suggest that the indigo pigment was synthetic, as natural, plant-based sources of indigo will contain indigotin, indirubin, and isatin.

However, researchers noted that the ability to absolutely discriminate between synthetic and natural indigo using LC-MS remains quite elusive. Keeping this in mind, the potential presence of synthetic indigo could still indicate production post 1897, when synthetic indigo was first synthesized by German manufacturer BASF (Smith et al. 6).

More encouragingly, when examining the green fibers, the synthetic dye Metanil yellow was identified in high concentrations. As a poor Raman scatterer, exhibiting near-infrared excitation, Metanil yellow would not have been identified during the initial Raman testing, corroborated by the result therein. Likewise, Metanil yellow was first synthesized in 1879 by C. Rumpff, and has thus only been found in textiles from the late 19th and early 20th centuries (Smith et al. 6).

For its part, the red fiber sample was found to contain predominantly synthetic dyes, along with a number of other compounds from natural sources in smaller concentrations. One of the natural compounds detected, ellagic acid, was consistent with the practice of applying weighting agents to silk in order to increase its price. In addition to the natural components, the presence of Metanil yellow was once again detected in the red fibers. Likewise, the presence of several other synthetic compounds was detected however a positive identification was regrettable not possible considering that they were the two major components identified. However, the profiles of both compounds were strikingly similar to that of Congo red. Researchers noted that these similarities suggest that the unknown pigments were related to Congo red, either as a synthetic by-product of its manufacture or a product of the subsequent reactions from or degradation of Congo red. Importantly, when researchers conducted light aging experiments on modern samples of Congo red, the compounds found in the unknown samples could not be replicated. The

inability to replicate the compounds suggested the possibility that an earlier form of Congo red, pre-dating 1970, could have been utilized. Until 1970, the early synthesis of Congo red utilized benzidine as a starting material, but the practice was ceased due to its carcinogenic nature. Researchers noted precedence for this possibility, citing a previous study of early Congo red that found similar contaminants to the current study, although in that study researchers also could not precisely identify the specific contaminants. Keeping this in mind, researchers tested a much older sample of Congo red found in a university stock room. From the packaging, researchers inferred a date somewhere in the early 20th century for the sample, though an exact date could not be determined. Upon testing, the same two unknown bands were found in significant relative concentrations to Congo red as seen in the carpet sample. Although, the specific compounds could not be identified, researchers cited the consistent presence of similar contamination patterns across older samples of Congo red in comparison to the carpet sample as possible evidence of a pre-1970's synthesis of Congo red. However, researchers noted that they could not definitively make a claim given the current uncertainties, though further efforts were already underway (Smith et al. 6-8).

Upon the conclusion of their study, researchers felt confident enough to assert that the carpet was of modern manufacture and not a 15th century Persian carpet as previously claimed. Taken together, the absence of indirubin in the indigo dye, the definitive usage of Metanil yellow, and strong possibility of Congo red usage, all point in the direction of synthetic dyes that would not have been available until the late 19th century. Given the evidence found, researchers felt that the need for invasive radiocarbon dating was

eliminated, and would not provide any significant additional evidence for the provenance of the fragment (Smith et al. 9).

Multi-faceted Investigation of 3 Alleged Jackson Pollock Paintings

In 2005, an independent, pro-bono analysis, was conducted by the Harvard Art Museums in to the provenance of a selection of 3 paintings from a lot of 32 attributed to the late Jackson Pollock (1912-1956). Through a multi-faceted approach, researchers hoped to paint a complete picture of the painting's relative dates of production. Extensive testing was performed on the paints and pigments utilized in order to provide a definitive answer on their provenance.

In 2002, Alex Matter, son of painter Mercedes Matter and photographer Herbert Matter, alleged to have uncovered 32 paintings from his father's Long Island Warehouse attributed to famed artist Jackson Pollock. The pieces in question, wrapped in brown paper, featured labels written on the wrapping that suggested production by Pollock during his life time. Per the labels, Matter believed the pieces were produced by Pollock, between 1946 and 1949, in Herbert Matter's New York Studio, utilizing paints from Swiss art supplier Robert Rebetz. Upon discovery of the works, Matter placed the pieces under the care of Mark Borghi Fine Art, and a conservator was found to treat the paintings not long after. Many of the paintings in question went on to be exhibited at the McMullen Museum of Art, however from the outset of their discovery the provenance has been the subject of scrutiny. By 2005, the Harvard Art Museums resolved to investigate the pieces, as part of a larger investigation into the materials and techniques utilized by 20th century artists. A selection

of 3 pieces, dubbed MBJP09, MBJP14, and MBJP29, was made with each subjected to a battery of testing in order to determine the age and composition of the materials used. The battery of test included: Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), pyrolysis-gas chromatography mass spectrometry (py-GCMS), carbon-14 dating, laser desorption ionization time-of-flight mass spectrometry, and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX). For their purposes, researchers utilized Raman spectroscopy, SEM-EDX, and LDI-MS to identify the pigments, FTIR was used to identify pigments and binding media, and Py-GCMS was used to identify binding media. Although the research team initially requested a diverse sampling of the 32 paintings, not all works were available and thus substitutions were made by the owner, resulting in the final selection of 3 works examined. Of the 3 pieces, MBJP29 was comparatively in the worst condition having suffered heavy damage in the past. Additionally, Mark Borghi claimed to have inadvertently altered the piece, having previously sent the piece for reassembly and restoration. Upon the pieces return, the painting had been almost completely repainted, however Borghi claimed to have removed a section of the repainting in order to provide some context into the original condition. As such, when selecting area for testing researchers avoided any known areas of restoration (Khandekar et al. 205-207).

For the purposes of carbon-14 dating, researchers decided upon sampling from the support material of the selected pieces. MBJP 14 and MBJP29 were selected for testing as the two pieces were not lined, and thus ideal for support sample recovery from the already damaged areas on the edges. MBJP09 was excluded because the piece was canvas lined, and therefore a support sample could not be taken without damaging the surface of the

image. For comparison, a piece of blue-coated cardboard from the Pollock/Krasner House and Study Center was also tested, and selected for its similarity to the supports used in the three works studied. The primary goal of the carbon-14 testing was to determine whether or not the selected samples contained traces of carbon-14 in elevated levels as a result of the 1955 nuclear bomb testing. Results indicated that all three boards contained no detectable levels of 'bomb' carbon-14, indicating manufacture prior to 1955. However, researchers noted that further research is required to refine the process of carbon-14 dating on cardboard, as the material is often comprised of materials from a variety of dates. Likewise, the time lag until 'bomb' carbon-carbon-14 is detectable in paper products also required additional research. Despite these drawbacks, results indicated that the blue-coated cardboard was significantly older than supports of the studied works, however exactly how much older could not be determined. Researchers noted that although the results indicated a pre-1955 manufacture date for the supports, the practice of utilizing new old stock is not uncommon in forgeries, as the stock could have been obtained at any time after its date of manufacture. It was also noted that two additional studies into the 32 paintings were conducted contemporaneously with the discussed study. In these studies, evidence was found indicating the use of materials created after Pollock's death, corroborating the ultimate findings of this study (Khandekar et al. 212).

Upon completion of research into the pigments utilized, several key findings became apparent. Among the pigments detected were a number of traditional pigments from the 19th and 20th century including yellow ochre, synthetic ultramarine blue, titanium white, cadmium red, and aniline black, among others. Likewise, several other components were identified such as calcite and barite, which have been common pigment extenders

since long before the 20th century. However, among the results found were several materials that would not have been available until after 1950 or even later. PO 43, a perinone, was found on both MBJP29 and MBJP14, and would not have been recognized as a pigment until 1950, and wouldn't have been industrially produced until 1953. PY 151, a benzimidazolone pigment was found on MBJP14, and has only been commercially available since 1971. Interestingly, PY 151 was found in lowest paint layer of MBJP14 indicating that everything above would have needed to have been painted after 1971. PR 254, a diketopyrrolopyrrole pigment found on MBJP29, was first reported by Farnum in 1974, and would not have come to market until 1986. Taken together, the presence of these pigments suggests a production date somewhere in the late 20th century after the death of Pollock (Khandekar et al. 208-210).

Similar to the results of testing on the pigments, testing of the binders revealed a number of other anachronisms in stark contrast of the proposed production dates. The black paint on MBJP09, was found to contain a polymer binder comprised of both n-butyl methacrylate and iso-butyl methacrylate. Although either one of the polymers could have been used as far back as 1930, the combination of the two would likely have not been used until 1965 when the first recorded use of a copolymer of this type was reported. Across several of the binders the presence of gum materials, styrene, and other additives was detected, all of which are commonly used in order to significantly expedite the production process and create an aged effect much sooner. Researchers noted these additions were reminiscent of the style of well-known forger John Myatt, who was reported to have regularly added KY-Jelly to his paints in order to alter the drying properties. However, researchers also noted these additions could have also been made for purely aesthetic

reasons, without trying to deliberately create an aged effect. On MBJP14, a copolymer of styrene and ethyl methacrylate was found, and though the exact date of introduction as a paint medium is difficult to pinpoint an early patent suggests a date no earlier than 1963. Researchers noted that significant research on this specific copolymer would not have occurred until the mid-1970's suggesting that the medium was not commercially available until then. Taken together, testing on the binders again suggests production dates falling in the mid to late 20th century after Pollock had already passed. Researchers additionally noted, that the unusual combinations of polymers with additives were observed across all three paintings studied, thus implying production by the same artist (Khandekar et al. 210-211).

Upon conclusion of the study, researchers determined a number of inaccuracies in contrast to the proposed dates of production were present. The use of materials not available until the late 20th century cast aspersion upon the claimed dates, and essentially rule out Pollock as the artist. Researchers noted that the study highlighted the importance of material studies in provenance research, and in the determination of authorship. In particular, researchers felt the results indicated the LDI-MS has an important role to play in conservation labs in order to identify modern organic pigments (Khandekar et al. 2012).

A Comparison of Hyperspectral Imaging and Raman Spectroscopy

In 2018, a group of researchers sought to evaluate the efficacy and reliability of hyperspectral imaging in the identification of pigments in historic works of art, and to ascertain if the use of HSI posed any advantages on its own or in conjunction with techniques like Raman spectroscopy. As such, for their purposes researchers would

compare results from HSI analysis with that of Raman spectroscopy analysis to determine the viability and reliability of hyperspectral imaging (Maybury et al. 1).

As a subject for testing, researchers selected a collection of Armenian manuscripts from the Bodleian Library at Oxford University. Researchers noted, that Armenian manuscripts have rarely been the subject of much scientific research, despite the fact that the Bodleian Library alone holds over 140 manuscripts as well as 250 early printed books in their Armenian collection. Researchers also noted that the collection spans nearly 1000 years and dates back as far as 1635. Armenian illuminators left no written account of their pigments, only having been partially identified in a 1974 study, which researchers noted was far from extensive. Due to the wide range of dates present in the collection, researchers felt the Bodleian was ideal for their study. From the collections, six manuscripts were chosen representing a period spanning from the 14th to the 18th century, including works from well-known artist Mezrop. The selections were subsequently subjected to both hyperspectral imaging analysis and Raman spectroscopy analysis (Maybury et al. 4).

Upon completion of testing, Raman spectroscopy identified 6 pigments: red lead, red lead+ vermillion, lapis, indigo+orpiment, vermillion, and indigo. Researchers noted that the pigment with highest concentration by far was vermillion, as further evidenced by the noticeable red color to the manuscripts. The results of the Raman spectroscopy analysis were then compared to hyperspectral imaging analyses utilizing data from 5 different databases ran through 3 different algorithms. Upon comparison, HSI was found to have an accuracy range varying between 9 and 93%, dependent on the specific combination of database and algorithm. As expected, the most effective databases were those closely

related to the pigments utilized in the manuscripts (Maybury et al. 9-11). As such, researchers noted that HSI analysis could be greatly improved by prior knowledge of the pigments utilized. Thus, researchers suggested that in subsequent testing techniques such as Raman spectroscopy be used first in order to identify the array of pigments, and HSI utilized to map out their arrangement. The proposed methodology would lend itself to the strengths of both processes while avoiding their weakness. Namely, Raman spectroscopy is best applied to small areas for precision detection, as the process is very accurate but also very slow, and likewise cannot cover a large area. Conversely, hyperspectral imaging is best applied to map a wide area of already identified pigments, as it can quickly analyze a wide area but requires a lot of algorithmic adjustments and database matching in order to provide accurate identifications of pigments. Researchers additionally noted, that HSI could be significantly improved through the use of much broader databases that cover a wider array of pigments (Maybury et al. 13).

Chapter Five

Conclusions

As evidenced above, the further development of art forgery detection techniques is critical in the continued identification of forgeries. Without the application of chemical analysis, the current authenticity determinations in many of the cases presented likely could not have been made. As a result, the debate over their authenticity may have raged on into perpetuity. Increased cross-disciplinary collaboration in the field of art forgery detection can lead to innovative new uses for already well-established analytical tools.

A fine example of the need for cross-disciplinary collaboration, as well as a good illustration of how determinations of authenticity can waiver over time is the debate over the Vinland Map. The controversy over the map's authenticity was been debated for over 60 years. Dozens of scholars from a multitude of disciplines have weighed in on the issue, both in support and in denial of its authenticity. From the moment the map was discovered questions were raised over it's authenticity on the grounds of historical evidence.

One of the most thorough critics was Kristen Seaver, who penned a publication in 2004 entitled *Maps, Myths, and Men: The Story of the Vinland Map*. Seaver, considered to be one of the foremost historians on the region the map was allegedly discovered, argued on the basis of historical evidence that it was highly unlikely that the map was authentic. Amongst her arguments, was the stunning accuracy with which Greenland was depicted. In her expert opinion, Seaver felt it would have been extremely unlikely that any mapmaker of that time period could have not only correctly depicted Greenland as an island, but more importantly that they could have been so stunningly accurate in its shape. R.A. Skelton

combated this by positing that it could have been an unusually warm period in 15th century Greenland, and thus the voyage could have been much simpler than Seaver believed.

However, Skelton himself admitted that the accurate depiction of Greenland was highly unusual (Harvey, 2006). Seaver argued against this assertion, claiming that while there may have been a “warm” period, the climate would not have been that much warmer than today. In her estimation, one would be hard pressed even in modern times if they were to use the technology of that era (Gugliotta, 2004).

In her publication, Seaver even proposed a possible culprit, Josef Fischer, in order to solve the burning question of why someone would forge the map in the first place. Seaver argued that Fischer, a prominent author on 15th century maps as well as the westward expansion of the Vikings, perhaps created the map circa 1955. His motivation, as Seaver posited, was in order to both tease Nazi scholars, as during this time the Nazi’s had closed the school and Jesuit house at which Fischer resided in response to their suspicion of the Roman Catholic Church. As Seaver explained, the map would have both fed into the Nazi’s belief in Nordic Superiority while simultaneously implying that it was part of the expansion of the church (Harvey, 2006).

Over the course of the debate, discourse from a scientific perspective was also repeatedly raised over the ink utilized on the work as well as the map. For example, in 1973, the McCrone Research Institute uncovered traces of anatase present on the map. This indicated at the time that the map was likely not produced until the 1920’s (Cascone, 2021). However, not long after, chemist Jacqueline Olin called the determination into question, claiming that far too few medieval inks had been tested to reliable make that assertion. Olin even went so far as to demonstrate that ilmenite could be used to create

anatase using a leaching process available during the medieval era. Moreover, Olin conducted radiocarbon dating on the parchment and found a date circa 1434. Not long after, researchers at the University of California conducted an x-ray analysis and discovered that the anatase was only present in very minute quantities further calling McCrone's determination into question (Gugliotta, 2004). It would not be until very recently, as discussed previously, that the matter of authenticity from a scientific perspective would finally find something resembling resolution. The case of the Vinland map is an excellent example of the need for cross-disciplinary collaboration, as well as evidence that determinations can change over time based upon the emergence and utilization of new technologies and the refinement of previous methods in order to paint a more accurate picture.

We can infer that further development of the presented techniques in the case studies mentioned, as well as the emergence of new technologies, can only serve to better the fields of forgery detection, and therein allow for more deceptions to be detected. In fact, there has been recent focus in the field on the use of artificial intelligence (A.I.) that has shown promising results in determining the authenticity of works.

In 2018, a competition called "Painter by Numbers" hosted on Kaggle tasked contenders with the challenge of developing a program which could identify paintings by the same artist. Challengers were given 79,433 instances, from 1,564 unique painters, from which predictions would need to be made for nearly 22 million pairs. The winner of the challenge, Nejc Illenic, was able to program a model that successfully extracted painters' unique styles and subsequently used machine learning to recognize these features in association with the artist. Surprisingly, Illenic's program was even successful in

identifying the difference between works by Vermeer and van Meegeren, which are nearly indistinguishable to the untrained eye. This was attributed in part to van Meegeren's methodology of copying styles from multiple works, while Vermeer of course had a style all his own (Huang, 2018).

Similarly, A.I. was successfully utilized in 2017 during a collaborative study from Rutgers University and the Atelier for Restoration & Research of Paintings in the Netherlands. As part of the study, researchers provided their A.I. with 300 line-drawings from a variety of artists including Matisse, Picasso, and Schiele, among others. Through the analysis of these works, the A.I. identified nearly 80,000 individual strokes and assigned each stroke to the given artist, and learned details such as line weight that could further differentiate the artist. Ultimately, it was found that the A.I. was successful in correctly identifying the works creator 80% of the time, and was able to successfully identify forgeries presented every time often needing to observe only a single stroke. Researchers touted this result claiming that no human could accomplish such a thing. It was additionally noted that this kind of analysis is unique in that it could identify stylistic characteristics of an artist that would not otherwise appear to a human observer, as in many cases the artist themselves may not have been entirely aware of them. Researchers posited that this kind of analysis could provide a cost-effective alternative, for the time being works paper, in contrast to the more costly methods of chemical analysis. Finally, researchers noted that because their A.I. was relying on line work in order to make determinations there is a clear limitation in the wider application of the technique, particularly an inability to analyze works with no visible lines or brushstrokes (Cascone, 2017).

In 2021, a series of tests utilizing A.I. determined that the famous masterpiece *Samson and Delilah* by Peter Paul Rubens was most likely a fake. For quite some time the piece's authenticity had been the subject of much discussion. Detractors for the piece's authenticity pointed to the cropping of Samson's toes, which were clearly present in a number of previous incarnations depicting the piece. Skeptics questioned the quality, style, and color palette of the work, with some going so far as to maintain websites compiling and outlining evidence of the piece's proposed issues. Considered most damning was the provenance of the work during the 20th century. The piece, originally commissioned in 1609, disappeared following the death of Nicolaas Rockox in 1640. The piece would not subsequently resurface until 1929 in Paris, at which point Ludwig Burchard, an expert on Rubens, signed a certificate attesting that the piece was legitimate. It would later be revealed following Burchard's death that he had falsely authenticated the work for his own benefit. As such, the current tests compared the work against 148 uncontested works attributed to Rubens on the basis of brushstroke patterns as well as a number of other indicators of Rubens style. Upon completion the algorithm utilized came to the conclusion that there was a 91% chance that the piece was fake. Researchers were so taken aback by the result that they repeated the experiment a number of times, with each returning results that there was more than a 90% chance that the piece was fake (Cascone, 2021).

This new emerging frontier seems promising for the future of forgery detection, perhaps easing the pressure on experts to make absolute determinations on the authenticity of pieces, and instead help inform the processes discussed above. In this way, the detection speed of forgeries can be significantly increased and thus the likelihood the institutions will take in forgeries is decreased. Taken in full, the interplay of stylistic

methods and chemical analysis methods is critical in the prevention of institutions obtaining future forgeries. With each new discovery of a forgery increased scrutiny is placed upon museums and collecting institutions in order to thoroughly vet their acquisitions prior to acceptance or purchase. In this way, museums themselves can become case studies. Over time, with the discovery of new information, museums will continue to call the authenticity of their pieces into question. The modern museum does not need to be afraid to admit that some of the acquisitions could have been falsified. This is supported by the continued refinement of techniques discussed previously, that allows museums to make determinations that would not have been feasible to have been made before. With the further development of techniques and methodologies, the window is opened to new possibilities for detection of flaws that are nigh invisible to the naked eye. The methods discussed above provide an arsenal of tools at the disposal of the institutions in order to ascertain as much information as possible in order to have a comprehensive picture of a piece's history, and thus determine the validity of provenance claims.

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