

**FROM EGG TO OIL:
THE EARLY DEVELOPMENT OF
OIL PAINTING
DURING THE QUATTROCENTO**

by

Kristin deGhetaldi

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Preservation Studies

Summer 2016

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ACKNOWLEDGEMENTS

I first became intrigued with the problems associated with characterizing binding media in Quattrocento Italian paintings in 2006 during a summer internship in the Paintings Conservation Department at the J. Paul Getty Museum in Los Angeles. I had only just recently been accepted into the Winterthur/University of Delaware Program in art conservation, a three-year graduate program that I attended from 2005 to 2008. Upon beginning my first graduate internship I realized that I still lacked an understanding of the relationship between historical materials and the various aesthetic qualities that we encounter in traditional Western easel paintings. In the back of my mind were the many paintings and frescoes that I had treated in Florence between 2002 and 2004. Finding it difficult to obtain the pre-program experience that is necessary to apply to the American graduate programs, I had enrolled in the Studio Art Centers International Post-Baccalaureate program (SACI) in 2002 where students are given the immediate opportunity to perform treatment on a number of objects including paintings. After completing the SACI program, I was hired by Stefano Garosi who had a successful private restoration studio located on Viale Lavagnini Spartaco near Piazza della Libertà. The number and quality of paintings that passed through his studio were eye-opening, and I was encouraged to learn as much as possible about the various schools and artists which I saw on a daily basis. By 2004 the internet was in full bloom, and I was suddenly able to access the *Journal of the American Institute for Conservation*. It was then that I realized I had far more to learn about the field. After making a difficult decision to leave Florence and return to the

United States, I enrolled in additional courses and internships and was accepted into a graduate program by the Fall of 2005. Despite all of these experiences, I still had an enormous gap in my knowledge of historical artists' materials. I had played around with fresco painting in Stefano's studio, and at SACI we were given the opportunity to paint with egg tempera. But by the time I reached the Getty, I was restoring paintings twice my size without any intimate knowledge of the oil technique. I called Dr. Joyce Hill Stoner my soon-to-be mentor at the University of Delaware and explained my concern. I quickly learned that the University was going to recruit a limited term researcher, who happened to have experience in painting as well as historical art materials. Brian Baade, who would eventually become my husband, worked very patiently with me as I re-created a painting "from the ground up": a copy of Rogier van der Weyden's *Portrait of a Woman* at the National Gallery of Art in Washington. As this was my first oil painting, Brian ensured that I experienced as many stages of the painting process as possible including planning the wooden support, extracting the glue size from parchment clippings, preparing the chalk-glue ground, sanding the panel, executing the underdrawing, mulling the oil colors, and applying the imprimatura, paint, and varnish layers. What became instantly clear is that historical pigments can be incredibly uncooperative. After corresponding with paintings conservator Catherine Metzger at the National Gallery of Art in Washington who had restored and examined the painting, we were given the appropriate analytical information relating to Rogier's use of pigments. The entire background was painted using coarse blue azurite with additions of carbon black, and I soon realized that applying the blue pigment can be likened to painting with oil and sand. I also learned how to manipulate the paint to create various effects such as scumbling, glazing, and

the precise, detailed lead-tin yellow highlights that are typically encountered in Flemish works.

After completing a summer internship at the Rijksmuseum, I began a year-long internship at the National Gallery of Art in Washington. I was given a range of treatments including a fifteenth-century Italian panel painting attributed to the school of Pesellino and Filippo Lippi. During visual examination of the panel, I found two characteristics particularly intriguing: the prominently raised foliage and the deep, transparent red lake glazes atop sections of the gold leaf. Neither of these attributes seemed to reflect what I had learned from my experience with tempera paints. During my morning gallery inspections I began to pay close attention to the labels in the Italian Renaissance galleries and found a wide range of descriptors relating to binding media. From “tempera and oil” to “tempera and oil(?)” to “tempera/oil,” the labels associated with Quattrocento paintings were confusing to say the least. I returned to the paintings conservator studio and began inquiring about the origin of these descriptions and whether they derived from results obtained from scientific analysis. I was told that these phrases had simply been assigned based on visual inspection by a curator-conservator team. By 2008, the London *National Gallery Technical Bulletin Series* had produced a number of wonderful publications that included detailed information relating to the medium analysis of easel paintings. I wondered if a similar study could be performed on the Italian Renaissance collection at the National Gallery in Washington, as the conservation department was fortunate to have a well-equipped scientific laboratory at its disposal. After learning that I had received the invitation to stay on as the Andrew W. Mellon Fellow, I pitched my research proposal to a panel of conservators and scientists and received a number of different responses. Some felt

(and rightly so) that the topic was much too broad while others stated that this research had already been explored (and “finalized”) by experts at the Doerner Institut. In addition, the scientists were apprehensive about the number of samples they would have to run as I was also planning on making a number of paint samples to serve as comparative references. Miraculously, I was somehow able to convince both departments to allow me to move forward with my proposed topic. I stated that I would narrow down the research to focus on a handful of paintings (case studies), that our findings could serve as complementary research to the studies performed at the Doerner, and that I would be willing to be trained on the analytical equipment so as not to burden the scientists with too many samples. What I then learned over the next three-years was rather disheartening. I found that of nearly all the tried-and-true analytical methods that were commonly used to characterize egg and/or oil-containing paints, none of them was generating the expected results. Perhaps the most memorable moment was when I performed staining tests on some of my very own paint cross-sections together alongside senior scientists, only to find that the stains (which many had relied on in previous technical studies) failed to give any definitive reactions that indicated the presence of egg yolk. While I found similar challenges when using FTIR, analysis using GC-MS presented an entirely different set of complications. Not only did certain pigments seem to affect the results, but every laboratory I researched appeared to be using different protocols for preparing samples. Throughout my fellowship, I was also given the opportunity to perform treatment on a number of Quattrocento paintings in addition to being exposed to other treatments being carried out in the paintings conservation studio. It became evident to me that some of the analytical challenges I was facing were likely due to the repeated restoration

campaigns that many of these paintings had experienced over the past 500 years. This, combined with the migration of fatty acids and the problems posed by reactive pigments, made it seemingly impossible to be able to accurately deduce whether an artist added a trace of partially heat-bodied walnut oil to his tempera paint in order to create a certain passage in the painting's composition. After all, much of the published literature on this subject appeared to suggest that such a deduction was entirely possible. This realization was fraught with potential problems: to admit that our previous assumptions about medium analysis required re-visitation was a notion that was not readily accepted by many. I was inclined to simply report my findings and shelve my research in the conservation files at the National Gallery and pursue other endeavors.

By late 2010 I was starting to wrap up my research and anticipate the next stage in my career after the completion of my three-year fellowship in Washington. I had found myself growing more and more interested in teaching and reached out to my previous mentors at the University of Delaware. After a meeting with professors Richard Wolbers, Debra Hess Norris, and Dr. Joyce Hill Stoner, I was encouraged to apply to the PhD Program in Preservation Studies (PSP). If accepted, I would be allowed to continue my research and given ample opportunities to improve my teaching skills. By the Fall of 2011 I was enrolled in the PSP program as the first student to focus on Old Master painting techniques. The series of events that followed were indeed serendipitous. I was graciously welcomed by Dr. W. Christian Petersen at the Scientific Research and Analytical Laboratory as he allowed me to work alongside him for nearly two years, learning the challenges associated with the world of chromatography-mass spectrometry. I enrolled in art history courses taught by Dr.

Perry Chapman to learn more about how art historians view and interpret the complex and vast body of technical information that is generated by the conservation field. I took independent courses with a chemometrician (Dr. Stephen Brown), a conservation scientist (Dr. Kenneth Sutherland), an analytical chemist (Dr. Murray V. Johnston), and an art historian (Dr. Carl Strehlke), all of whom ended up impacting my resulting dissertation. During my second year as a PhD student, I began to wander the halls of the Chemistry department at the University of Delaware, hoping for an impossible scenario: to locate an analytical instrument that showed some promise in picking apart the egg-oil question. I knocked on the door of the Surface Analysis Facility run by Dr. Thomas Beebe, Jr. and ran into my soon-to-be colleague Zachary Voras, a PhD student in Chemistry who was also in his second year. We began our collaboration immediately. I procured cross-sectional samples from gracious colleagues at the Walters Art Museum in Baltimore of Italian paintings while Zach continued to refine our sample preparation using my reference samples. Our results obtained using Time-of-Flight Secondary Ion Mass Spectrometry were revealing. Not only were we able to image areas of glue, egg, and oil, but the technique could also be applied to already existing cross-sections, eliminating the need to collect additional samples from works of art. Furthermore the images we collected revealed other unexpected findings. I was able to connect with Dr. Jaap J. Boon who generously shared with us his years of expertise using SIMS applied to samples collected from Dutch and Flemish paintings nearly a decade prior. We relied heavily on early GC-MS studies to help locate which chemical markers we were to look for. While much remains to be explored using this exceptionally sensitive surface analysis technique, it appears to show great promise for the future study of paint cross-sections. Perhaps the most important lesson I have

learned throughout the past eight years of researching this topic is that we must constantly re-assess analytical techniques used in cultural heritage, particularly those that we have come to rely heavily upon. If I had not forced myself to work with historical materials early on in my graduate career, I realize that many the issues summarized in this dissertation relating to the analysis of Old Master paintings would have likely gone unnoticed. Those of us who continue to be stewards of historic collections and the interpreters of deceased artisans must be ever vigilant in our ability to question what is presented in the literature whilst maintaining close dialogues and friendships with colleagues in our sister fields of the arts and sciences.

Dissertation Committee

I would like to extend my utmost gratitude to the members of my dissertation committee who have worked so patiently alongside me throughout my dissertation: Dr. Joyce Hill Stoner (committee chair), Edward F. and Elizabeth Goodman Rosenberg Professor of Material Culture Studies and Director of the Preservation Studies Doctoral Program, University of Delaware Department of Art Conservation; Dr. Murray Johnston, Professor and Chair, University of Delaware Department of Chemistry and Biochemistry; Dr. W. Christian Petersen, Associate Professor in the Winterthur/University of Delaware Program of Art Conservation/Conservation Scientist, Winterthur Museum; Dr. H. Perry Chapman, Professor and Associate Chair, University of Delaware Department of Art History; and Dr. Meredith J. Gill, Professor and Chair, Department of Art History and Archaeology, University of Maryland.

Museums, Institutions, and Individuals

I am indebted to many institutions and individuals for assisting me throughout

the early stages of my research and throughout my dissertation. Brian Baade, Assistant Professor of Historic Art Materials at the University of Delaware, has continually served as my sounding board and loving critic. Dr. Joyce Hill Stoner has served as my mentor well before I began this research and without her knowledge, support, and expertise, managing the world of dissertation writing would have proved next to impossible. Debra Hess Norris, Chair and Professor of the Department of Art Conservation, and Henry Francis DuPont Chair in Fine Arts, University of Delaware, has provided me with a never-ending stream of encouragement and support. Dr. W. Christian Petersen has been incredibly patient, introducing me to the complex world of organic analysis and all of its beautiful mysteries. Without assistance from my colleague Zachary Voras, a PhD candidate in Chemistry at the University of Delaware, many of the analytical findings presented in this dissertation would not have been possible. Dr. Thomas Beebe Jr. was most generous with his students as well as his instruments at the Surface Analysis Facility, as was Dr. Karl Booksh, both highly accomplished scientists at the University of Delaware. Dr. Steven Brown, the Willis F. Harrington Professor in Chemistry and Biochemistry at the University of Delaware, patiently helped me to develop a better understanding of multivariate analysis while Dr. Murray Johnston (mentioned previously) generously devoted his time to answering my many questions relating to analytical techniques. Dr. David Stone, Art History Professor and Director of the Curatorial Track Program at the University of Delaware, and Dr. Perry Chapman (mentioned previously) served on my dissertation exam committee, while both Dr. Chapman and Dr. Monica Dominguez Torres, Associate Professor and Director of Undergraduate Studies, shared their knowledge with me relating to cross-cultural exchanges during the Renaissance. I am

also indebted to Professor Richard Wolbers, Associate Professor, Coordinator of Science and Affiliated Paintings Professor at the University of Delaware and Matthew Cushman, Conservator of Paintings at Winterthur Museum, for sharing their expertise with me throughout my research. Dr. Jennifer Mass, formerly head of the Scientific Research and Analytical Laboratory at Winterthur Museum, and Catherine Matsen, Conservation Scientist, were also generous with their time, allowing me full access to the analytical equipment housed at Winterthur Museum.

My list of outside readers and contributors includes many established professionals, for whom I hold the utmost respect, both for their knowledge and expertise as well as the time that each person devoted to poring over various chapters. Dr. Noëlle Lynn Wenger Streeton, Associate Professor of Conservation Studies (IAKH) at the University of Oslo, provided me with invaluable comments and edits concerning my Introduction and second chapter. The same can be said of Lara Broecke, an independent painting conservator who single-handedly undertook the re-translation of Cennino Cennini's *Il Libro dell'Arte*. Her insight and suggestions contributed greatly to my summary of primary sources covered in chapter three. Alan Phenix, Conservation Scientist and Paintings Conservator at the Getty Conservation Institute in Los Angeles, provided me with useful suggestions and insight regarding my overview of analytical techniques outlined in chapter five. Dr. Patrick Dietemann, Graduate Chemist at the Doerner Institut graciously provided me with many of his articles (some not yet published). He was extremely willing to share and exchange ideas with me regarding the complex world of binding media analysis. Dr. Jaap J. Boon of JAAP Enterprise for Art Scientific Studies was instrumental in helping me interpret and comprehend the rather daunting amount of information we obtained

using ToF-SIMS. His expertise with SIMS technology relating to the analysis of easel paintings has proved immensely helpful to myself and my chemistry colleagues as he has always been available to offer advice and guidance relating to our findings.

I would also like to thank Dr. Carl Brandon Strehlke, former Curator of the John G. Johnson Collection at the Philadelphia Museum of Art, who was also exceptionally generous with his time serving as a proctor on my dissertation exam committee. Thanks to Dr. Strehlke, I was given the opportunity to participate in the *Around Antonello* Conference at the Istituto Universitario Olandese di Storia dell'Arte in Florence on October 18, 2012. I am also indebted to paintings conservators Teresa Lignelli and Mark Tucker, also at the Philadelphia Museum of Art, who graciously allowed me access to the conservation files. Dr. Kenneth Sutherland, Conservation Scientist at the Art Institute of Chicago (formerly at the Philadelphia Museum of Art), also generously consulted with me on topics relating to multivariate analysis used in cultural heritage. Many of the new analytical findings presented in this dissertation would not have been possible without the generosity and devotion demonstrated by my colleagues at the Walters Art Museum. Eric Gordon (Head of Painting Conservation), Karen French (Senior Paintings Conservator), Pamela Betts (Associate Painting Conservator/Exhibitions Conservator), and Dr. Glenn Gates (Conservation Scientist) provided me with several precious cross-sections from Italian paintings in the Walters collection. Finally, Abbie Vandivere, Paintings Conservator at the Mauritshuis, and Dr. Gwenaëlle Gautier, former Associate Conservation Scientist at the Art Institute of Chicago, generously shared their dissertations with me, both of which proved invaluable resources throughout my research.

I have many people to thank during my four years in the Paintings Conservation Department at the National Gallery of Art in Washington, DC. Sarah Fisher, former Head of the Paintings Conservation Department, as well as Ross Merrill, former Head of the Conservation Department, were both particularly supportive of my research interests. Former Senior Paintings Conservator David Bull graciously allowed me to examine and sample Italian paintings that he was treating in the conservation studio during my fellowship. I am indebted to my supervisor, Michael Swicklik, Senior Paintings Conservator, and to Carol Christiansen, for their support, advice, and expertise. René de la Rie, former Head of the Scientific Research Department, was extremely generous and supportive, allowing me to work closely with his staff throughout my entire time as an intern and fellow. Dr. Michael Palmer, Dr. Melanie Gifford, and Dr. Barbara Berrie assisted me in the interpretation of cross-sectional paint samples and protocols used for staining. Conservation scientists Dr. Suzanne Q. Lomax and Dr. Christopher Maines devoted many hours, graciously training me to run the FTIR and GC-MS and patiently helping me with the interpretation of dozens of spectra and chromatograms. Dr. John K. Delaney enthusiastically worked with me in an attempt to design a non-destructive method of characterizing egg-oil paints using NIR hyperspectral imaging. I was also given the opportunity to consult with conservation scientists Dr. Michael Schilling at the Getty Conservation Institute and Julie Arslanoglu at the Metropolitan Museum of Art, both of whom shared their expertise with me regarding GC-MS and ELISA, respectively. My discussions with Julie would later lead to further studies exploring the potential interference caused by certain pigments when identifying proteins in paint samples using ELISA. I also thank the conservation scientists David A. Peggie, Marika Spring,

and Rachael Billinge for generously allowing me to meet with them to discuss the organic analysis of Italian paintings in the collection of the National Gallery, London. Finally, I could not have generated and produced the many paint samples without the materials provided by Dr. Georg Kremer of Kremer Pigmente Farbmühle and George O'Hanlon of Natural Pigments.

Funding

This dissertation has been made possible by numerous funding sources and awards over a five-year period. Academic funding sources through the University of Delaware have included the Paul Coremans Endowment Art Conservation Research Fellowship, an award through the University of Delaware Public Humanities Institute (NEH Challenge Grant in Public Engagement), Professional Development for Graduate-level students, and the College of Arts and Sciences Dean's Doctoral Scholarship awards. External funding sources have included a Chemical Heritage Foundation Fellowship Award, a Rotary District Award for Public Outreach/Academic Excellence through the Gundaker Foundation, and Professional Development Awards through the Foundation for the American Institute for Conservation (FAIC), the Indigo Arts Alliance, and the Renaissance Society of American/Italian Art Society.

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ABSTRACT

This dissertation demonstrates that a more accurate assessment of Quattrocento painting practice can be accomplished only if the original stratigraphy of the paint and ground layers is preserved during organic analysis. The evolution of oil painting in Renaissance Italy must now be re-examined due to advancements in the analysis of binding media and recent improvements in primary source research. Contemporary conceptions of Western European painting techniques stem from a complex history associated with conservation science, treatment methodologies, and connoisseurship. New findings suggest that Italian painters working in and around the Veneto were likely introduced to the oil technique well before 1400 while analysis and visual examination of fifteenth-century works from southern Italy also demonstrate an acute familiarity with the northern medium and aesthetic. The decision to use an egg vs. an oil binder is inextricably tied to an artist's technique and arguably as important as the conscious selection of certain pigments. Such considerations will help to further elucidate the dissemination of oil painting south of the Alps during the fifteenth century.

In this dissertation I demonstrate that problematic and even incorrect assumptions have been made regarding the characterization of binding media in early Italian paintings. This is shown through the creation of historically representative paint reconstructions that can help in determining the visual qualities and chemical components of traditional egg tempera and oil paint as well as the analysis of actual works of art. In addition, Contamination from restoration materials, the migration of

fatty acids, the presence of reactive pigments, and the formation of degradation products are now known to affect the detection of certain chemical markers that are key in helping scientists to identify the binders present in a work of art. Newly recognized inaccuracies relating to early analytical protocols have prompted scientists to develop more sophisticated methods for distinguishing egg tempera from oil paints, and earlier technical studies of Quattrocento paintings must now be re-evaluated. A new discourse is needed to develop a more accurate understanding of Quattrocento painting techniques, workshop practices, attribution, and the diffusion of artistic processes throughout Europe.

Chapter 1

INTRODUCTION

Italian painting experienced a significant transition during the fifteenth century as artists moved away from traditional egg tempera paints and began to embrace the oil technique. Technical evidence suggests that a handful of artists, such as Giovanni Bellini (1430 -1516), Domenico Ghirlandaio (1449 - 94), and Antonello da Messina (1430 - 79), played a substantial role in facilitating the adoption of oil painting in Italy, a skill that painters working north of the Alps had already managed to master several decades prior.¹ Early twenty-first century exhibitions and publications have prompted a resurgence of interest in the cultural exchanges that occurred between Italy and the Low Countries; in some instances Italian artists were compelled to incorporate the oil medium into their daily workshop practice in an attempt to emulate their northern counterparts.² The following chapters will demonstrate

¹ Joyce Townsend and Erma Hermens, “Binding Media” in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce Hill Stoner and Rebecca Rushfield (London: Routledge, 2012), 208-11.

² Refer to the following sources for more information on North-South cross-cultural exchanges: Bernard Aikema and Beverly Louis Brown, eds., *Renaissance Venice and the North: Crosscurrents in the Time of Durer, Bellini, and Titian* (New York: Rizzoli Intl. Publishing, 2000); Marco Lucco, Dominique Thiebault, and Marco Collareta, *Antonello da Messina. L'opera completa* (Milano: Silvana Editoriale S.p.A., 2006); Bert W. Meijer, ed., *Firenze e gli antichi Paesi Bassi, 1430-1530 dialoghi tra artisti: da Jan van Eyck a Ghirlandaio, da Memling a Raffaello* (Firenze: Istituto Universitario Olandese di Storia dell'Arte di Firenze, 2008); Jill Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery* (New Haven and London: Yale University Press and National Gallery Publications, 1991), 193-204; Kieth Christiansen, “The View from Italy,” in *From Van Eyck to Bruegel: Netherlandish Painting in the Metropolitan Museum of Art*, ed. Maryan W. Ainsworth and Kieth Christiansen (New York: Metropolitan Museum of Art, 1998), 39-62.

that the evolution of oil painting in Renaissance Italy must now be re-examined due to recent advancements in scientific analysis and improvements in primary source research. Only by improving the ability to characterize egg and oil paints can technical researchers aid scholars in developing a more accurate assessment of how Quattrocento painting practice evolved during this transitional period in Italian art.

The decision to use an egg vs. an oil binder is inextricably tied to an artist's technique and arguably as important as the conscious selection of certain pigments. Egg tempera and drying oil have little in common, so the new medium presented challenges to the early Italian painter. Pigments mixed with oil can produce colors with rich, deep qualities, enabling the artist to achieve subtle gradations and transparent paint layers. Oil paint takes much longer to dry than tempera or other aqueous-based media, and allows the artist to blend and further manipulate the paint long after it has been applied to the support. If a drying oil was prepared incorrectly, however, the paint film could take months to adequately dry and even lead to significant yellowing and wrinkling of the paint.³ On the other hand, tempera paint, created by mixing pigments with diluted egg yolk, does not lend itself well to blending as the paint dries almost immediately after it is applied to the substrate, hence the characteristic hatched strokes that are often visible on tempera paintings (see Figure 1.1). Visual inspection and scientific analysis of Quattrocento paintings have also pointed towards the use of mixed techniques, layering oil atop egg tempera paint or even mixing the two together, creating a paint referred to as *tempera grassa*.⁴

³ It should be noted that certain pigments can also slow the drying rate of oil, particularly lake pigments and bituminous browns/blacks.

⁴ John Mills and Raymond White, "Analyses of Paint Media," *National Gallery Technical Bulletin* 1 (1977): 57-9; Jill Dunkerton and Ashok Roy, "The Materials of a Group of Late Fifteenth-century Florentine Panel Paintings," *National Gallery Technical Bulletin* 17 (1996):



Figures 1.1 (left) and 1.2 (right): Visual comparison of traditional egg tempera paint (left) with traditional oil paint (right). Details taken from reconstructions (created by Brian Baade and the author) of Duccio di Buoninsegna's *The Virgin and Child with Saints Dominic and Aurea* (c. 1312-1315) and Hans Memling's *St. Veronica* (c. 1470/1475).

In this dissertation I will address questions posed by historians, collectors, conservators, and scientists regarding the gradual shift from egg tempera to oil, as it is a topic that continues to challenge our understanding of traditional painting practices. By reviewing past technical studies of fifteenth-century artworks and exploring new methods of paint analysis, I intend to demonstrate how this information impacts our current perception of Italian artists working at the beginning of the Renaissance. Newly recognized inaccuracies relating to early analytical protocols reveal that more sophisticated methods are required in order to accurately distinguish egg tempera from oil paints, methods that will be explored further in the final chapters of this dissertation. These findings reveal that early conclusions

20-31; Michael Hirst and Jill Dunkerton, *Making and Meaning: The Young Michelangelo - The Artist in Rome, 1496-1501* (London: National Gallery London, 1994), 100-1.

relating to binding media used throughout the history of painting in Italy and much of Western Europe must now be reconsidered.

Leonardo da Vinci's double-sided *Ginevra de Benci* in Washington DC provides an informative visual example of this transition: egg tempera paints were used to depict the emblematic symbol on the reverse, while rich, transparent oil colors were reserved for the more prominent portrait of Ginevra. Leonardo's conscious decision to adopt the oil technique can be partly linked to the numerous north-south cultural exchanges, many of which will be explored in greater detail in the second chapter. Several factors helped to spur this gradual shift towards oil painting in Italian workshops: socio-economic relationships between countries north and south of the Alps and religious events that occurred during the aftermath of the 1378 Papal Schism.⁵ These factors helped to set the stage for artists who were open to learning new painting methods, generating a market for Italian artworks that were heavily influenced by the northern aesthetic. The gradual influx of northern art into Italy must have been both fascinating and intimidating to Italian painters of the early 1400s, compelling them to rethink the traditional Italian aesthetic in order to compete with Flemish works that were beginning to appear in courtly collections and in the marketplace. Thanks to recent collaborative research among art historians, scientists, and conservators, scholars are now able to re-examine these early Italian oil painters in a more appropriate cultural context.

As a thorough understanding of early workshop practices in early Renaissance Italy has not yet been achieved, I will address this topic of treatises at length in chapter three. Before the explosion of technical painting analysis in the 1960s and '70s, information

⁵ Raymond A. de Roover, *The Rise and Decline of the Medici Bank: 1397-1494* (Washington DC: Beard Books, 1999), 240-254; Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Art Press, 2004), 89-93; Walter Ullmann, *The Origins of the Great Schism* (Hamden: Archon Books, 1948), 1-101.

regarding early Renaissance painting techniques was based on Giorgio Vasari's *Lives of the Artists*, Cennino Cennini's *Il Libro d'Arte*, as well as a few other lesser known sources.⁶ While both Vasari's and Cennini's texts are invaluable resources, each has led to misconceptions and over-generalizations regarding early Italian painting technique. For example, while Vasari did occasionally give a nod to Jan van Eyck and Rogier van der Weyden in his *Lives of the Artists*, perhaps due to his pervasive Tuscan pride, he glossed over the enormous impact that northern art had on a number of Italian painters during this period. Unfortunately, Vasari's elaborate tale recounting the spread of oil painting in Italy falsely credited a single Italian artist with disseminating the technique associated with this "secret" medium; technical studies have now shown that artists working before Antonello da Messina may have simultaneously embraced the oil medium.⁷ Furthermore, some of these early manuscripts, such as Cennino's frequently cited *Il Libro d'Arte*, appear to have suffered from certain forms of corruption and mistranslations, a symptom that may have been overlooked by scholars such as Mary P. Merrifield, Sir Charles Eastlake, and Daniel V. Thompson whose publications continue to be widely used today.⁸ While Cennino's text does refer to the practice

⁶ Mark Clarke, *Mediaeval Painters' Materials and Techniques: The Montpelier 'Liber Diversarum Arcium' (c. 1200-1400)* (London: Archetype Publications, 2011), 10-92; Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte,'* trans. Daniel V. Thompson, Jr. (1933; repr., New York: Dover Publications, 1954), 57; Giorgio Vasari, *Vasari on Technique*, trans. Louise S. Maclehorse (1907; repr., New York: Dover Publications, 1960), 228-30, 294-7.

⁷ Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197-204.

⁸ Charles Lock Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vols. I & II (1847; repr., New York: Dover Publications, 2001); Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vols. I & II (1849; repr., New York: Dover Publications, 1999); Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte,'* trans. Daniel V. Thompson, Jr. (1933; repr., New York: Dover Publications, 1954).

of oil painting (the text was likely written no earlier than 1398), it is important to consider how and whether this treatise was used by artists, especially in light of recent technical studies and newly translated versions of the manuscript.⁹ The word “temperare” in Italian, for example, has a wide range of meanings as the term can refer to the act of mixing colors into a binder or it can refer to a particular type of binder depending on the context.¹⁰ Lara Broecke’s 2015 translation of Cennino Cennini’s *Il Libro d’Arte* reassesses Thompson’s 1954 translation, more accurately describing the historical text and correcting more than 400 errors.¹¹ While certain texts should be revisited, others still await translation or transcription; it is entirely possible that future scholarship will uncover information that sheds additional light on Quattrocento painting practice.

Certainly Michelangelo, Leonardo, and Raphael were masters of the oil medium; chapter four, however, will explore the materials and techniques used by their predecessors, Italian painters who were among the first to deviate from artistic tradition. Much of the information covered in chapter four summarizes technical studies of Quattrocento paintings outlined in the *National Gallery Technical Bulletin* series, as well as other publications associated with the Gallery. Since the *Bulletin*’s inception in 1977 there has been an international growth in technical studies, giving rise to a relatively new field now termed “technical art history,” which focuses on the materiality of art and how such information can

⁹ Lara Broecke, *Cennino Cennini’s ‘Il Libro dell’Arte’: A new English translation and commentary with Italian translation* (London: Archetype Publications, 2015), 5; See also Carl Brandon Strehlke and Cecilia Frosinini, eds., *The Panel Paintings of Masaccio and Masolino: The Role of Technique* (Milan: 5 Continents Editions srl, 2002).

¹⁰ Broecke, *Cennino Cennini’s ‘Il Libro dell’Arte’: A new English translation and commentary with Italian translation*, 268.

¹¹ *Ibid.*, 1.

be used to better inform our understanding of an object.¹² Technical studies have appeared in publications that have in turn help to elucidate certain aspects relating to early Italian painting practice. Paula Nuttal's *From Flanders to Florence* has been a seminal text for this dissertation and offers a fairly recent perspective on how northern art impacted Italian painting technique (through the eyes of an art historian).¹³

An artwork that continues to be re-evaluated with various analytical techniques over an extended period of time can be used to effectively communicate the history of conservation science to a wider audience. Perhaps one of the most successful examples that emphasized this complex history is the analysis of the Ghent altarpiece, a story that is brilliantly summarized in Noelle Streeton's *Perspectives on the Painting Technique of Jan van Eyck*.¹⁴ What is unique in the case of the Ghent altarpiece is that these oil paintings have been revisited by scholars and scientists every ten to twenty years, each time with the intent of testing new analytical methods in an effort to prove or disprove how the masterpiece was created. The study of the Santa Maria Maggiore Altarpiece by painters Masolino and Masaccio (see Figure 1.3) is one of the closest comparative examples that the Italian Renaissance has to the "Ghent altarpiece narrative"; the Masolino/Masaccio project has involved multiple groups of scientists, art historians, and conservators working together over a

¹² Maryan Ainsworth, "From Connoisseurship to Technical Art History: The Evolution of the Interdisciplinary Study of Art," *Getty Conservation Institute Newsletter* 20 (2005): 4-10; Ashok Roy and Jill Dunkerton, "Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London," in *Early Italian Paintings: Approaches to Conservation*, ed. Patricia Sherwin Garland (New Haven: Yale University Art Gallery, 2002), 120-31.

¹³ Nuttal, *From Flanders to Florence*, 87-199.

¹⁴ Noelle Streeton, *Perspectives on the Painting Technique of Jan van Eyck* (London: Archetype Publications, 2013), 10-106.

period of almost ten years in an effort to better characterize the painting methods used by both artists.¹⁵ Numerous analytical techniques were performed by some of the world's leading conservation science laboratories, ending with the most recent evaluation performed in 2002 using some of the more up-to-date technology and instrumentation.¹⁶ The resulting conclusions from this collaborative study were groundbreaking for Italian scholars focusing on the evolution of oil painting and will be discussed at length in chapters four and five. However, subsequent discussions conducted with scholars at both the Philadelphia Museum of Art and the National Gallery of Art, London indicate that the interpretations of the analytical results of the Masaccio/Masolino project continue to change. While it is relatively easy to follow shifting perspectives in the hard sciences and in art history, art conservation has further to go, as it is more difficult for those outside of the profession to trace changing viewpoints regarding the analysis of easel paintings as I will explain below.

In chapter five, I will attempt to outline the evolution of analytical techniques as they relate to the characterization of egg and oil paints; chapter six will summarize a select number of methods that are commonly being used in today's institutional laboratories. Although art historians are becoming more familiar with technical analysis and its various benefits, there remains a lack of dialogue about how far certain analytical capabilities can extend. The scientific instruments used to examine Leonardo's works some fifty years ago are rudimentary

¹⁵ See also Carl Strehlke and Cecilia Frosinini, eds., *The Panel Paintings of Masaccio and Masolino: The Role of Technique* (Milan: 5 Continents Editions srl, 2002).

¹⁶ Kenneth Sutherland, "Masaccio and Masolino Scientific Report – 11 December, 2002" (Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art).

Figure removed due to copyrighting

Figure 1.3: Digital reconstruction of the Santa Maria Maggiore Altarpiece (c. 1427-28) by Masaccio and Masolino da Panicale. The double-sided wings and central panel are now divided between the National Gallery, London (left, *Saints Jerome and John the Baptist/A Pope (Saint Gregory?) and Saint Matthias*), the Museo Nazionale di Capodimonte, Naples (central panel, *The Founding of Santa Maria Maggiore*), and the Philadelphia Museum of Art (right, *Saints John the Evangelist (?) and Martin of Tours/Saints Peter and Paul*).

compared to the instruments we use today.¹⁷ Today conservators and scientists are charged with the daunting task of staying up to date with ongoing scientific advancements, a

¹⁷ Kristin deGhetaldi, "The Organic Analysis of Artworks: Early Challenges and Future Directions," *Western Association for Art Conservation* 34 (September 2012): 12-17; Joyce Townsend and Jaap Boon, "Research and Instrumental Analysis in the Materials of Easel Paintings," in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 341-366; David Pegg, "The Chemistry

significant challenge for such a small field with limited economic and technological resources. In addition, sampling artwork is a precarious endeavor, one that is often difficult to repeat if an object is in pristine condition and/or highly valued. Collecting even the tiniest of samples still requires removing original material from an artwork; therefore *if*, *why* and *where* an object should be sampled become crucial questions when conducting organic analysis. Consequently, when an analytical method is suddenly determined to be problematic, or an interpretation found to be misguided, it is even more imperative that these issues are effectively communicated throughout the conservation community particularly to avoid unnecessary sampling.

To date there has been little discussion among conservators on how to address these issues; when a technique is deemed outdated or a previous conclusion is found to be problematic, the small field of art conservation is ill-equipped to carry out appropriate measures of widespread communication in contrast to its much larger, sister fields in the hard sciences. Failure to address ongoing changes in the interpretation of organic analysis has directly impacted research on early Italian painting technique: while the conservation and science communities slowly begin to re-evaluate analytical methods, art historians continue to look to older and sometimes outdated technical studies. One reason that some scholars remain unaware of this “scientific evolution” may be explained by the overwhelming number of variables, making it difficult to compare one study with the next. For example, different

and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century,” in *Science and Art: The Painted Surface*, eds. Antonio Sgamellotti, Brunetto Brunetti, and Costanza Miliani (Cambridge: The Royal Society of Chemistry, 2014), 209-29; Roy and Dunkerton, “Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London,” 120-31. See also Francesca G. Bewer, *A Laboratory for Art: Harvard’s Fogg Museum and the Emergence of Conservation in American, 1900-1950* (Cambridge: Harvard Art Museums and Yale University Press, 2010).

laboratories possess different instruments; the same instruments can even generate different results depending on a variety of factors and so on. An accessible overview of scientific methods used to identify proteins (e.g. egg, casein, animal glues), resins, oils, and other materials is therefore summarized in chapter five, including a clear and concise summary of how these methods have evolved and changed over the past seventy-five years.

Studies performed since the 1990s, particularly those published by the National Gallery, London, that focus on early Italian painting techniques, have generally presented a clear interpretation of organic materials.¹⁸ While many of these studies still offer useful technical information, they have also over-simplified the convoluted processes involved with the interpretation of these 500-year-old works of art. Many of these fifteenth-century artworks continue to undergo chemical changes and have been subjected to numerous restoration campaigns, all of which can affect what our scientific instruments are able to tell us about the original materials and techniques used to create the work. The growth in technological advancements has generated a need to revisit previously assumed notions, particularly notions that were once thought to be straightforward. This is certainly the case with fifteenth-century Italian paintings; works today are given arbitrary labels that provide the viewer with vague descriptions of binding media. By the 1990s, technical studies began to suggest that Italian painters during this period occasionally employed *tempera grassa* (mixtures of egg and oil) as a painting medium.¹⁹ However, recent research has revealed that a number of factors can

¹⁸ Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 161-204; Roy and Dunkerton, "Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London," 120-31.

¹⁹ Jill Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, eds. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997): 29-35.

interfere with the characterization of drying oils and egg tempera; reactive pigments, for example, such as copper-based colorants and lead white can complicate organic analysis and ultimately lead to misconceptions relating to the identification of binding media used by Italian artists.²⁰ While this issue is now recognized by most practicing conservation scientists, the conservation and art history communities are less aware of these complicating factors. But perhaps even more problematic is the misconception associated with fatty acids, chemical markers that have been used to draw definitive conclusions about the media used by Italian artists working more than 500 years ago. Some conservation publications continue to perpetuate these problematic guidelines, ones that are derived from an earlier time when the current technology suggested that fatty acid ratios were thought to convey concrete information about the characterization of a drying oil, whether a mixture (e.g. egg and oil) was possibly present, and even how a drying oil was prepared (e.g. heat-bodied, partially heat-bodied, etc.).²¹ While these ratios can still provide important data, twenty-first century

²⁰ Ester B. Ferreira, Jerre van der Horst, and Jaap Boon, "Chemical aspects of the binding media of the Oranjezaal ensemble: an insight into 17th century Netherlandish materials and methods" in *ICOM Committee for Conservation, 14th Triennial Meeting, The Hague, 12-16 September 2005: Preprints*, ed. Isabelle Verger, vol. I (London: James & James, 2005), 12-16; Marika Spring and Catherine Higgitt, "Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media," in *Medieval Painting in Northern Europe: Techniques, Analysis, Art History*, ed. Jilleen Nadolny (London: Archetype, 2006), 223-29; Peggie, "The Chemistry and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century," 209-29.

²¹ John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects* (1987; repr., Oxford: Butterworth-Heinemann Ltd., 1996), 14-30; Ferreira et al., "Chemical aspects of the binding media of the Oranjezaal ensemble: an insight into 17th century Netherlandish materials and methods," 12-16; Larry Keith et al. "Leonardo da Vinci's 'Virgin of the Rocks': Treatment, Technique and Display," in *National Gallery Technical Bulletin* 32 (2011): 48.

scientists realize that we are only at the beginning of our understanding of how to accurately characterize historical paint systems.

In chapters five and six I will also demonstrate that a more accurate assessment of Quattrocento painting practice can be accomplished only if the original stratigraphy of the paint and ground layers is preserved during organic analysis. Conservators and scientists continue to struggle with the challenges of identifying glues, oils, resins, and other organics, and it is the location of these materials within a painting which matters greatly. For example, if an instrument is detecting protein in a paint sample, where is the protein coming from? Could it be from the animal glue that is often present in traditional Italian grounds? To further complicate matters, many paintings that date to the fifteenth century have been previously restored, thus a protein signal may be due to the presence of an animal glue that was used to consolidate the painting during a previous restoration campaign as opposed to an animal glue that is original to the artwork. Unless the examiner is able to develop a better sense of the location associated with the protein signal in a microscopic paint cross-section, it is difficult to make conclusions relating to the materials and technique used by the artist.

My research involves the application of imaging Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to samples collected from Quattrocento paintings, research that has relied heavily upon the pioneering work of conservation scientists Dr. Katrien Keune and Dr. Jaap J. Boon.²² ToF-SIMS is able to provide both spatial and analytical information,

²² Katrien Keune and Jaap J. Boon, "Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden," *Analytical Chemistry* 76 (2004): 1374–85, doi: 10.1021/ac035201a; Jaap J. Boon, Katrien Keune, and Joyce Zucker, "Imaging Analytical Studies of Lead Soaps Aggregating in Preprimed Canvas Used by the Hudson River School Painter F.E. Church," *Microscopy and Microanalysis* 11 (2005): 444–5, doi: 10.1017/S1431927605505579; Boon et al., "Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych," in *Proceedings of the Sixth Infrared and Raman Users Group, Florence, 29 March – 1 April 2004*, ed. Marcello Picollo (Il Prato:

generating spatial “maps” that can assist the analyst in determining where proteins and oil-containing materials exist within a paint sample; however, egg tempera paints and animal glues *both* contain protein, introducing yet another complication. Earlier incarnations of ToF-SIMS technology were not as successful at imaging each of the individual amino acids present in protein-containing materials. Thanks to recent improvements in ion beam technology, this type of instrument can now distinguish between egg yolk and animal glue based on the presence of certain amino acids.²³ An additional benefit that is offered by ToF-SIMS is its ability to gather new information on organic materials from old paint cross-sections, including those that have been residing in museum laboratories for decades. In some instances this may even eliminate the need for re-sampling certain works of art, yet another reason for museums to consider an accessible, permanent storage system for samples collected from artworks over the years. While the potential benefits of this technique are explored at length in chapter six, it should be noted that no technique should be used *alone* to deduce definite conclusions relating to organic analysis. Finally, it must be stressed that ToF-SIMS is at its strongest only when used in conjunction with other analytical methods, especially when examining objects that possess complicated restoration histories.

Padova, 2004) 66–74; Katrien Keune. “Binding medium, pigments and metal soaps characterised and localised in paint cross-sections” (PhD diss., University of Amsterdam, 2005).

²³ Zachary Voras, Kristin deGhetaldi, Brian Baadem Eric Gordon, Glenn Gates, and Thomas P. Beebe, “Comparison of oil and egg tempera paint systems using time-of-flight secondary ion mass spectrometry” *Studies in Conservation* (2016), doi:10.1179/2047058414Y.0000000154; Matthew S. Wagner and Daniel G. Castner, “Characterization of Adsorbed Protein Films by Time-of-Flight Secondary Ion Mass Spectrometry with Principal Component Analysis,” *Langmuir* 17: 4649–60, doi: 10.1021/la001209t; Annemie Adriaens and Mark G. Dowsett, “Applications of SIMS to Cultural Heritage Studies,” *Applied Surface Science* 252: 7096–101, doi:10.1016/j.apsusc.2006.02.193.

During the early stages of research that led up to this dissertation topic, I had the opportunity to examine and perform analysis on a number of fifteenth-century paintings, many of which will be presented as case studies in this dissertation. While many publications continue to offer important insights into the technical analysis of Italian paintings, detailed information relating to *organic* analysis is commonly relegated to footnotes or omitted altogether. Often, the most helpful resources for piecing together the analytical history of an object are the conservation and scientific reports housed in museum conservation and curatorial files. Interviews and discussions with professionals who specialize in technical art history can also yield useful information. Perhaps the greatest challenge throughout this dissertation has been gaining access to such sources, access that in some cases could not have occurred without personal connections combined with the generosity of particular institutional staff members. These experiences provided me with a unique insight into the complex world of conservation science and also the external pressures that are felt by some professionals when they are unable to provide conservators and art historians with clear, concise answers about the specific characterization of binding media.

Over the last fifty years, scholars have looked to the profession of conservation for material evidence to help clarify this exceptionally complex moment in the history of art. Useful and surprising information can be gleaned from the organic analysis of works originating from the Quattrocento period, information that can 1) help to elucidate trade routes concerning art materials and techniques 2) shed light on issues relating to provenance and workshop practice and 3) help in tracing the gradual dissemination of oil from the north. Most scholars in pursuit of “secret” techniques practiced by Renaissance artists appear to be driven by a shared desire to learn more about historical materials and workshop traditions. While Quattrocento painters continue to attract the attention of scholars, the field of conservation has undergone its own changes, developing an intimate relationship with the hard sciences in

order to develop a better understanding of our own cultural heritage. If more is to be learned from this transitional period in Italian art, many of the abovementioned topics must be further integrated into the dialogue among art historians, scientists, and conservators, a dialogue that effectively communicates the ongoing changes that are occurring within the conservation field. I hope that this project will provide groundwork for future research relating to the transition of egg to oil painting throughout the Renaissance by evaluating both successful and unsuccessful methods that have been used to examine organic binders used by early Italian painters.

Chapter 2

THE INFLUENCE OF THE NORTH

The evolution of oil painting in Italy did not occur as a singular event divorced from the peninsula's ever-changing economic and social setting. Towards the end of the fourteenth century, a succession of religious events continued to bring representatives of the Christian Church together from both sides of the Alps. Artistic movements were consequently shaped by these religious exchanges and indirectly spurred the adoption of oil painting in Italy. As with other private Italian collectors, clergymen also began to develop a taste for northern illuminated manuscripts and eventually paintings done in oil. Such patronage was one of the driving forces behind the gradual implementation of oil painting south of the Alps. Several years after the Papal Schism of 1378, many of the Italian city-states witnessed a steady rise in economic prosperity, financial success that can be partly attributed to the marriage between the Catholic church and the Medici bank. The bank expanded throughout Europe, with Italian bankers and merchants moving abroad to manage international business affairs and consequently seeking opportunities to exercise their foreign patronage; many collectors sent exquisite, and sometimes monumental, objects back to their native cities in Italy.²⁴ Such commissions played a crucial role in compelling traditional Italian painters to turn away from egg tempera and embrace northern techniques.

²⁴ See Marina Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe* (Cambridge: Cambridge University Press, 2012).

2.1 Cultural Exchanges and the Papal Schism

It is difficult to know how conscious religious patrons were of the “new” oil medium used by northern artists. Italian ecclesiasts would likely have encountered numerous oil paintings along pilgrimage routes such as the famous Camino di Santiago that extended from northern Italy to sites in France, Spain, and Germany (see Figure 2.1).²⁵ Higher ranking

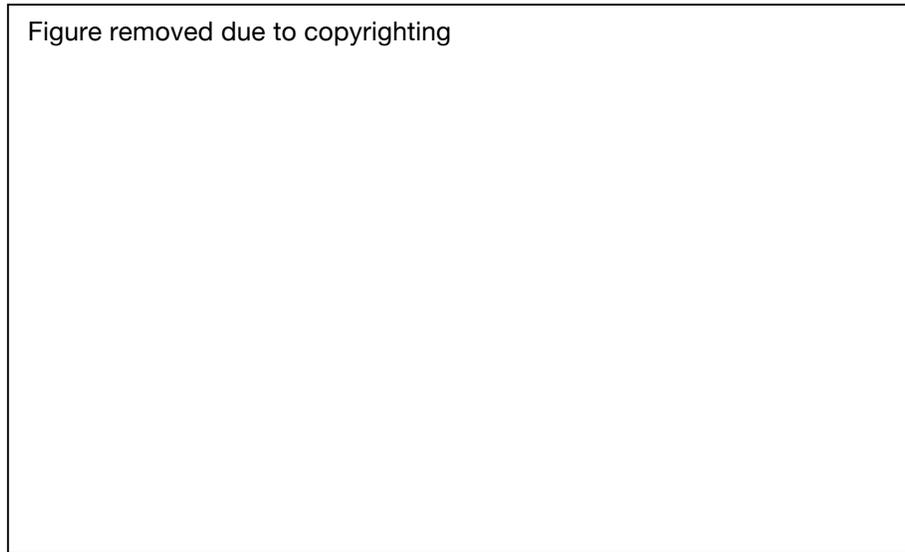


Figure 2.1: Modern day map illustrating various site destinations related to the Camino di Santiago pilgrimage route (also known as St. James Way). The route played a crucial role in encouraging cultural exchange between western European countries during the Medieval and Renaissance periods.²⁶

²⁵ Simon Yarrow, “Pilgrimage” in *The Routledge History of Medieval Christianity: 1050-1500*, ed. Robert N. Swanson (New York: Routledge, 2015), 159-72.

²⁶ “Camino di Santiago,” last modified May 2, 2016, http://en.wikipedia.org/wiki/Camino_de_Santiago.

officials in the Catholic Church were obliged to attend council meetings, yet another avenue for cultural exchange between international delegates. Hundreds of portable diptychs, triptychs and other painted works intended for private devotion have survived from this period and it is likely that religious delegates, especially those who held prominent positions within the church, often traveled accompanied by such objects. By the late-fourteenth century, disagreements within the church led to a series of council meetings resulting in increased interactions between Italian delegates and their northern counterparts well into the 1450s.²⁷ Selected cities became temporary sites for international religious debates, beginning first in Pisa in 1409.²⁸ While the Council of Pisa was comprised mostly of cardinals from Italian city-states, a handful of representatives from France, Germany, and England were also present; for many of the Italian cardinals this may have been one of their first encounters with the northern aesthetic. Universities based in Oxford, Paris, and Cologne also sent more than 300 scholars who were well versed in theology and canon law. These religious and scholarly ambassadors from the north made haste to reach Pisa in time and were likely accompanied by a variety of devotional objects, including intricately decorated manuscripts or diptychs and triptychs painted in oil. While the Council of Pisa lasted only a few months, a subsequent meeting held in Constance lasted for several years, creating a far more effective environment for cultural

²⁷ Walter Ullmann, *The Origins of the Great Schism* (Hamden: Archon Books, 1967), 1-101; Joseph Gill, *The Council of Florence* (Cambridge: Cambridge University Press, 1959), 1-16. The Schism began with Pope Gregory XI's retreat to Rome in 1378, abandoning the papal bureaucracy in Avignon, France and prompting a rift within the Church, one that lasted for more than 40 years.

²⁸ John Holland Smith, *The Great Schism: 1378* (New York: Weybright and Talley, 1970), 167-82; Louis Salembier, "Council of Pisa," in *The Catholic Encyclopedia*, vol. 12 (New York: Robert Appleton Company, 1911), accessed November 1, 2014, <http://www.newadvent.org/cathen/12112b.html>.

exchange. From 1414 to 1417, religious delegates met in the German city finally putting an end to the schism with the election of Pope Martin V.²⁹ During this three-year period, a number of Italian religious authorities temporarily relocated to the German city to sit alongside their northern colleagues.

The meetings at Constance and Pisa undoubtedly generated a series of cultural exchanges between religious patrons that would eventually impact artistic communities working south of the Alps; however, scholars have only been able to make direct connections with the Council of Ferrara to concrete examples of early north-south artistic exchange.³⁰ Originally intended to be held in Basel, the Council of Ferrara was primarily called to address conflicts between members of the Greek and Latin Church; however, the Greek embassy was unable to reach Basel in time prompting delegates to postpone the congregation.³¹ By 1438 the council reconvened in the city of Ferrara, home to the wealthy family of Niccolo III of the d'Este family, a dynasty that is well known for their patronage of northern artists.³² As with earlier councils, these religious representatives must have brought with them icons, diptychs,

²⁹ This particular council was one of the most significant in Catholic history, with an international assembly so large that both Latin and German were used to issue proclamations. John Julius Norwich, *The Popes: A History* (London: Chatto & Windus, 2011), 226-228; Smith, *The Great Schism: 1378*, 185-220; Francis Oakley, "1378: The Great Papal Schism," *Christian History* 28 (1990), accessed November 3, 2014, <http://www.christianitytoday.com/ch/1990/issue28/2824.html>.

³⁰ "Haec Sancta, Council of Constance, Session 5 (April 6, 1415)," in *Decrees of the Ecumenical Councils, I, Nicaea I to Lateran V*, ed. Norman P. Tanner (London: Sheed & Ward and Georgetown University Press, 1990), 409.

³¹ Gill, *The Council of Florence*, 95-117.

³² Ibid.

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Figures 2.2 (left) and 2.3 (right): Jan van Eyck, *Portrait of a Man, Possibly Cardinal Niccolo Albergati* (left, c. 1431, Kunsthistorisches Museum, Vienna; left) and Workshop of Jan van Eyck (attr.), *St. Jerome in his Study* (right, c. 1442, Detroit Institute of Arts; right).

reliquaries, and books of hours, objects that would have made a lasting impression on the d'Este family.³³ In the years immediately following the meeting, the city continued to offer a unique working environment for artists, providing job opportunities for both Italian and foreign artisans. The d'Este family were not the only Italian patrons of northern art present at the Council of Ferrara; Cardinal Albergati, Eugenius IV, and members of the Medici family have all been linked to artworks or commissions involving northern artists.³⁴ Some scholars

³³ Frances Ames-Lewis, "Fra Filippo Lippi and Flanders," *Zeitschrift für Kunstgeschichte* 4 (1979), 272, accessed October 20, 2015, <http://www.jstor.org/stable/1481985>; Lorne Campbell, "Cosmè Tura and Netherlandish Art," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Stephen J. Campbell (Boston: Isabella Stewart Gardner, 2002), 71-105. Artworks from the north began appearing at the d'Este court as early as the 1430s.

³⁴ Gerald Christianson, Thomas M. Izbicki, and Christopher M. Belitto, *The Church, the Councils, & Reform: The Legacy of the Fifteenth Century* (Washington DC: Catholic University of America Press, 2008), 183; Guido Messling, "The Art of Drawing before Van Eyck," in *The Road to Van Eyck*, eds. Stephan Kemperdick and Friso Lammertse (Rotterdam: Museum Boijmans Van Beuningen, 2012), 66-7. It should be noted that not all scholars agree as to the identity of the sitter in the Vienna portrait; the precise date of the St. Jerome panel is also a matter of some debate.

have determined that Albergati's portrait by van Eyck (now in Vienna, see Figure 2.2) as well as an image of St Jerome (now in Detroit, see Figure 2.3) were both painted precisely around this period.³⁵ Cardinal Albergati, a native of Bologna, may have encountered northern works well before the Council of Ferrara as he is noted to have ventured north of the Alps to attend the Council of Basel several years earlier.³⁶ Albergati was an active foreign diplomat and his brief sojourn in Bruges in December 1431 may well account for his portrait by Jan van Eyck.³⁷ Albergati's embassy is documented traveling from Florence to Arras, where his entourage was brought to see the new altarpiece in the Abbey Chapel painted by a pupil of Robert Campin.³⁸ The altarpiece was praised by Albergati and his fellow ecclesiasts from Tuscany, notably Nicolas V who continued to provide patronage to a group of Arras artisans even after they had relocated to Siena.³⁹ Pope Eugenius IV also shared Nicolas V and Albergati's acquired taste for northern art. Eugenius IV was appointed Pope in 1431 and soon

³⁵ John Hunter, "Who Is Jan van Eyck's 'Cardinal Nicolo Albergati'?", *The Art Bulletin* 75 (1993): 207, doi: 10.2307/3045945. The Detroit *St. Jerome* was likely painted for Albergati but eventually purchased by the Medici as it appears in the Medici inventory of 1492.

³⁶ Frances Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," in *Cultural Exchange Between the Low Countries and Italy, 1440-1600*, ed. Ingrid Alexander-Skipnes, (New York: Brepols Publishers, 2007), 53.

³⁷ Hunter, "Who Is Jan van Eyck's 'Cardinal Nicolo Albergati'?", 207; Jean C. Wilson, *Painting in Bruges at the Close of the Middle Ages: Society and Visual Culture* (University Park: Pennsylvania State University Press, 2010), 64.

³⁸ Wilson, *Ibid*; Ames-Lewis, "Fra Filippo Lippi and Flanders," 271-2. The primary intention of Albergati's journey was to attend the Congress of Arras that was convened to address diplomatic issues between France and England during the latter part of the Hundred Years War.

³⁹ *Ibid*. Nicolas V commissioned a set of tapestries from Jacquet, son of Benoit d'Arras, who was operating in Siena by the 1450s.

after his arrival in Ferrara, he summoned Jean Fouquet from Tours to paint his portrait (whereabouts currently unknown), presumably after the pope had reached Rome.⁴⁰ Such a portrait may have been proudly displayed by the Pope during his stay with the d'Este family in Ferrara and may account for Niccolo d'Este's decision to commission Fouquet to paint a likeness of Ferrara's court jester Gonella in 1440 (see Figure 2.4).⁴¹

⁴⁰ Erik Inglis, *Jean Fouquet and the Invention of France: Art and Nation after the Hundred Years War* (New Haven: Yale University Press, 2011), 15-9; Lorne Campbell, *Renaissance portraits: European portrait-painting in the 14th, 15th, and 16th centuries* (London & New Haven: Yale University Press, 1990), 228-33; Peter C. Clancy, "The Illusion of a 'Fouquet Workshop': The 'Hours of Charles de France,' the 'Hours of Diane de Croy,' and the 'Hours of Adelaide de Savoie,'" *Zeitschrift für Kunstgeschichte* 56 (1993): 207, doi: 10.2307/1482636; Wolfgang Stechow, *Northern Renaissance Art, 1400-1600: Sources and Documents* (New Jersey: Prentice-Hall, Inc., 1966), 145-6. While it is still debatable whether Fouquet visited Italy sometime between 1443 and 1449, Filarete the Florentine architect describes in 1465 a portrait of Pope Eugenius IV painted by a certain "Grachetto francioso." Furthermore, the humanist writer Florio, who had been living in Tours since 1467, associates this "Grachetto" with Jean Fouquet.

⁴¹ Erik Inglis, *Jean Fouquet and the Invention of France: Art and Nation after the Hundred Years War*, 15; Campbell, *Renaissance portraits: European portrait-painting in the 14th, 15th, and 16th centuries*, 228-33.

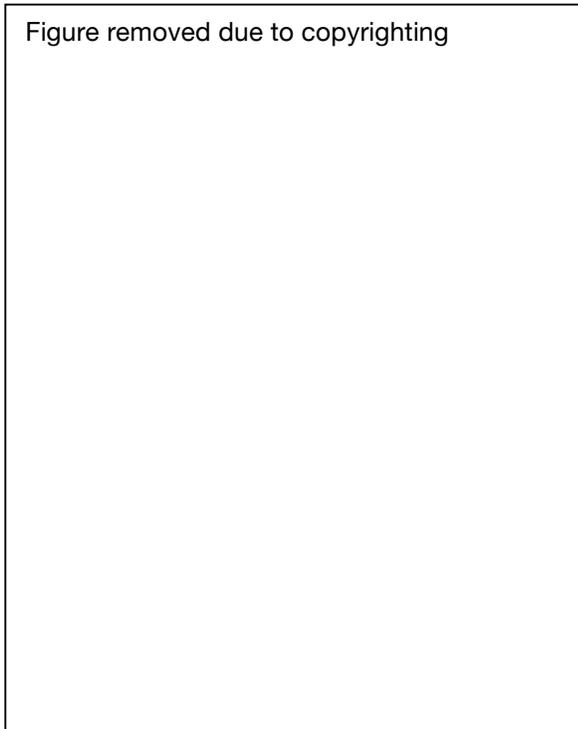


Figure 2.4: Jean Fouquet, *Portrait of Jester Gonella* (c. 1447-1450, Kunsthistorisches Museum, Vienna).

2.2 Merchants, Bankers, and Dealers: The Expansion of the Medici Bank

While developments within the Christian Church gradually led to changes in artistic taste, the success of the Italian merchant class and expansion of the Medici Bank appears to have had a more immediate impact on Italian collectors. Financiers and tradesman working north of the Alps became accustomed to paintings executed in oil, acquiring northern works for their personal collections and in some instances sending pictures back to their native city-states. Scholar James M. Murray discusses the role that many Italians played in the economic

environment of Bruges during the fourteenth century.⁴² A number of successful pawnbrokers working in the city were frequently referred to as the “lombards” or the *Caorsini* as many, but not all, originated from the Piedmont region in northern Italy particularly from Chieri and Asti.⁴³ Italian merchants also organized themselves into five merchant colonies (Lucca, Genoa, Florence, Milan, and Venice) before the Medici bank established in the thriving city of Bruges.⁴⁴ The bank had remained relatively unimportant during the late 1300s until its founder, Giovanni di Bicci de’ Medici, elected to support Baldassare Cossa in his plight to restore the papacy to Rome.⁴⁵ When Cossa was consecrated Pope John XXIII in 1410, the Medici Bank was granted the official role of overseeing all financial transactions carried out by the Roman Curia, thus assuming a position of unmeasurable power.⁴⁶ By 1402, the bank opened its third branch in the thriving international port city of Venice, where artisans, both native and foreign (*oltramontani*), were able to find work.⁴⁷ Over the next forty years, other branches would open in Geneva, London, Avignon, and eventually Bruges, the latter serving

⁴² Charles S. Murray, *Bruges, Cradle of Capitalism, 1280-1390* (Cambridge: Cambridge University Press, 2005), 138-41, 223-37, 258. Contrary to what is proposed by Raymond A. de Roover in *The Rise and Decline of the Medici Bank: 1397-1494*, Murray goes into great detail outlining the complexities involving the financial systems that dominated the economic scene in fourteenth-century Bruges, stating that “the financially precocious Italians played the leading, albeit not the solo, part.”

⁴³ *Ibid.*, 138, 141. Murray lists the di Caloccio, Roerio, and Deal families as prominent pawnbrokers working from 1281-1420.

⁴⁴ *Ibid.*, 223.

⁴⁵ Raymond A de Roover, *The Rise and Decline of the Medici Bank: 1397-1494* (Washington DC: Beard Books, 1999), 202-3.

⁴⁶ Vincent Cronin, *The Florentine Renaissance* (New York: E.P. Dutton & Co., Inc., 1967), 59-78.

⁴⁷ de Roover, *The Rise and Decline of the Medici Bank: 1397-1494*, 41, 240-254.

as an important station for Italian merchants involved with financial affairs both within the city and in nearby Antwerp or Middleburg.⁴⁸ The cultural atmosphere of the Flemish financial center may have had the greatest impact on contemporary artistic tastes among the Italian elite, a notion that is corroborated by the provenance history associated with a number of extant northern artworks.

With Cosimo de' Medici's return to Florence in 1434, the bank began to explore alternate methods for northward expansion rather than relying on Lucchese merchants, such as Marco Giudiccioni and Giovanni di Nicolao Arnolfini, who often worked as private contractors for larger companies.⁴⁹ Today, the Arnolfini name is perhaps better known for the family's taste in art thanks to the survival of two Flemish paintings: a portrait now in Berlin (which may depict Giovanni in his later years) as well as the famed portrait of 1434 housed in the National Gallery, London. The *Arnolfini Portrait* is one of the earliest testaments to Italy's burgeoning interest in Flemish art (see Figure 2.5), with van Eyck's Dresden altarpiece following close behind (see Figure 2.6; recently the altarpiece was linked to members of the Giustianni family from Genoa who also had ties to Bruges, Middelburg, London, and Antwerp).⁵⁰ Arnolfini not only acquired objects for his own collection but also acted as

⁴⁸ Ibid., 254-338.

⁴⁹ Ames-Lewis, "Fra Filippo Lippi and Flanders," 271-2; Lorne Campbell, "The Arnolfini Double Portrait," in *Investigating Jan van Eyck*, eds. Susan Foister, Sue Jones, and Delphine Cool (Turnhout: Brepols, 2000), 19; Paul Nuttal, "Jan van Eyck's Paintings in Italy," in *Investigating Jan van Eyck*, eds. Susan Foister, Sue Jones, and Delphine Cool (Turnhout: Brepols, 2000), 169-82.

⁵⁰ Noelle L.W. Streeton, "Jan van Eyck's Dresden Triptych: new evidence for the Giustiniani of Genoa in the Borromei ledger for Bruges, 1438," *Journal of Historians of Netherlandish Art* 3 (2011), accessed November 5, 2014, <http://jhnalive.pielabmedia.com/index.php/past-issues/vol-3-1/136-janvaneycksdresden>.

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Figure 2.5: Jan van Eyck, *Arnolfini Portrait* (1434, The National Gallery, London).

an intermediary, exemplified by his involvement in dispatching a set of tapestries to Rome for Pope Martin V in 1423.⁵¹

The panel on which the *Portrait of Giovanni Nicolao Arnolfini* is painted has been linked to two additional paintings using dendrochronology, a technique typically used to identify and match wood species as well as to approximate the age of wooden panels. This method was used to confirm that the *Portrait of Giovanni Nicolao Arnolfini* was cut from the same wooden plank as Jan van Eyck's *Portrait of Baudouin de Lannoy* (c. 1435) and a

⁵¹ Ames-Lewis, "Fra Filippo Lippi and Flanders," 272.

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Figure 2.6: Jan van Eyck, *Dresden Triptych* (1434, Gemaldegalerie Alte Meister, Dresden).

painting in Philadelphia depicting *St. Francis receiving the Stigmata* (also attributed to Jan van Eyck).⁵² The latter picture was likely owned by yet another Italian merchant family residing in Bruges (see Figures 2.7 and 2.8).⁵³ The Adornes were originally from Genoa but became quite involved in Bruges's civic, political and religious circles throughout the

⁵² Stephan Kemperdick and Friso Lammertse, "Painting around 1400 and Jan van Eyck's Early Works," in *The Road to Van Eyck*, eds. Stephan Kemperdick and Friso Lammertse (Rotterdam: Museum Boijmans Van Beuningen, 2012), 106-7.

⁵³ Katherine Crawford Lubber, "Patronage and Pilgrimage: Jan van Eyck, the Adornes Family, and Two Paintings of 'Saint Francis in Portraiture,'" *Philadelphia Museum Bulletin* 91 (1998): 33, doi: 10.2307/3795461; Stephan Kemperdick, "Copies after Jan van Eyck and his Predecessors" in *The Road to Van Eyck*, eds. Stephan Kemperdick and Friso Lammertse (Rotterdam: Museum Boijmans Van Beuningen, 2012), 80. The wooden supports from the *St. Francis* in Philadelphia as well as the two Berlin portraits were analyzed by Dr. Peter Klein and found to be from the same tree.

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Figures 2.7 (left) and 2.8 (right): The Philadelphia panel (left) and the Turin panel (right) depicting *Saint Francis Receiving the Stigmata* (both are attributed to Jan van Eyck and dated c. 1430-32).⁵⁴

fifteenth century.⁵⁵ Oppicino Adornes was the first to relocate to the Flemish city and may have been the first *Jeruzalemvaadar* of the Adornes family, a term referring to those who

⁵⁴ Katherine Crawford Luber, “Patronage and Pilgrimage: Jan van Eyck, the Adornes Family, and Two Paintings of ‘Saint Francis in Portraiture,’” 33; Kemperdick, “Copies after Jan van Eyck and his Predecessors,” 80; — and Lammertse, “Painting around 1400 and Jan van Eyck’s Early Works,” 106-7. Infrared reflectography performed on the Turin panel revealed changes in the preliminary underdrawing and underpainting, confirming that the Turin panel is likely the original. Based on this finding, most scholars consider the Turin panel to be an autograph work while the Philadelphia panel may have been done by a studio assistant.

⁵⁵ Mitzi Kirkland-Ives, “‘Capell nuncapato Jherusalem noviter Brugis’: The Adornes Family of Bruges and Holy Land Devotion,” *The Sixteenth Century Journal* 39 (2008), 1041-3, doi: 10.2307/20479137. The family was also responsible for erecting a private mortuary chapel in Bruges called the Jerusalemkerk, in Honor of the Holy Sepulchre.

frequently embarked on pilgrimages to the Holy City as Oppicino did in 1269.⁵⁶ The family's pilgrimage routes as well as an extant copy of Anselm Adornes's will of 1470 have both been used by Lubber to connect the family to not one but two panels depicting St. Francis, both attributed to Jan van Eyck and his circle.⁵⁷ Lubber has speculated that at least one of these versions was present in Florence during the early 1470s as several prominent Italian artists (among them Filippino Lippi and Botticelli) subsequently included van Eyck's craggy landscape in their own compositions (see Figures 2.7 and 2.8).⁵⁸ This is further supported by documents detailing Anselm's pilgrimage to Jerusalem in 1470, during which he and his son stopped in Rome, Genoa, and Florence.⁵⁹ The small format of these compositions and their Italianate depiction of St. Francis (pictured without a prominent wound on his side or rays connecting his stigmata) suggests that the images were intended as portable objects meant for private devotion during extended travels.

Both the Arnolfini and Adornes family belonged to the Confraternity of the Dry Tree, a closed confraternity in Bruges that had become immensely popular amongst foreign merchants and dignitaries. The confraternity was clearly supportive of international cultural exchange and can be traced to several Italians who would eventually play an instrumental role

⁵⁶ Kirkland-Ives, "Capell nuncapato Jherusalem noviter Brugis": The Adornes Family of Bruges and Holy Land Devotion," 1041.

⁵⁷ Lubber, "Patronage and Pilgrimage: Jan van Eyck, the Adornes Family, and Two Paintings of 'Saint Francis in Portraiture,'" 25; Kemperdick, "Copies after Jan van Eyck and his Predecessors," 80; — and Lammertse, "Painting around 1400 and Jan van Eyck's Early Works," 106-7.

⁵⁸ Lubber, "Patronage and Pilgrimage: Jan van Eyck, the Adornes Family, and Two Paintings of 'Saint Francis in Portraiture,'" 27.

⁵⁹ *Ibid.*, 28.

in introducing the northern aesthetic to their counterparts back home. Martens has noted that this particular confraternity (whose unique name refers to the infertility of the Virgin) possessed an unusually “high percentage of foreign merchants, especially Florentines” including members of the Tani, Altoviti, Ricasoli, Villani, and Cavalcanti families.⁶⁰ By the time the Medici Bank had firmly established itself in Bruges, the confraternity was experiencing a period of rapid growth (by this time the group boasted notable members such as Phillip the Good and Petrus Christus), and eventually adopted a Florentine representative of the Medici Bank, Tommaso Portinari, as a leading member.⁶¹

The Portinari family was essential in establishing the Bruges branch of the Medici bank from the very beginning; in 1436, Tommaso’s cousin Bernardo traveled to city to survey the prospects of establishing the new branch and likely met with other Italian merchants who had already made Bruges their home. Bernardo would have found that many of these merchant families, in particular the Arnolfinis, the Adornes, and the Guistinani, had already developed a taste for northern works, particularly those executed *ad olio* or in oil.⁶² By 1469 the Bruges Branch of the Medici Bank was officially established, attracting even more Italian bankers and merchants to the Flemish city. Tommaso Portinari had assumed a more prominent position within the Bank by the mid-1460s, becoming the official manager of the

⁶⁰ Maximiliaan P. J. Martens, "Petrus Christus: A Cultural Biography," in *Petrus Christus: Renaissance Master of Bruges*, ed. Maryan W. Ainsworth (New York: Metropolitan Museum of Art, 1994), 16.

⁶¹ Ibid, 16; Jessica Buskirk, “Hugo van der Goes’s Adoration of the Shepherds: Between Idealism and Urban Networks in Late Medieval Flanders,” *Journal of Historians of Netherlandish Art* 6 (2014), accessed November 19, 2014, <http://www.jhna.org/index.php/past-issues/volume-6-issue-1-2014/250-buskirk-hugo-van-der-goess-adoration-of-the-shepherds>.

⁶² Ames-Lewis, “Fra Filippo Lippi and Flanders,” 272.

branch and eventually establishing himself as an active leader of the Confraternity of the Dry Tree. The cultural scene in Bruges left an impression on Tommaso; he no doubt began to notice his Italian colleagues patronizing local artisans and exporting works back to the homeland. He soon began purchasing works in both Bruges and Antwerp for Piero di Medici's collection in Florence and by 1470 was acquiring works for his own collection.⁶³ By this time Hans Memling had become popular among Italians working north of the Alps so it is not surprising that Portinari ultimately chose Memling to execute a small triptych for private devotion. Unfortunately the central panel (which likely featured an image of the Virgin and Child) is now lost; however, Memling's detailed portraits of the banker and his new bride currently reside at the Metropolitan Museum of Art (see Figures 2.9 and 2.10).⁶⁴

Tommaso Portinari, along with his Italian competitor (and ex-manager) Angelo Tani, are responsible for the commission of two monumental northern altarpieces, both of which were originally bound for Italian destinations. Tani's altarpiece depicting the *Last Judgment* (by Hans Memling; see Figure 2.11) would have been one of the first large-scale northern paintings to appear in Italy if it had not been intercepted by pirates en route. Instead, that legacy was ultimately claimed by Portinari; his famous altarpiece by Hugo van der Goes is perhaps one of the most significant paintings from this period, a symbol of Italy's newfound

⁶³ Susanne Franke, "Between Status and Spritual Salvation: The Portinari Triptych and Tommaso Portinari's Concern for His Memoria," *Simiolus: Netherlands Quarterly for the History of Art* 33 (2007/8): 124-6.

⁶⁴ Ibid.

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Figures 2.9 (left) and 2.10 (right): Hans Memling, *Portrait of Tommaso di Folco Portinari* (1428-1501) and *Portrait of Maria Portinari* (Maria Maddalena Baroncelli, 1456-?) (c. 1470, The Metropolitan Museum of Art).

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Figure 2.11: Hans Memling, *Last Judgement* (1476-70, National Museum, Gdansk).

taste for the northern aesthetic.⁶⁵ Thanks to the competitive relationship between Angelo Tani and Tomasso Portinari, Hugo van der Goes was eventually commissioned by Portinari in 1476 to fabricate a devotional altarpiece that rivalled Memling's newly completed *Last Judgment*.⁶⁶ The Portinari altarpiece, painted by a northern artist, was perhaps the first large format oil painting to arrive in Italy (see Figure 2.12). In 1481, this monumental northern masterpiece was met with an extraordinary celebration in Florence when it was paraded through the city to its final resting place within the Portinari family's church of Sant'Egidio.⁶⁷ Merchants from other Italian cities also followed suit; Andrea della Costa of Genoa 1483 sent a Flemish triptych to adorn his newly built church in 1483, and Paolo Pagagnotti very likely had a hand in commissioning Hans Memling to create a triptych for his uncle in Florence, the Bishop of Vaizon.⁶⁸ Despite the bank's eventual failure in 1478, the Portinaris continued to commission several paintings by northern artists, either returning home with their purchases or sending them back to members of the family.⁶⁹ Italy continually looked to Bruges for

⁶⁵ Franke, "Between Status and Spiritual Salvation: The Portinari Triptych and Tommaso Portinari's Concern for His Memoria," 140; Christiansen, "The View from Italy," 45-6. Considerably smaller in scale is Nicolas Froment's altarpiece depicting the *Resurrection of Lazarus* (1461, Galleria degli Uffizi), commissioned by Francesco Coppini, Bishop of Terni as a gift for Cosimo de Medici during a pilgrimage to the Netherlands and England.

⁶⁶ Ibid.

⁶⁷ Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Press, 2004), 61-3.

⁶⁸ Nuttal, *From Flanders to Florence*, 89; Steven A. Epstein, *Genoa and the Genoese, 958-1528* (Chapel Hill & London: The University of North Carolina Press, 2000), 297.

⁶⁹ Nuttal, *From Flanders to Florence*, 70-2. In 1480 Tomasso's nephew Lodovico commissions a diptych from the Master of the St. Ursula Legend and in 1487 another nephew, Benedetto, commissions Hans Memling to create a small triptych.

aesthetic inspiration until the city was eventually displaced by nearby Antwerp at the end of the sixteenth century.

Figure removed due to copyrighting

Figure 2.12: Hugo van der Goes, *Portinari Altarpiece* (c.1475, Galleria degli Uffizi, Florence).

2.3 Northern Paintings South of the Alps

Many of Netherlandish paintings that managed to survive the subsequent waves of iconoclasm in the sixteenth century owe their existence in part to many of the Italian collectors and religious dignitaries mentioned in the previous narrative. These international clergymen and merchants, in turn, helped to foster a growing appreciation for the *ars nova* style among prominent collectors throughout Italian city-states.⁷⁰ The term *ars nova*, coined

⁷⁰ Erwin Panofsky, *Renaissance and Renascences in Western Art* (New York: Harper Row, 1969), 165.

by Panofsky in the 1960s, has become synonymous with the aesthetic accomplishments of northern artists, including their attention to precise detail, their realistic depiction of nature, and their use of rich, transparent colors to capture the effects of light.⁷¹ In *Flanders to Florence*, Paula Nuttal describes a steady influx of northern art into Italy throughout the fifteenth century, often through intermediate dealers acting on behalf of wealthy Italian collectors, collectors who were consciously seeking artworks that not were created in the traditional tempera technique. Nuttal and art historian Joanne Wright have described a number of fifteenth-century Italian documents suggesting a reverence for painting done *ad oilo* and possibly works done in distemper (animal glue). As Italian collectors began to develop a taste for the *ars nova* aesthetic, native Italian artisans were eventually compelled to embrace different working methods. By the mid-fifteenth century, artworks that differed drastically from traditional egg tempera paintings could be found in several major Italian collections, a shift that was spurred by the continued relationships between international religious, business officials, and influential collectors up and down the peninsula.

A tremendous amount of scholarship has been devoted to the Tuscan city of Florence and its role as an epicenter of artistic traditions in Renaissance Italy. However, Florence was not solely accountable for the distribution and dissemination of Netherlandish paintings at the beginning of the fifteenth century. Genoa, Ferrara, and the Kingdom of Naples all hosted ruling families or wealthy merchants who began looking to northern artists years before their

⁷¹ Ibid. Note: The term *ars nova* was also meant to offer a more sympathetic descriptor for Flemish paintings as opposed to the traditional label of “flemish primitives” that was adopted around the turn of the century. While *ars nova* is typically associated with musical movements of the period, the term can be used to reflect the innovative style and beauty of northern art in a general sense.

counterparts in Florence, Milan, and to some extent, the Veneto.⁷² Genoa, for example, began to experience a slight influx of northern works during the early 1400s, a cross-cultural exchange that was not only reliant on artistic patronage but also on the fact that city had already established successful commercial ties with the north.⁷³ By the dawn of the Renaissance, Genoa's merchant class was firmly established within the international business community, a fact that is further corroborated by the number of Genoese patrons that appear to be connected with Netherlandish paintings dating to the early 1420s. The Lomellini family reportedly owned a number of Flemish works, some of which were described in detail by the humanist writer Bartolomeo Facio (c. 1400-1457).⁷⁴ This successful family of merchants is

⁷² Keith Christiansen, "The View from Italy," in *From Van Eyck to Brueghel*, eds. Maryan W. Ainsworth and Keith Christiansen (New York City: Metropolitan Museum of Art, 1998), 40-3; Penny H. Jolly, "Antonello da Messina's 'St. Jerome in His Study': A Disguised Portrait?", *The Burlington Magazine* 124 (1982): 26-29, accessed October 15, 2015, <http://www.jstor.org/stable/3050320>; Margaret Koster, "Reconsidering 'St. Catherine of Bologna with Three Donors' by the Baroncelli Master of Bruges," *Simiolus: Netherlandish Quarterly for the History of Art* 26 (1998): 4-17, doi: 10.2307/3780870.

⁷³ Christiansen, "The View from Italy," 43.

⁷⁴ Epstein, *Genoa and the Genoese, 958-1528*, 296; Carol M. Richardson, Kim W. Woods, and Michael W. Franklin, eds., *Renaissance Art Reconsidered* (Chicester: John Wiley and Sons, Ltd., 2007), 187-9; Frances Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 55-7; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 182-3. In the 1450s, Facio reported seeing a painting depicting a bath scene by Rogier van der Weyden, a portrait by Jan van Eyck, and a triptych by Jan van Eyck (possibly the Lomellini triptych). Marina Belozerskaya includes Facio's description of this triptych in *Rethinking the Renaissance*: A remarkable picture in the private apartments of King Alfonso, in which there is a Virgin Mary notable for its grace and modesty, with an Angel Gabriel, of exceptional beauty and with hair surpassing reality, announcing that the Son of God will be born of her; and a John the Baptist that declares the wonderful sanctity and austerity of his life, and Jerome like a living being in a library done with rare art: for if move away from it a little it seems that it recedes inwards and that it has complete books laid open in it, while if you go near it is evident that there is only a summary of these. On the outer side of the picture is painted Battista Lomellini, whose picture it was – you would judge he lacked only a voice – and the woman whom he loved, of outstanding beauty; and she too is portrayed exactly as she

also documented conducting business in Bruges, where Battista Lomellini likely commissioned van Eyck to paint his portrait (whereabouts unknown) as well as a triptych that depicted the Annunciation (complete with flanking wings with images of St. Jerome and Battista and his wife, whereabouts currently unknown).⁷⁵ The family may have also been connected to a smaller triptych attributed to Petrus Christus, the wings of which are now housed at the National Gallery in Washington (see Figures 2.13 and 2.14).⁷⁶

Neighboring collectors both in and around the port city of Genoa were likely affected by the gradual influx of northern works, developing a taste for paintings done in oil. For example, several compositions associated with Rogier van der Weyden have been linked to the small town of Chieri just outside of Turin. Chieri was populated by members of the Villa family whose role as money-lenders in the Lombard region probably led to an interest in Flemish art.⁷⁷ Recent research suggests that the Villa family commissioned Rogier's workshop to paint an *Annunciation* (c. 1434) as well as a *Crucifixion* scene (c.

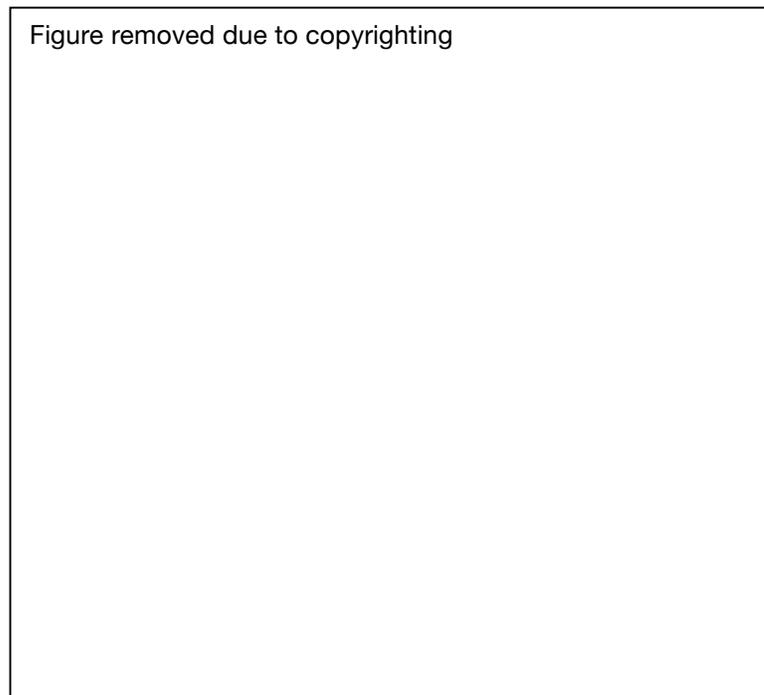
was. Between them, as if through a chink in the wall, falls a ray of sun that you would take to be real sun-light.

⁷⁵ David Summers, *Vision, Reflection, and Desire in Western Painting* (North Carolina: UNC Press Books, 2007), 130; Christiansen, "The View from Italy," 43; Ann Tzeuschler Lurie, "A Newly Discovered Eyckian St. John the Baptist in a Landscape," *The Bulletin of the Cleveland Museum of Art* 68 (1981): 87-109, accessed October 5, 2015, <http://www.jstor.org/stable/25159721>; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197.

⁷⁶ Maryan Ainsworth, "Portrait of a Male Donor; Portrait of a Female," in *Petrus Christus: Renaissance Master of Bruges*, ed. Maryan Ainsworth (New York: Metropolitan Museum of Art, 1994), 131.

⁷⁷ Lorne Campbell et al., "'The Virgin and Child Before a Firescreen': History, Examination, and Treatment," *The National Gallery Technical Bulletin* 15 (1994): 21-35.

1430-40), altarpieces meant to adorn a private or public chapel for their home in Italy (see Figures 2.15 and 2.16).⁷⁸ Other Genoese patrons followed suit; nearly a decade later Giusto d'Allemagne (Joos Amman of Ravensburg) was commissioned to execute an Eyckian Annunciation fresco scene for the cloister of Santa Maria di Castello, and several years later Andrea della Costa commissioned an anonymous Master of Bruges to create a triptych for his church.⁷⁹ Foreign artists like the Master of Bruges (and later on the French Ludovico Brea) were welcome in Genoa, perhaps due to the city's commercial function as an international



Figures 2.13 (left) and 2.14 (right): Petrus Christus, *Portrait of a Male Donor/Portrait of a Female Donor* (c. 1455, The National Gallery of Art, Washington DC).

⁷⁸ Christiansen, "The View from Italy," 43; Lynn F. Jacobs, *Opening Doors: The Early Netherlandish Triptych Reinterpreted* (Harrisburg: Pennsylvania State University Press, 2012), 92-7.

⁷⁹ Epstein, *Genoa and the Genoese, 958-1528*, 297.

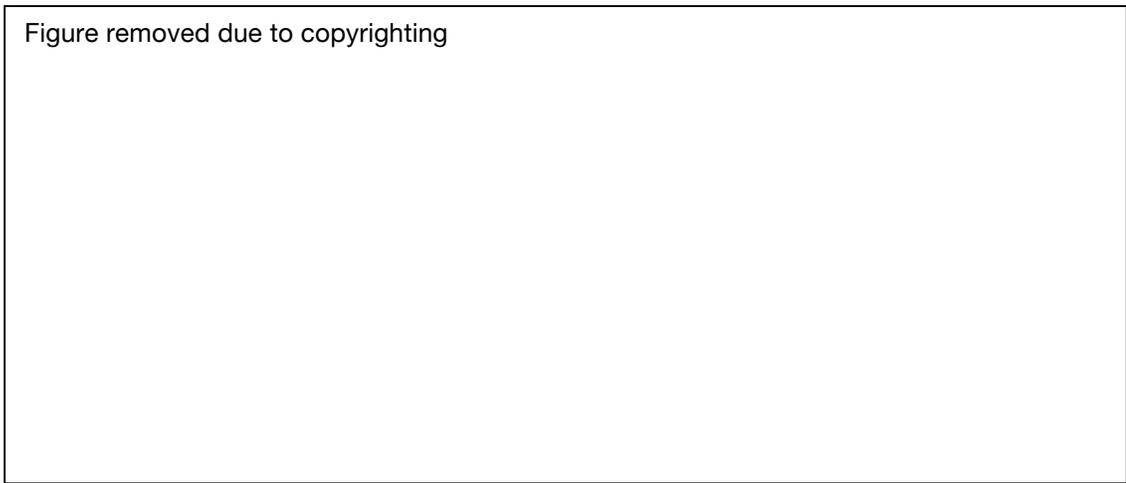


Figure 2.15: Rogier van der Weyden, *Annunciation Triptych* (c.1434, Musée du Louvre, Paris).

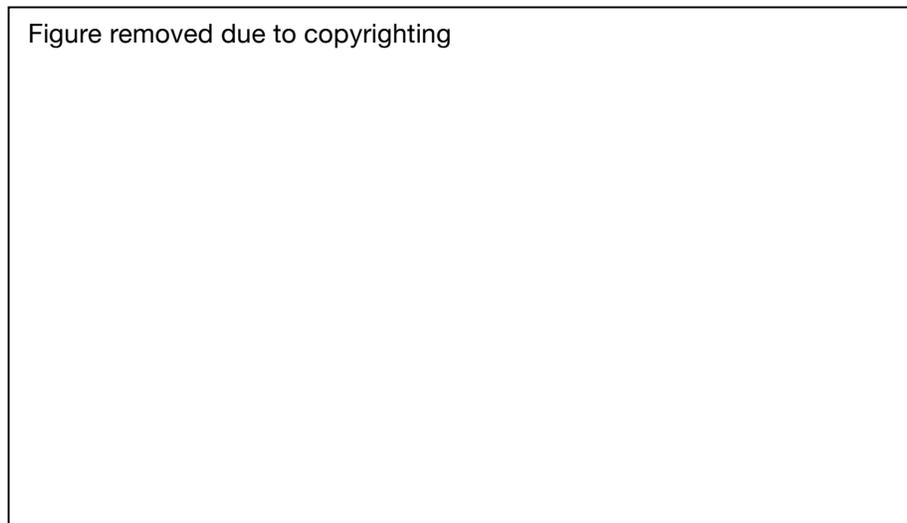


Figure 2.16: Rogier van der Weyden, *Abegg Triptych* (c. 1438-40, Abegg-Stiftung, Riggisberg).

port center.⁸⁰ By the mid-fifteenth century Genoa's neighboring city of Milan had risen to considerable power as Francesco Sforza was able to establish an alliance with Cosimo de Medici in 1454.⁸¹ The Sforza family continued to cultivate the city's cultural atmosphere, patronizing a number of artists including the Milanese painter Zanetto Bugatto (birth unknown – 1476).⁸² Evidently the Sforza family was familiar with Rogier van der Weyden's reputation as the Duchess of Milan, Bianca Maria Visconti, sent Zanetto to Brussels to train under Rogier from 1460 to 1463.⁸³ Upon Zanetto's return the Duchess extended her thanks to Rogier, implying that her court painter had much improved.⁸⁴ Zanetto may have continued working in a northern style during the latter part of his career as he was summoned north once more to Paris, in 1468, to paint a portrait of Bona of Savoy, sister to the queen of France.⁸⁵

⁸⁰ Ibid.

⁸¹ Kenneth Meyer Setton, *The Papacy and the Levant, 1204-1571: The Fifteenth Century* (Philadelphia: The American Philosophical Society, 1976), 156.

⁸² Luke Syson, "Zanetto Bugatto, Court Portraitist in Sforza Milan," *The Burlington Magazine* 138 (1996): 300-308, accessed November 12, 2015, <http://www.jstor.org/stable/886901>; Dunkerton, et al., *Giotto to Durer: Early Renaissance Painting in the National Gallery*, 197; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 194-7.

⁸³ Syson, "Zanetto Bugatto, Court Portraitist in Sforza Milan," 300; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 194-7; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 49-50. At least three letters survive that relate to Zanetto's apprenticeship under Rogier van der Weyden; a letter from Francesco Sforza to the Dauphin of France describing the Sforza's wish to send Zanetto to Brussels, a letter from Bianca Maria Sforza to Rogier describing her gratitude towards the Netherlandish painter, and a dispatch letter describing Zanetto's problematic behavior during his apprenticeship under Rogier, purportedly caused by drunken misconduct.

⁸⁴ Syson, "Zanetto Bugatto, Court Portraitist in Sforza Milan," 300; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 194-7; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 49-50.

⁸⁵ Syson, "Zanetto Bugatto, Court Portraitist in Sforza Milan," 300.

Art historian Luke Syson suspects that during his travels Zanetto was likely influenced by Rogier and French artists such as Jean Fouquet and may have encountered more northern oil paintings in Lodovico Gonzaga's collection in Mantua in 1471.⁸⁶ Whether or not Zanetto learnt the oil technique is unknown; however, it seems that the artist was at least skilled in emulating northern works. Such a skill left a lasting impact on Zanetto's patron Galeazzo Sforza even after the artist's death, inspiring Galeazzo to seek the services of Antonello da Messina, another painter who was known for his "flemish" style.⁸⁷

Ferrara's connection with the Papal Schism has already been associated with the city's early role as a cross-cultural artistic center. Northern artworks began to arrive in the city in the early the fifteenth century, possibly beginning with Niccolo d'Este's commission for heraldic tapestries from Bruges, in 1434, through the Lucchese merchant Paolo Miliani.⁸⁸ Leonello, Niccolo's son, acquired his father's taste and may be credited with summoning some of the first northern artists to the city, recruiting a Jacopo de Angelo di Fiandra to repair a series of tapestries in April of 1436.⁸⁹ Like his father, Leonello relied on both Paolo Milani as well as another Lucchese merchant, Paolo di Poggio, to identify possible works in Bruges and in other northern cities that met the standards of the d'Este collection.⁹⁰ In 1443, Poggio is recorded spending 3,000 ducats in Bruges on several tapestries for Leonello; he also

⁸⁶ Ibid.

⁸⁷ Ibid.

⁸⁸ Campbell, "Cosmè Tura and Netherlandish Art," 71-105.

⁸⁹ Ames-Lewis, "Fra Filippo Lippi and Flanders," 272.

⁹⁰ Campbell, "Cosmè Tura and Netherlandish Art," 71.

purchased additional paintings for the Ferrara court in 1447 and 1451.⁹¹ Poggio must have had close contact with notable painters in Bruges; in 1450 the merchant made multiple payments to Rogier van der Weyden on behalf of Leonello, and Poggio's wife, Donna Agata, was found in possession of a Pieta by Jan van Eyck, in Lucca in 1480, well after her husband's death.⁹² Leonello d'Este purportedly purchased at least four paintings from Rogier, including a triptych that depicted the Deposition and the Fall of Man (whereabouts unknown).⁹³ Rogier's workshop appears to have continued its relationship with the d'Este family; Steven Campbell has also connected a portrait of Leonello's illegitimate son Francesco (c. 1460) to the artist (see Figure 2.17).⁹⁴ The d'Este family were dutiful patrons of northern art, a devotion that directly impacted the Italian artists who were recruited to realize Leonello's vision for his future *studiolo* at the Belfiore Palace.

⁹¹ Ibid.

⁹² Ibid; Nuttal, "Jan van Eyck's Paintings in Italy," 169.

⁹³ Campbell, "Cosmè Tura and Netherlandish Art," 75; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 54.

⁹⁴ Ibid. Note that the portrait, now at the Metropolitan, was likely painted for Francesco at the Burgundian Court and may have never been in Ferrara.

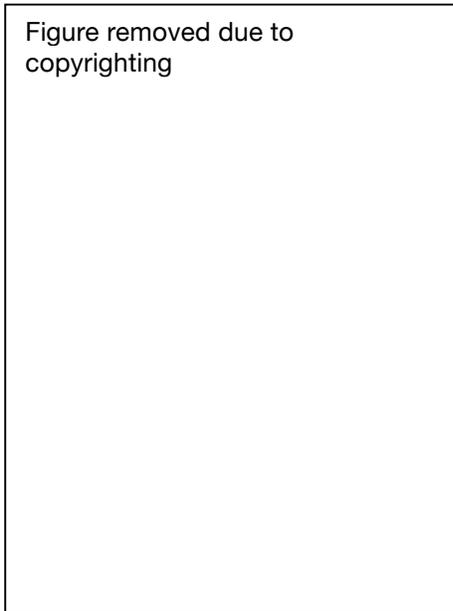


Figure 2.17: Rogier van der Weyden, *Portrait of Francesco d'Este* (c. 1460, Metropolitan Museum of Art).

Scholarship focusing on artistic movements and painting materials associated with the *Mezzogiorno* during the early Renaissance is sadly deficient. Yet this region, which is comprised of the southern half of the Italian peninsula, was integral in facilitating cultural exchanges between the north and south throughout the fifteenth century as will be discussed in greater detail in the following chapter. Despite an ongoing succession of feuds between the Spanish and French, the works from this region have managed to survive demonstrate a strong stylistic connection to the northern aesthetic. By 1438, Rene of Anjou had seized the throne of Naples and subsequently recruited a local Italian painter to join his court named

Niccolo Colantonio to join his court.⁹⁵ If northern works were readily accessible to Colantonio, these paintings may have been purchased by Rene or were already present in the collection of the Neapolitan court. Rene's keen interest in the arts is well documented; Christiansen has suggested that Rene may have also brought along his own painter from Provence, an artist referred to as the Master of the Annunciation of Aix who more recently has tentatively been identified as Barthelemy d'Eyck would have had a lasting influence on the newly recruited Colantonio whose extant paintings emulate a northern aesthetic (see Figure 3.4).

In 1442 Alfonso of Aragon expelled Rene from Naples but opted to retain Colantonio as a court painter, likely due to his propensity for emulating the northern style. Alfonso's own collection at Castelnuovo has been studied more extensively and consisted of works by Iberian, Hungarian, Flemish, and French artists, including a series of paintings depicting the Passion by Rogier van der Weyden (whereabouts unknown).⁹⁶ The Spanish

⁹⁵ Joanne Wright, "Antonello da *Messina*, the Origins of His Style and Technique," *Art History* 3 (1980): 41-2; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50, 55-6.

⁹⁶ Christiansen, "The View from Italy," 40; Carl Brandon Strehlke, "Review: Quattrocento Aragonese, Naples," *Burlington Magazine* 140, no. 1139 (1998): 144, accessed October 22, 2015, <http://www.jstor.org/stable/887721>; Carol Richardson, ed. *Locating Renaissance Art* (New Haven: Yale University Press, 2007), 93; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 180-7. Keith Christiansen notes that this series may in fact have been a set of tapestries as they have been cited as paintings on canvas although the author argues that it is equally possible that there were painted using the distemper method or that they were mislabeled during inventory. Marina Belozerskaya also discusses a set of tapestries (described by Pietro Summonte) designed by Rogier van der Weyden that were purchased by Alfonso.

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Figure 2.18: Barthelemy d’Eyck, *Aix Annunciation Altarpiece* (1443-1445, Église de la Madeleine, Aix-en-Provence; Rijksmuseum, Amsterdam; Museum Boijmans van Beuningen, Rotterdam).

ruler had developed an affection for Flemish art well before his move from Aragon to Naples. Alfonso sent one of his court painters, Lluís Dalmau, to study from the Flemish masters in Bruges as early as 1431.⁹⁷ Alfonso’s son, Ferrante I of Napoli, followed suit, sending his court painter Giovanni di Giusto da Basilio to study with painters residing in Bruges in 1469.⁹⁸ Wright has pointed out that the Franco-Flemish painting tradition had a significant impact on artisans working in Iberia starting in the early fifteenth century.⁹⁹ Like his French

⁹⁷ Dunkerton, et al., *Giotto to Durer: Early Renaissance Painting in the National Gallery*, 197.

⁹⁸ Nuttall, *From Flanders to Florence*, 4.

⁹⁹ Wright, "Antonello da Messina, the Origins of His Style and Technique," 42. Wright states that "in 1427, Van Eyck himself was in Valencia with the Burgundian Embassy" and it is known that the artist painted a portrait of Isabelle of Portugal as part of this embassy.

predecessor, Alfonso also brought selected artisans from the north including the Valencian painter Jacomart Baço whose only surviving works date to his Catalan period (see Figure 2.19).¹⁰⁰ Jacomart would have likely adopted a more Flemish style of painting in order to appease Alfonso's taste during his tenure as court painter. Alfonso's fascination with the northern aesthetic was also noted by his new Italian neighbors, particularly the Lomellini family. Battista Lomellini opted to present the new Neapolitan ruler with a triptych by Jan van Eyck during a Genoese delegation trip to the south in 1444.¹⁰¹ This particular work, now lost, was described by the humanist writer Bartolomeo Facio, and must have been a notable gesture on the part of Battista as it was the very same personalized triptych (referred to as the Lomellini triptych) that he commissioned from van Eyck in Bruges.¹⁰² Joanne Wright also suggests that Alfonso acquired two more paintings by Jan van Eyck, an image of St George in 1445 (given as a gift from the Valencian general Berenger Mercader) and another depicting the Adoration (both whereabouts unknown).¹⁰³ The northern works in Alfonso's vast collection clearly had a significant impact on local practicing artisans, including a rising Italian painter, the young Antonello da Messina.

¹⁰⁰ Strehlke, "Review: Quattrocento Aragonese, Naples," 144-5.

¹⁰¹ Christiansen, "The View from Italy," 40.

¹⁰² Richardson, Woods, and Franklin, eds., *Renaissance Art Reconsidered*, 187-9; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 55-7; Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe*, 182-3.

¹⁰³ Wright, "Antonello da Messina, the Origins of His Style and Technique," 42-3.

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Figure 2.19: Jacomart Baco, *The Last Supper* (c.1460s, Cathedral of Segorbe, Spain).

Just as Naples was the international hub of the south, the Veneto served a similar role in the north. The probability of Italian painters interacting with northern painters in Venice was much higher than in other cities. Venetian bottegas and independent artists were therefore more prone to embrace novel painting techniques, especially if it meant keeping up with the demands of the market. With *La Serenissima*'s close proximity to the Alps, cities in and around the Veneto region would have also been a likely home for northern collections not to mention northern artisans looking for work. In his discussion of the Sloane manuscript, Sir Charles Eastlake (1793-1865) mentioned the presence and influence of foreign artists in

Venice during the fourteenth and fifteenth centuries.¹⁰⁴ A German artist, whom Eastlake called Master “Paulus, pictor theotonicus,” may have also worked in and around Venice during the early fourteenth century, supplying churches with altarpieces and paintings on cloth, possibly in collaboration with a Franciscan monk.¹⁰⁵ Eastlake also mentioned other commissions involving *artistichi tedeschi*; a painter known as “Frederico” is listed working in Padua between 1395 to 1424 as well as a group of northern artists who specialized in fresco painting.¹⁰⁶ Venice also provided a work environment that encouraged relationships between Italian collectors and foreign craftsmen. Recent scholarship suggests that portraits may have been some of the first northern works to populate private collections. Marco Barbarigo, who became the Doge of Venice, and Zaccaria Contarini, the ambassador to France, both had their portraits painted by northern artists while the famed Venetian ambassador Bernardo Bembo may have also been responsible for the commission of a diptych by Hans Memling (now divided between the National Gallery of Art in Washington and Alte Pinakothek in Munich). The Italian humanist Marcantonio Michiel visited several Venetian collections during the 1520s and ‘30s and noted specific encounters with northern works including works by Rogier, Jan Gossaert, and Memling. The latter was particularly favored by Domenico Grimani, a

¹⁰⁴ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 90-3.

¹⁰⁵ Ibid. There is a receipt that describes payment made to Paulus for an altarpiece that created for St. Mark’s Cathedral, perhaps created around the same time as another painting currently in Vincenza that is inscribed “1333 – Paulus di Veneciis pinxit hoc opus.” Eastlake also connects this “Master Paulus” with a “Maestro Marco,” who had recently joined the Minor Franciscans.

¹⁰⁶ Bernd Roeck, “Venice and Germany: Commercial Contacts and Intellectual Inspirations,” in *Renaissance Venice and the North: Crosscurrents in the Time of Durer, Bellini, and Titian*, Bernard Aikema and Beverly Louis Brown, eds. (New York: Rizzoli Intl. Publishing, 2000), 46.

cardinal whose collection comprised of at least sixteen northern paintings (among them works by Bosch and Patinir) and a series of illuminations attributed to Simon Benning.¹⁰⁷

By the mid-fifteenth century, northern artists began to receive an increasing number of commissions from both private collectors and religious institutions throughout the Veneto. An artist named “Piero de Fiandra,” who some scholars believe to be linked to Petrus Christus, completed an altarpiece in 1451 for the no-longer-extant Santa Maria della Carita. Dieric Bouts’s *The Entombment*, painted around 1450, was possibly part of an elaborate polyptych intended for a Venetian church while another painted cloth by “Gianes da Brugia” has been described by Marcantonio in the collection of Leonico Tomeo in Padua.¹⁰⁸ One of the most poignant examples of cross-cultural artistic collaboration, however, involves the fresco cycles within the Ovetari chapel located in Padua (destroyed in World War II). This commission was initiated by the widow of Antonio Ovetari in 1451 and will be discussed in greater detail in chapter four; however, Giovanni d’Alemagna, brother-in-law of the Italian painter Antonio Vivarini, was among the team of recruited artists.¹⁰⁹ Little is known of his early years but it is assumed that Giovanni apprenticed in Germany where he was likely trained in oil painting. There is evidence that the artist was active in Padua prior to registering with the guild in 1441, as he was purportedly commissioned to polychrome the tomb of Raffaello Fulgosio at the Santo in Padua in 1431; art historian Ames-Lewis speculates that Giovanni d’Alemagna could very well be the same “Giovanni da Ulma” who is recorded

¹⁰⁷ Christiansen, “The View from Italy,” 40-43.

¹⁰⁸ Richardson, *Locating Renaissance Art*, 93.

¹⁰⁹ Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 48; Ian Holgate, “Giovanni d’Alemagna, Antonio Vivarini and the Early History of the Ovetari Chapel,” *Artibus et Historiae* 24 (2003): 9-29, accessed January 20, 2016, <http://www.jstor.org/stable/1483758>; Campbell, “Cosmè Tura and Netherlandish Art,” 119.

decorating the walls in the palace of the Bishop in Padua “all in oil.”¹¹⁰ Eastlake’s 1847 manuscript also refers to an altarpiece that is inscribed “Johannes de Alamania et Antonius de Murano, p. 1445,” possibly the *Coronation of the Virgin* that is presently at the Galleria dell’Accademia in Venice (see Figure 4.65).¹¹¹ Sometime after 1440, Giovanni d’Alemagna became partners with Antonio Vivarini; the two artists completed their first major commission the following year, *The St. Jerome altarpiece* for the Venetian church of the Augustinian Hermits. Giovanni’s reputation and northern aesthetic became so widely respected that San Pantaleone Martire hired the native Venetian artist Michele Giambono to produce a copy of Giovanni’s *Coronation of the Virgin* for one of its chapels (Figure 2.20). Giovanni d’Alemagna’s northern background may have had a dramatic impact on Antonio Vivarini’s workshop and eventually the young Andrea Mantegna, two painters whose works challenge the traditional aesthetic associated with Italian tempera technique.

¹¹⁰ Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 48; Holgate, “Giovanni d’Alemagna, Antonio Vivarini and the Early History of the Ovetari Chapel,” 9-29. A signed contract dating to 1437 indicates that the Bishop Pietro Donato stipulated a “Giovanni da Ulma” to paint the walls of the Chapel of S. Massimo “all in oil.” Holgate observes that Giovanni d’Alemagna began his practice first in Padua, possibly registering with the guild as “Giovanni Tectonico” in 1441, with Antonio Vivarini joining him later on in Venice

¹¹¹ Sir Charles Lock Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I (1847; repr., New York: Dover Publications, 2001), 111. Antonio Vivarini would occasionally sign his paintings as “Antonius de Murano” since the Viviarini workshop was based on the island of Murano for several years; however, it should be noted that the *Coronation of the Virgin* is presently dated 1446.

Figure removed due to copyrighting

Figure 2.20: Giovanni d'Alemagna, *Coronation of the Virgin* (1446, Galleria dell'Accademia, Venice).

As the fourteenth century progressed, Tuscany soon became a thriving economic center for artistic trade between the north and south. In Florence, banking was not the only market that was witnessing a period of extraordinary growth. By 1383 the Florentine silk market was full of merchants selling painted cloths from the north, objects that had become increasingly popular with the Italian middle and upper middle classes.¹¹² These

¹¹² Nuttal, *From Flanders to Florence*, 89.

painted fabrics were considerably more affordable than elaborate woven tapestries. While some were created to serve as patterns for the latter, others may have been produced for the simple reason that they could be manufactured and distributed more quickly than oil paintings, wall murals, or tapestries. Both Villers and Nuttal have shown that these textiles were considered to be works of art in their own right, familiarizing Italian patrons with the *ars nova* aesthetic of the north.¹¹³ Members of the Strozzi family began importing these painted cloths or *pannetti dipinti* into Florence in the 1460s; Filippo Strozzi purchased five northern pictures through the Medici bank in Bruges, and Alessandra Strozzi acquired several cloth paintings from her son Lorenzo in Bruges.¹¹⁴

As the Italian elite continued to develop a taste for painted cloths from the north, Nuttal's work reveals that these objects also made their way into Florentine workshops. Technical examination of a painted cloth (depicting the Virgin and Child) from the workshop of Hugo van der Goes revealed that the composition was later modified by artists associated with Ghirlandaio's workshop (see Figure 2.21).¹¹⁵ Only a handful of fifteenth-century *pannetti dipinti* have managed to survive, all of which were executed using a distemper (animal glue) technique; however, it is not impossible that artists occasionally used oil to produce these painted cloths.¹¹⁶ An account from 1462 provides a rare glimpse into some of

¹¹³ Nuttal, *From Flanders to Florence*, 77-8; Caroline Villers, "Paintings on Canvas in Fourteenth Century Italy" in *Zeitschrift für Kunstgeschichte* 58 (1995): 338-57, doi: 10.2307/1482818.

¹¹⁴ Nuttal, *From Flanders to Florence*, 77-8; Richardson, *Locating Renaissance Art*, 93; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 56-7.

¹¹⁵ Nuttal, *From Flanders to Florence*, 138.

¹¹⁶ Christina Young, "History of Fabric Supports," in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (New York: Routledge, 2012), 125-7.

Figure removed due to copyrighting

Figure 2.21: Hugo van der Goes and workshop of Ghirlanda, *Madonna and Child* (c. 1470s-80s, Staatliche Museum, Kassel).

the challenges facing Italian artists as their patrons became increasingly attracted to the aesthetic associated with these northern *pannetti dipinti*. Tommaso Portinari opted to hire artists from his native Florence to execute a series of painted cloths that were intended to serve as preliminary designs for a set of tapestries.¹¹⁷ Tommaso noted that his *pannetti dipinti*

¹¹⁷ Nuttal, 81. Portinari was enthusiastic about the experiment, recommending Giovanni de Medici to adopt it for all future tapestry commissions, as it enabled his ideas to be more satisfactorily realized; However he stressed that “the painter must be reminded not to apply the colors so thickly.”

began to deteriorate soon after they were completed; he complained that they had become *mezzo chascato*, or suffering from several losses in the paint layer.¹¹⁸ The precise reason behind the failure of Tommaso's painted cloths may never be known, but it is possible an Italian artist, unfamiliar with this northern technique, attempted to emulate the aesthetic quality of distemper cloths by using a traditional Italian egg tempera method; egg tempera paint would have flaked away from the fabric soon after the composition was completed. Andrea Mantegna, an artist working in close proximity to the north, seems to have been the sole artist who adopted and mastered the technique of painting on cloth using a range of aqueous media.¹¹⁹ As Mantegna trained in Padua, Dunkerton has suggested that there was also a market for these objects in northern Italy, stating that "early canvas paintings seem to have survived from centres north of the Apennines" as evidenced by surviving examples of cloth paintings encountered in Bologna and Padua.¹²⁰

Documents from the Medici archives confirm that the Medici were avid patrons of northern artists. An inventory from 1492 reveals that out of 142 paintings owned by the Medici, about a third were northern, many of which were on cloth.¹²¹ While many of these

¹¹⁸ Ibid., 81.

¹¹⁹ Young, *The Conservation of Easel Paintings*, 126; Andrea Rothe, "Andrea Mantegna's 'Adoration of the Magi,'" in *Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995*, eds. Arie Wallert, Arie, Erma Hermens, and Marja F.J. Peek, (Los Angeles: Getty Publications, 1995), 111-6; —, "Mantegna's Paintings in Distemper," in *Andrea Mantegna*, ed. Jane Martineau, (London & New York: The Royal Academy of Arts and The Metropolitan Museum of Art, 1992), 80-8; Jill Dunkerton, "Mantegna's Painting Techniques," in *Mantegna and 15th Century Court Culture*, eds. Frances Ames-Lewis and Anka Bednarek (London: Birkbeck College, 1993), 26-38.

¹²⁰ Dunkerton, "Mantegna's Painting Techniques," 31.

¹²¹ Nuttal, *From Flanders to Florence*, 150.

works are misattributed by the author of the inventory, it is interesting to note that the medium associated with each painting is rather accurately described. When paintings (particularly portraits) have been executed in oil this is specifically noted by the compiler “as if it were something special, a constituent of their precious and rare quality.”¹²² The Medici also kept their most precious northern paintings in their *scrittorio*, not unlike Leonello d’Este and Duke Alfonso of Aragon who also stored their northern treasures in private rooms.¹²³ Aside from a number of canvas paintings (many of which have not survived), notable works included a *St Jerome* by van Eyck, a portrait of a woman by Petrus (now in Berlin), and at least two paintings attributed to Rogier van der Weyden (a *Virgin and Child*, now in Frankfurt and a *Lamentation*, now at the Uffizi; see Figures 2.22 and 2.23).¹²⁴ The fact that this celebrated collection possessed such a significant number of paintings attributed to northern painters is noteworthy as they would have surely been seen by a number of distinguished collectors as well as Italian artists who frequented the Medici court, including Antonio Pollaiuolo, Fra Filippo, and later on, Filippino Lippi.¹²⁵

While only a fraction of these delicate cloth paintings have survived, they seem to have been common items in Italian markets throughout much of the fifteenth century, introducing a wider group of patrons and collectors to an aesthetic that was intimately tied with technique. Cloth paintings arriving from the north (often referred to as *tuchleins*) tended to be executed using a distemper technique; however, it is difficult to confirm if Italian artists

¹²² Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome*, 122; Nuttal, *From Flanders to Florence*, 161.

¹²³ Nuttal, *From Flanders to Florence*, 117.

¹²⁴ Christiansen, “The View from Italy,” 44-45.

¹²⁵ Nuttal, *From Flanders to Florence*, 113.

turned to other types of media (such as egg yolk or drying oils) in an effort to compete in this ever-growing area of the art market. Although Portinari's account suggests that Italian artists struggled to successfully produce *pannetti dipinti*, there is evidence that a handful of painters were able to compete in this particular market using oil paints. Alison Wright discusses the elaborate cloth paintings that have been commissioned from Paolo Uccello, Pesellino, Piero Pollaiuolo and Piero della Francesca, some which were recorded as having been done in oil.¹²⁶ An inventory of the Medici's collection dating to 1598 states that Uccello's large painted cloths, hanging beside his *Battle of Romano*, had suffered from tears and losses in the paint.¹²⁷ Although it is not possible to confirm whether or not these large wall hangings were executed in oil, they were apparently prone to damage and paint loss (possibly due to the inherent acidity of the medium and its effect on the canvas support). All of these accounts provide additional insight into how the influx of northern works helped to shape workshop practice through the demands of the marketplace.

¹²⁶ Alison Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome* (New Haven & London: Yale University Press, 2005), 80. Wright describes Pollaiuolo's three canvases depicting the labors of Hercules for the great hall of the Medici palace in Florence as well as lost canvas paintings of animals and mythological subjects by Pesellino and Uccello that were in the camera grande terrena of the Medici Palace. Vasari claims that another cloth painting attributed to Pollaiuolo (the gonfalone of the Archangel Michael made for Arezzo) was painted in oil; Wright links this to another painted cloth from the same decade (a confraternity banner in Arezzo executed in oil) by Piero della Francesca. See also Marina Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe* (Cambridge: Cambridge University Press, 2012), 202.

¹²⁷ Villers, "Paintings on Canvas in Fourteenth Century Italy," 349.

Figure removed due to copyrighting

Figure 2.22: Rogier van der Weyden, *Virgin and Child* (c. 1460-4, The Städel, Frankfurt).

Figure removed due to copyrighting

Figure 2.23: Rogier van der Weyden, *Lamentation* (c. 1460-3, The Uffizi Gallery, Florence).

Chapter 3

WRITTEN ACCOUNTS RELATING TO THE EARLY USE OF OIL IN QUATTROCENTO ITALY

The transitional period in fifteenth-century Italian painting can be contextualized by closely examining a wide range of written accounts, tracing the recorded development of oil painting in Northern Europe to its gradual adoption by artists working south of the Alps. In manuscripts, treatises, and other documents dating to the Medieval and Renaissance periods, the amount of information relating to pigments and dyes far outweighs the number of references that specify the preparation and use of painting media (e.g. drying oils, egg, etc.). When detailed entries relating to binding media are encountered, they rarely indicate whether such materials are meant to be employed as binding media, as coatings, or even as mordants. Nonetheless, scholars have still managed to trace references relating to the preparation of drying oil(s) back to the second and third century AD, corroborating the fact that artists were familiar with the oil technique well before the age of Jan van Eyck.¹²⁸ By the twelfth century, written documents included details concerning the application of oils, proteins, gums, and resins, beginning with Theophilus's text followed by Cennino Cennini's *Il Libro dell'Arte*.¹²⁹ Fifteenth- and sixteenth-century writers also offer a different perspective; anecdotal

¹²⁸ Sir Charles Lock Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vols. 1 & II (1847; repr., New York: Dover Publications, 2001), 28.

¹²⁹ Frances Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," in *Cultural Exchange Between the Low Countries and Italy, 1440-1600*, ed. Ingrid Alexander-Skipnes (New York: Brepols Publishers, 2007), 47-62. See also Theophilus, *On Divers Arts: The Foremost Medieval Treatise on Painting, Gildsmaking and Metalwork*, trans. John G. Hawthorne and Cyril Stanley Smith (1963; repr., New York: Dover Publications, 1979).

commentaries encountered in letters and later historical texts, such as Giorgio Vasari's *The Lives of the Painters, Sculptors and Architects* and Karel van Mander's *Het Schilderboek*, provide important social viewpoints regarding Quattrocento painting practice. This chapter will examine a wide range of written accounts that relate to the development and mastery of oil painting, tracing early oil paint technology to the Italian Renaissance and beyond.

3.1. Before Cennini: Ancient Texts and the Early Development of Oil Painting

Until fairly recently, the evolution and context of early written accounts relating to early Medieval and Renaissance painting practices have rarely been discussed or considered.¹³⁰ Any given manuscript may exist as numerous copies divided among multiple locations, with each rendition having been subjected to various translation/transcription campaigns by different generations of copyists.¹³¹ Scribes were traditionally charged with the task of copying these manuscripts and were likely more familiar with the art of illumination than with sculpture, wall/easel painting, or other artisanal professions.¹³² Furthermore, as

¹³⁰ Mark Clarke, "Asymptotically approaching the Past: Historiography and Critical Use of Sources in Art Technological Source Research," in *Art Technology: Sources and Methods*, eds. Stefanos Kroustallis, Joyce H. Townsend, Elena Cenalmor Bruquestas, Ad Stijnman, and Margarita San Andres Moya (London: Archetype Publications, 2008), 16-22.

¹³¹ Raymond Clemens and Timothy Graham, *Introduction to Manuscripts* (Ithaca and London: Cornell University Press, 2007), 39; Salvador Munoz Vinas, "Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts," *Studies in Conservation* 43 (1998): 114-24, doi: 10.2307/1506648.

¹³² Mark Clarke, "Codicological indicators or practical medieval artists' recipes," in *Sources and Serendipity: Testimonies of Artists' Practice*, eds. Erma Hermens and Joyce Townsend (London: Archetype Publications, 2009), 8-17. Clarke states that "it seems that for some of these manuscripts the writer's intention was not to provide a text for practical use, but to copy it for some ulterior reason. Art technological source research must therefore attempt to distinguish between those medieval recipe-containing manuscripts that were written down

sections of bound volumes were commonly separated from their original formats, re-circulated, and copied, manuscripts could become susceptible to misinterpretation or faulty translation.¹³³ The word “temper” for instance, stems from the Latin word meaning “to mix,” and can easily be interpreted as a reference to an aqueous binder (in particular egg tempera), an issue that is relevant when tracing the evolution of oil painting in Italy through written sources. Finally, there is the matter of accurately dating ancient texts; while evidence of old binding techniques and even watermarks can provide some information, these features are not always available. All of these factors must be considered when weighing the possible impact these manuscripts may have had on Italian artists active in the fourteenth and fifteenth centuries. Several of the ancient manuscripts covered in the following section still warrant further inspection and re-examination, much like the newly revised editions of Cennino Cennini’s *Il Libro dell’Arte* and the *Liber diversarum arcium*, in order to place them in an appropriate context relating to the development of oil painting in Renaissance Italy.¹³⁴ Early written sources confirm that particular technologies associated with drying oils, such as the use of heat, solvents, and/or siccatives (materials containing copper or lead that are added

with the intention that artists would use them, and those manuscripts written for other motives.”

¹³³ Clarke, “Asymptotically approaching the Past: Historiography and Critical Use of Sources in Art Technological Source Research,” 16-22; Stefanos Kroustallis, “Reading the Past: Methodological Considerations for Future Research in Art Technology,” in *Sources and Serendipity: Testimonies of Artists’ Practice*, eds. Erma Hermens and Joyce Townsend (London: Archetype Publications, 2009), 23-7.

¹³⁴ See the following sources: Mark Clarke, *Mediaeval Painters’ Materials and Techniques: The Montpelier Liber diversarum arcium (c.1200-1400)* (London: Archetype Publications, 2011), Lara Broecke, *Cennino Cennini’s ‘Il Libro dell’Arte’: A new English translation and commentary with Italian translation* (London: Archetype Publications, 2015), and Cennino Cennini, *The Craftsman’s Handbook, ‘Il Libro dell’Arte,’* trans. Daniel V. Thompson, Jr. (1933; repr., New York: Dover Publications, 1954).

to quicken the drying rate of oil), were either available or known to artists well before the Renaissance.¹³⁵ The early development of oil painting can be traced back to the second and third centuries, with a surprisingly early reference to the use of driers.¹³⁶ Based on his interpretations of writings by the Greek physician Aelius Galenus, Sir Charles Eastlake suspected that many Italian painters were unaware of siccatives and their properties; this may explain why many Italians avoided the new medium until the early fifteenth century.¹³⁷ Artists had the option of adding small amounts of dry pigments (such as verdigris or lead white) that would naturally speed the curing process of the oil film or adding materials to the oil medium at high temperatures (such as litharge), dissolving and dispersing the siccative throughout the oil. The latter would likely have created a much faster drying medium than the former and certainly the addition of resins would have also counteracted the slow drying rate of oils extracted from linseed or walnuts (Eastlake noted that the medical writer Aetius

¹³⁵ For information on the early use and development of turpentine and other essential oils see Alan Phenix, *Some Instances in the History of Distilled Oil of Turpentine, the Disappearing Painters' Material* (Los Angeles: Alan Phenix, 2015). Phenix concludes that turpentine was likely available to painters around 1300.

¹³⁶ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 28. Sir Charles Eastlake has noted Galen's observations regarding the siccative properties of oil when mixed with other materials: "Litharge dries like all the other metallic medicinal preparations" and "white lead and litharge are astringent and drying." Galen, also known as Aelius Galenus or Claudius Galenus was an accomplished Greek physician and philosopher. While only about a third of his writings have survived, some scholars feel that Galen may have written nearly 600 treatises, many of which were widely circulated and well known throughout Europe well after his death. Sir Charles Eastlake has noted Galen's observations regarding the siccative properties of oil when mixed with other materials: "Litharge dries like all the other metallic medicinal preparations" and "white lead and litharge are astringent and drying."

¹³⁷ *Ibid.*, 65.

recorded the preparation of drying oils from walnuts as early as the fifth/sixth century).¹³⁸ Siccatives were not the only means used to speed the drying rate of oils. As Eastlake recorded, the Greek physician, botanist, and pharmacologist Pedanius Dioscorides described the process of “sun-thickening” in his widely circulated *De Materia Medica* (portions of which date between the fifth and seventh centuries), although it seems that the original intent of Pedanius’s recipe is to rid the oil of its yellow color in preparation for painting.¹³⁹ Dioscorides’s writings may well be the earliest existing reference to the use of oil as a paint medium; a recipe for the preparation of a pigmented oil has been located in the *Mappae*

¹³⁸ Ibid., 19. Aetius has included rather lengthy descriptions of drying oils and their relation to art in his records. Although he does not speak directly of oil being used as a paint binder he does indicate that encaustic painters and gilders use oil to protect their artworks (likely referring to oil-resin varnishes). He relates the preparation of oleum cicinum (oil obtained from the Croton tree in Egypt/India) to the preparation of linseed oil, the earliest known reference to linseed oil as opposed to nut oil: “Walnut oil is prepared like that of almonds, either by pounding or pressing the nuts, or by throwing them, after they have been bruised, into boiling water. The (medicinal) uses are the same: but it has a use besides these, being employed by gilders or encaustic painters; for it dries, and preserves gildings and encaustic paintings for a long time.”

¹³⁹ Ibid., 25-6; Clarke, *Mediaeval Painters’ Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 19-20. Dioscorides’s *De Materia Medica* is recorded as being one of the most influential written works on herbal science. Composed of five volumes, *De Materia Medica* was widely circulated in the form of illuminated manuscripts up until around 1600 AD. In one of his volumes, he does provide instructions on the preparation of oil for colors. Eastlake includes an excerpt of the recipe with additional commentary: “Oil is bleached in this manner. Select it of a light color, and not more than a year old; pour about 5 gallons into a new earthenware vessel of an open form, place it in the sun, and daily at noon dip and pour back the oil with a ladle, beating up its surface till, by constant agitation, it is thoroughly immixed and made to foam.” The oil is thus treated for several days; the ingredients afterwards added (macerated Trigonea and resinous pine-wood shavings) are unimportant; but in conclusion it is observed, if “the remainder” of oil (the aqueous portion being evaporated) “be not sufficiently bleached, place it again in the sun, repeating the above operation, till it becomes colorless.”

Clavicula (dating to the ninth, tenth, and twelfth centuries), but the resulting material is intended to function as a glaze over metal leaf as opposed to a primary paint binder.¹⁴⁰

Perhaps the most relevant written accounts relating to the early use of oil paint in medieval and Renaissance Europe are those attributed to Theophilus Presbyter (a Benedictine monk who likely flourished between 1070-1125) as well as an individual referred to as “(H)Eraclius” of which very little is known; recipes pertaining to the use of oil- and egg-based paints were cited by both authors and continued to reappear in later manuscripts dating to the

¹⁴⁰ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 19-23; Vinas, “Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts,” 115-6; Cyril S. Smith and John G. Hawthorne, “Mappae Clavicula: A Little Key to the World of Medieval Techniques,” *Transactions of the American Philosophical Society* 64 (1974): 44, doi: 10.2307/1006317; Clarke, *Mediaeval Painters’ Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 20-1; Silvia Biana Tosatti, *Trattati Medievali di Tecniche Artistiche* (Milan: Editoriale Java Book SpA, 2007), 34. Written in northern Europe, this collection of recipes has strong connections with the Lucca Manuscript with many of the same references also appearing in other codices such as the Spanish *Codex Matritensis*. The *Mappae Clavicula* exists primarily as fragments, with its central core originating from around 800 AD, an addition dating to the tenth century, and several later additions presumably made during the late eleventh/early twelfth century (these are referred to separately as the *De coloribus et mixtionibus* by Daniel V. Thompson in 1933). These later additions probably originated from northern France or southern England and contain references to both the preparation of oil for use in varnishes, as glazes for metal leaf, and also as a mordant: “The following three chapters [are for use] when it is necessary to work in gilding with leaf. Chapter 113 -The recipe for linseed oil – 2 pounds of linseed oil, 1 ounce of gum, 1 ounce of pine resin, Grind all these and cook down in an earthenware pot. Chapter 113A - Linseed oil for gilding - 2 pounds of linseed oil, 2 ounces of gum, 1 ounce of pine resin, 2 soldi of saffron. Mix these three as above. Chapter 114 – The procedure for laying out [gilding] – If gold leaf is to be laid out on a firmly stretched raw skin coated with white lead or any pigment, the gold leaves are laid down and after they are dry, coat them with linseed oil using the mixture described above, where we say it is mixed with saffron. [] Chapter 116 - Coloring tin leaf - Take 1 ounce of clean saffron, 2 oz of the best split orpiment, add half [an ounce] of gum and half ounce of linseed oil. Mix in rain or fresh water, and boil it. Mix the preparation together, grinding it well, and taking it up with a sponge, coat the leaf with it.”

thirteenth, fourteenth, and fifteenth centuries.¹⁴¹ Theophilus's *Schedula diversarum artium* (or *De diversis artibus*) is often quoted for its early reference to drying oils. The extraction process used to prepare linseed oil is described in the text as well as the addition of oil to pigments that can be applied over metal leaf and on wooden surfaces; however, the author appears to be unfamiliar with siccatives used to accelerate the drying rate of linseed oil which may explain why he describes the process of working with oils as "tedious."¹⁴² In the same chapter, Theophilus offers an alternative, faster drying "resin" (the gum from a cherry or plum tree) that can be mixed with most colors, a material that would be far less effective than the addition of driers:

Book 1, Chapter 20 – How to Redden Doors; and Linseed Oil

¹⁴¹ Vinas, "Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts," 115-17; Clark, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber diversarum artium (c.1200-1400)*, 20, 29-32; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 42, 345; Theophilus, *On Divers Arts: The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork*, xv-xxxv; Mary P. Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vols. I & II (1849; repr., New York: Dover Publications, 1999), 166-79; Tosatti, *Trattati Medievali di Tecniche Artistiche*, 40-8, 91. Theophilus is thought to have lived in France or Germany during the eleventh and/or twelfth century. His *Schedula diversarum artium* is considered to be a systematic literary work rather than simply a collection of various unrelated recipes as often seen with other ancient texts. Book I focuses on painting techniques, Book II on glasswork, and Book III on metalwork and other miscellaneous recipes. Eastlake states that Theophilus in particular used words of Germanic origin to further clarify his Latin. The origin of *De coloribus et artibus romanorum* is less secure as the actual identity of the writer "(H)eraclius" is still debated amongst scholars. Books I and II (written in verse by one hand and date to approximately the tenth century) comprise a majority of the original text and appear to originate in Germany or Flanders, while Book III (written in prose) appears to have been added in sections throughout the twelfth and thirteenth centuries and may be from Northern France or Southern England.

¹⁴² Theophilus, *On Divers Arts: The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork*, 27-32. A recipe is also included involving the preparation of varnishes (Chapter 21) that calls for the addition of resin to linseed oil.

If you want to redden doors, get linseed oil which you should make in this way. Take some flax seed and dry it in a pan over the fire without water. Then put it in a mortar and pound it with a pestle until it becomes a very fine powder. Put it back in the pan, pour in a little water, and heat it strongly. Afterwards wrap it in a new cloth and put it in the press where oil is usually pressed from olives, nuts, and poppy seeds, and press out this oil also in the same way. Grind some minimum or cinnabar with this oil on a stone without water, spread it with a brush on the doors or panels that you want to redden and dry them in the sun. Then coat them a second time and dry them again. Finally spread on top of it the gluten called varnish...

Book 1, Chapter 24 – Tin Leaf

.....Then take the pigments that you want to apply, grind them carefully with linseed oil without water, and make the mixtures for faces and robes just as you made them with water above. Vary the animals or birds or foliage each with their proper colors, as you please.

Book 1, Chapter 25 – Grinding Pigments with Oil and Resin

All kinds of pigments can be ground with this same oil and laid on woodwork but only on things that can be dried in the sun, because, whenever you have laid on one pigment, you cannot lay a second over it until the first has dried out. This process is an excessively tedious one in the case of figures...¹⁴³

While Theophilus appears to have been unaware of driers and their properties, siccatives are described in Eraclius's *De Coloribus et artibus Romanorum*, a portion of which Mary P. Merrifield suspected may have been written by a compiler who lived in or originated from Italy.¹⁴⁴ Eastlake noted that unlike Theophilus, Eraclius "does not restrict oil painting to

¹⁴³ Ibid.; Clark, *Mediaeval Painters' Materials and Techniques: The Montpelier Liber diversarum arcium (c.1200-1400)*, 29; Tosatti, *Trattati Medievali di Tecnica Artistica*, 91. This particular manuscript is considered to be a structured literary work rather than simply a collection of various unrelated recipes as often seen with other ancient texts. Book I focuses on painting techniques, Book II on glasswork, and Book III on metalwork and other miscellaneous recipes.

¹⁴⁴ Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vol. I, 170; Clarke, *Mediaeval Painters' Materials and Techniques: The Montpelier Liber diversarum arcium (c.1200-1400)*, 20; Tosatti, *Trattati Medievali di Tecnica Artistica*, 40; Vinas, "Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts," 115; Vinas points out that scholars feel portions of the manuscript were written in Italy while other sections may have been written in France or Germany. Clarke also lists all three countries as likely places of

surfaces that are only to be exposed to the sun”; recipes from Book III of the manuscript include instructions for painting columns, the preparation of oil using additions of lime, lead white, and the heat of the sun, and a reference to the problematic nature of orpiment in oil:

Book III, Chapter 24 – How wood is to be prepared before painting on it. -And when you have made it smooth, as I was saying, mix plenty of white-lead very finely ground, with linseed oil, and lay an excessively thin coat of it wherever you intend to paint with a brush....When this is dry, lay on, as you did before, another and a thicker coat of it, not thicker by having a greater quantity of color, but by having less oil in it.

Book III, Chapter 25 – How a column is prepared for painting. – If you wish to paint on a column or slab of stone, first let it dry very perfectly in the sun or before a fire. Then take white, and grind it very finely with oil upon a marble slab. Afterwards, the column being well smoothed and polished, without any crevices, lay on it two or three coats of that white, with a broad paintbrush. Then run very stiff white over it with your hand or with a brush, and let it remain a short time. When tolerably dry, press your hand strongly over the white surface, drawing your hand towards you. Continue to do this until it is as smooth as glass. You will then be able to paint upon it with all colors mixed with oil. But if you wish to imitate the veins of marble on a general tint (brown, black, or any other color), you can give the appearance, when the ground so prepared is dry. Afterwards varnish it in the sun.

Book III, Number 28 - Of the General Practice in grinding all colors. - You must know, however, that all colors may be ground with clear water, if they are afterwards allowed to dry; and then with the white of egg, or oil, or gum-water, or wine, or cervisia, when they are mixed or tempered.

Book III, Number 29 - How oil is prepared for tempering colors – Put a moderate quantity of lime into oil and heat it, continually scumming it; add ceruse to it according to the quantity of oil, and put it in the sun for a month or more, stirring it frequently. And know that the longer it remains in the sun, the better it will be. Then strain and keep it, and distemper colors with it.

Book III, Number 32 - How yolk of egg is prepared – orpiment is ground and prepared with the yolk of egg in the following manner, and the yolk of egg is thus prepared: - Take the yolk in the middle of your hand, and prick it with a thorn or a needle, and, putting your finger upon it, press it out, and

origin. This theory is also supported by the presence of recipes relating to glass technology that can be found within the manuscript, recipes that suggest a familiarity with the glass industry in and around the *Veneto* region.

receive it in a vase; and, adding a drop of water to it, mix with the orpiment. If you mix with oil it will never dry. Mix it therefore with the yolk of egg.¹⁴⁵

Sections from both Theophilus's and Eraclius's manuscripts are believed to have first arrived in Italy around 1409, brought to Milan by the writer Johannes Alcherius.¹⁴⁶ Between 1398 and 1411, Alcherius is documented traveling between Paris and Milan gathering recipes from a number of artists including a Johannes de Modena from Bologna, a Michelino da Besozzo (presumably from Milan), a "Theodore" from Flanders, a Jacob Cona in Paris, a miniature painter Antonio di Compendio, an Italian monk Dioniso, and Peter de St. Omer from France.¹⁴⁷ Peter de St. Omer (or Audemar) left an intriguing compilation referred to as *De coloribus faciendus* (c. 1300) that Alcherius incorporated into his manuscript:

150. The way to make a green color with salt – [...] This color may be distempered and mixed with water, or still better, with vinegar, and also with linseed-oil, or even with white of egg.

152. How to make and temper white and green – [...] Take the white, dry it, and grind it, and temper it with wine, and use it for painting on parchment, and mix it with oil for painting on wood and on walls. In the same manner grind and temper the green with oil, and use it for painting on wood; but on walls with wine, or if you prefer, with oil, but you must temper it with very clear and good wine, or with vinegar.

¹⁴⁵ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 63; Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vol. I, 232; Tosatti, *Trattati Medievali di Tecniche Artistiche*, 48.

¹⁴⁶ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 42-3; Vinas, "Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts," 118; Merrifield, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 112-62; Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 25-6. Although sections of Eraclius's text may have been written in Italy, Alcherius's travels to Milan may have helped in making Eraclius's recipes more widely available.

¹⁴⁷ Ibid.

158. Also to make green – [...] This is tempered first with water, and afterwards with egg on wood or on walls...

168. How azure is prepared and purified – [...] This color is used on walls with egg and water; but on wood it is ground with oil, like other colors.

172. How to make a black color in various manners – [...] If you wish to lay black over other colors on parchment, you must not put incaustum, but know that you must take charcoal distempered with egg, and the same on walls either with water or with egg, and on wood with oil...

176. How to make minimum, otherwise called sandaraca – [...] and in laying on walls it is ground with gum water; but never with egg. It can, however, be laid upon parchment with egg; but on wood, with oil.¹⁴⁸

Technical studies of Medieval northern artworks confirm what is intimated in St. Peter de Omer's manuscript: by the early fourteenth century, northern artists appear to have been familiar with the working properties of both tempera and oil.¹⁴⁹ Along with Theophilus's

¹⁴⁸ Merrifield, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 116-22, 126, 134, 138, 140; Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 25-6; Vinas, "Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts," 117; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 42, 83, 277. Note that the recipe outlined under 150 is actually placed within the text of the preceding chapter that details the preparation of vinegar for making "salt green." Clarke also points out that Peter of St. Omer was most likely not the original compiler of the manuscript but that the text was named after him. In addition to recipes relating to pigments there is also a recipe for using oil and resin as a binder to glaze over metal leaf as well as a rather complex set of instructions for decorating a wooden box using saffron mixed with egg, followed by an application of oil to make it "shine." These particular recipes can also be found in a fourteenth-century manuscript *Incipit Tractatus de Coloribus Illuminatorum seu Pictorum* (also referred to as the *Liber di Coloribus illuminatorum sive pictorum*) in the British Museum; however, driers are meant to be added to an oil binder before colors are tempered with it.

¹⁴⁹ For technical studies on the early use of oil painting in northern Europe see the following sources: Jilleen Nadolny, ed., *Medieval Painting in Northern Europe: Techniques, Analysis, Art History* (London: Archetype Publications, 2006), Unn Plahter et al., eds., *Painted Alter Frontals of Norway, 1250-1350*, vols. I, II & III (London: Archetype Publications, 2004), and Cyriel Stroo, ed., *Pre-Eyckian Paintings in the Low Countries* (Brussels: Brepols Publishers, 2009).

description of preparing oils for painting, these recipes made their way into Alcherius's collection; however, it is still unclear whether his manuscript had a direct impact on Italian artists at the beginning of the fifteenth century, specifically those working in and around the city of Milan which Alcherius was known to have frequented.¹⁵⁰ The Strasburg Manuscript, a Germanic text dating to the same period, specifically states that this particular oil technique is not yet known to all painters in a passage that includes instructions for the preparation of oil (with the addition of siccatives) as well as which pigments are suitable for mixing with oils and varnish:

How to temper all oil colors - Now, I will also here teach how all colors are to be tempered with oil, better and (more) masterly than other painters; and in the first place how the oil is to be prepared for the purposes, so that it may be limpid and clear, and that it may dry quickly.

How to prepare oil for all colors – Take oil of linseed, or of hempseed, or old nut oil, as much as you please, and therein bones that have been long kept, calcined to whiteness, and an equal amount of pumice stone; let them boil in the oil, removing the scum. Then take the oil from the fire, and let it well cool; and, if it is in quantity about a quart, add to it an ounce of white copperas; this will diffuse itself into the oil, which will become quite limpid and clear. Afterwards strain the oil through a clean linen cloth into a clean basin, and place it in the sun for four days. Thus it will acquire a thick consistence, and also become as transparent as a fine crystal. And this oil dries very fast, and makes all colors beautifully clear, and glossy besides. All painters are not acquainted with it: from its excellence it is called *oleum preciosum*, since half an ounce is well worth a shilling; and with (this) oil all colors are to be ground and tempered. All colors should be ground stiffly, and then tempered to a half-liquid state, which should be neither too thick nor too thin.

These are the colors which should be tempered with oil. Vermilion, minium, lake, brasil red, blue bice, azure, indigo, and also black, yellow orpiment, red orpiment, ochre, face brown red, verdigris, green bice, and white lead. These are the oil colors and no more. Here observe that these colors are to be well ground in oil, and at last with every color mix three (that is a few)

¹⁵⁰ As Alcherius's text includes sections from Theophilus's *Schedula* and Eraclius's *De Coloribus et artibus Romanorum*, he was at least aware of the technologies that were associated with the preparation of oil.

drops of varnish, and then place every colors by itself in a clean cup, and paint what you please.

With all the above mentioned colors a small quantity of calcined bone may be mixed, or a little white copperas about the size of a bean, in order to make the color dry readily and well.¹⁵¹

The process by which this particular drying oil is prepared (using both heat and siccatives) was evidently regarded as “better and more masterly” than other methods, suggesting that northern painters were better acquainted with the technological challenges posed by the oil medium than were their Italian counterparts, a notion further corroborated by manuscripts written in the decades to follow. It is possible that drying oils, solvents, and other materials prepared north of the Alps were made accessible to medieval Italian painters through apothecaries; Florentine guild statutes from the early 1300s for the *Medici e Speciali* (to which painters and artisans belonged) list linseed oil, *ragia* (pine resin), and *trementina* (likely oil of turpentine) as products that were readily available for purchase.¹⁵² By the fourteenth century, texts relating to art materials were written in the vernacular instead of in Latin, a feature that some scholars feel is indicative of an author’s first-hand experience or observation of a painting technique.¹⁵³ Mark Clarke stipulates that texts or portions of texts written in the vernacular including the *Segreti per colori* (or Bolognese Manuscript), the *Liber diversarum arcium* (also referred to as the Montpellier MS), and Cennino Cennini’s *Il Libro*

¹⁵¹ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 126-31; Vinas, “Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts,” 119. See also Viola and Rosamund Borradaile, *The Strasburg Manuscript: A Medical Painters’ Handbook* (New York: Transatlantic Arts, 1966).

¹⁵² Phenix, *Some Instances in the History of Distilled Oil of Turpentine, the Disappearing Painters’ Material*, 12. See also Raffaele Ciasca, *L’arte dei medici e speciali nella storia e nel commercio fiorentino dal secolo XII al XV* (Florence: L.S. Olschki, 1927).

¹⁵³ Clarke, *Mediaeval Painters’ Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 12.

dell'Arte, are therefore more representative of workshop practice in the fourteenth and fifteenth centuries.¹⁵⁴ Comparatively speaking there are far fewer references involving the oil medium in the *Segreti per Colori* (likely written around the second quarter of the fifteenth century); however, the seventh chapter specifically refers to the painting technique of a Spanish painter, a “Magister Jacobus de Tholeto.”¹⁵⁵ Although many of the recipes call for the use of gum-water and egg there is a specific reference to an egg-oil emulsion (although only egg white is involved in this instance) when red lakes are mixed with lead white; other notable recipes involve the preparation of an oil-resin mordant and another involving *acqua di ragia*, quite possibly referring to oil of turpentine.¹⁵⁶ Though none of these recipes involve the preparation of oil paints, it suggests that by this period Italian artists were at least familiar with solvents such as turpentine, a material that would have facilitated painting with a potentially viscous medium such as oil:

¹⁵⁴ Ibid; Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vol. II, 328-30; Vinas, “Original Written Sources for the History of Mediaeval Painting Techniques and Materials: A List of Published Texts,” 119. See also Lara Broecke, *Cennino Cennini’s ‘Il Libro dell’Arte’: A new English translation and commentary with Italian translation* (London: Archetype Publications, 2015).

¹⁵⁵ Merrifield, *Medieval and Renaissance Treatises on the Arts of Painting, Original Texts with English Translations*, vol. II, 328-30. Merrifield has also pointed out that there was a Spanish college in Bologna during this period as well a hospital, Santa Maria Maddalena, built by the Spanish in 1342.

¹⁵⁶ Ibid. A recipe involving the distillation of turpentine is mentioned in Chapter 7, No. 246. Merrifield also states that in No. 238 “the distillation of linseed oil is written about with a note that colors mixed with it will last forever.” This statement is confusing as linseed oil (and other drying oils) is not prepared using distillation techniques; it is possible Merrifield was unaware of the actual chemical process involved with distillation or that this particular chapter was misinterpreted or mistranslated. Further study is needed to confirm which techniques this particular recipe alludes to.

Chapter 6, No. 152 – To make a mordant for gilding on walls- Take calcined bone, ground fine with weak glue, such as parchment glue, and let it dry; and when quite dry grind it up afresh with linseed oil, and make it rather stiff; then take a little liquid varnish, and incorporate it with the bone-dust. Add to it a little saffron, sufficient to give it color, and make it rather stiff. When you wish to put the gold on the wall, the mortar must be dry, and the mordant must not be applied too thick. Let it remain 5 or 6 days, and put on the gold.

Chapter 7, No. 201 – To make a rose color, very good and beautiful – Take 1 ½ oz. of lac, and the same quantity of ceruse; grind them with linseed oil and prepared white of egg, and apply upon paper.

Chapter 7, No. 204 – To make a certain water which is good for applying on figures and miniatures – Take oil of aloes, linseed oil, and liquid varnish, of each equal quantities; boil these ingredients together, and put them into a flask. When you wish to use the liquor, anoint it with the figures or miniatures when they are dry, and not before, and they will be shining and very beautiful.

Chapter 7, No. 205 – To make linseed oil – Take one quart of clean and pure linseed, damp it a little and then put it into a vase over the fire and stir it up with a spoon, and then push the spoon several times to the bottom so as to moisten all the seeds. You must add a little water in order to soften them; then put the seeds into a strong woolen cloth, place it in the press, and the oil will flow out.

Chapter 7, No. 206 – To make liquid varnish – Take the gum of juniper (sandarac), two parts, and one part of linseed oil, boil them together over a slow fire, and if the varnish appears to be too stiff, add more of the oil and take care not to let it catch fire, because you would not be able to extinguish it, and even if you could extinguish it, the varnish would be dark and unsightly. Let it boil for half an hour, and it will be done.¹⁵⁷

While the Bolognese Manuscript (c. 1425-50) may be one of the earliest texts to cite the use of an egg-oil paint, the *Liber diversarum artium* (originally written in France or England sometime around 1300) involves an egg-oil painting technique that is far more involved. This particular text, like Alcherius's collection, contains recipes that are also found in Theophilus and Eraclius's *De Coloribus et artibus Romanorum* and is considered to have

¹⁵⁷ Ibid.

been copied around 1430 in northern Italy.¹⁵⁸ The existence of this copy implies that the “secret” of oil painting (likely some of the preparatory processes described earlier) may have been common knowledge within certain circles of Italian painters. Clarke points out that the structure of the *Liber diversarum artium* is unique as it is divided according to binding media with individual sections devoted to water-based materials, oil-based, and mural painting (in this instance lime).¹⁵⁹ One particular passage in the *Liber diversarum artium* refers to various layering systems using oil paint and egg tempera while another section on panel painting techniques makes a clear distinction between colors used on paper and colors used on panel:

On the preparation of linseed oil - 4th chapter – Linseed oil is made thus; take flax seeds and dry in a pan over the fire, without water, then put in a mortar, and beat with a pestle until it shall be a very fine powder, again put it in the pan and pour in a little water; heat it strongly thus, then wrap it in a new cloth, and put it in a press where it (the oil), will be expressed; made with such a protocol (as if it were some other pressed oil).

Which colors are used on wood - 9th chapter - On wood are used the same colors just as on a page, and the same mixtures and matizas; their tempering however is dissimilar. [...] And some colors are excepted: folium, sanguine (probably brazil), grain (kermes), ink, dragonsblood. All types of colors may be ground (with the same oil) and applied on a wooden work, on those things which can be dried in the sun.

Note. Because every time you apply a color, another may not be put onto it, without the first being dried: on figures (ymaginibus) that is prolonged, and very tiresome.

Note. If you however want to speed up your work, (take) gum of cherry or plum mixed with water, and poured into a vessel, on the fire in winter, or in the sun in summer, such that they may liquefy, or colors may be ground up with clear egg white mixed with water and applied. Yet you should

¹⁵⁸ Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber diversarum artium (c.1200-1400)*, 89-90. Clarke states that this manuscript is a complete handbook for painters and appears to have been copied in northern Italy, possibly Venice, by a doctor as the recipes relating to painting practice are embedded in a number of medical texts.

¹⁵⁹ *Ibid*, 39.

place the required amount of minium and ceruse and carmine with glaire and water. Spanish green (verdigris) should not be mixed with juice.

Note. Lead white, however, if mixed (with the aforementioned gums) darkens, whence it is always applied with oil, and not (just) varnished, for costly works. Azure, if tempered with oil, darkens. Whence white is added to it until it is recalled to pristine.

Note: Paint fields (campis) or figures (ymaginibus) thus: two or three layers must be applied of that color with which you want to make a field or image; nevertheless the first and second layer can be made from a weaker color, with the last pure color; and two (coats) (must be) with egg white, and the last (coat) in oil; or all of them in oil; except when an image must be detailed with gold leaf, when the first coat should be applied with oil, but the last with water and egg.

For example: first apply in oil one layer of pale blue, and dry; there will follow: one of azure in oil, and dry; and finally one with water and egg, and dry. If you want to detail with gold, first detail with the color which is applied under the gold leaf. If indigo is tempered with oil it will not dry, whence it is applied with glaire and water. Put cinnabar second, on (a first layer of) minium, such that it shall dry, if it is tempered with oil.¹⁶⁰

The presence of the *Liber diversarum arcium* in Venice by 1431 is another indication that the technique of oil painting had reached northern Italy by the early fifteenth century at

¹⁶⁰ Ibid, 140-1; Lara Broecke, e-mail message to author, 4 January, 2016. Clarke points out that while some of these recipes may refer to the painting of polychrome painting as opposed to traditional easel painting but that technical studies of both polychrome sculpture and easel paintings from the period indicate that the differences in technique are “trivial.” Clarke also feels that the gum and glaire are meant to be used as alternatives for painting on panel as opposed to additives to the oil medium; Lara Broecke offers another explanation for the various layering systems proposed by the author: The first option, with two coats in egg and then one in oil, is a glazing system – you establish an opaque base colour in a quick-drying medium and then apply a rich oil colour over the top. This gives a covering, deep, rich effect that cannot be achieved with egg alone, without having to wait for lots of layers of oil to dry. The third option, with egg over oil, is probably a release system. If you need to mordant gild onto an area painted in oil, the gold leaf will stick to the oil paint surrounding the mordant even if it appears to be dry. Coating the oil paint with a layer of egg white means that the gold leaf can be applied to a mordant laid over the egg white and it will not stick to the surrounding egg white. The egg white can then be washed off if necessary with swabs of water. The recipe here seems to be an alternative where the egg is pigmented and is left in place (or maybe the recipe compiler misunderstood and assumed that the egg layer was a paint layer when actually it was just a release layer).

the latest, likely before cities like Florence and Siena.¹⁶¹ The suggestion to alternate layers of oil and/or egg is a curious one and may or may not have been followed in northern European workshops; however, it is perhaps more significant that the *Liber diversarum arcium* does not contain any references to the use of siccatives in the preparation of oil.¹⁶² Such technology would have been instrumental to artists working in the humid climate of Venice or in any damp environment; cold-pressed oil would have taken months to dry, a characteristic that would have likely deterred many an Italian painter who was familiar with the quick-drying egg tempera medium. Cennino Cennini's *Il Libro dell'Arte* confirms that while siccatives were used to create mordants they do not appear to have been commonly incorporated into oil paints. Drying oils prepared with siccatives and/or heat may have been available in apothecaries in major cities by the fourteenth century; however, it appears that the processes involved with the successful preparation of the medium may have been known only by a select number of Italian painters, likely those working in northern Italy. As art manuals and treatises continue to be discovered and revisited, these primary sources may be able to provide scholars with a more complete chronology outlining the development and dissemination of oil paint technology.

3.2. Cennino Cennini and Renaissance Perspectives

Just as the *Liber diversarum arcium* reflects fourteenth century northern painting practice, Cennino Cennini's text offers a comprehensive summary of techniques employed in

¹⁶¹ Ibid, 90.

¹⁶² While the use of heat would have helped with the pre-polymerization process to a certain extent, small additions of siccatives containing lead or copper would have helped facilitate the drying process (arguably more so).

Italy before the birth of the Renaissance. While many of the manuscripts discussed in the previous section are compilations of pre-existing texts, Cennini's *Il Libro dell'Arte* stands apart as it is written solely in Italian, by an Italian painter, and offers almost all new material regarding historical painting practices.¹⁶³ In revisiting one of the most celebrated complete treatises of the Quattrocento, scholar Lara Broecke has recently provided a new assessment of Cennini's background, why he was compelled to write such a text, and a re-evaluation of the script itself.¹⁶⁴ One important distinction between Broecke's translation of the manuscript compared to earlier English translations, is the decision to use more descriptive terms such as "binder" or "mixture" in an effort to avoid using the generic word "tempera"; the differentiation between egg and oil-based binders (or any organic binders in fact) is imperative when exploring the evolution of oil paint in Italy.¹⁶⁵ While some scholars feel

¹⁶³ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 9.

¹⁶⁴ Ibid, 1-17. An earlier assessment of Cennini's text suggested that the treatise was likely commissioned by the Florentine Guild in an attempt to further control (and restrict) artists from experimenting with new techniques and materials. See Carl Brandon Strehlke, "The Case for Studying Masolino's and Masaccio's Panel Paintings in the Laboratory" in *The Panel Paintings of Masaccio and Masolino: The Role of Technique*, eds. Carl Brandon Strehlke and Cecilia Frosinini (Milan: 5 Continents Editions, 2001), 23-4, and Roberto Bellucci and Cecilia Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings" in *The Panel Paintings of Masaccio and Masolino: The Role of Technique*, eds. Carl Brandon Strehlke and Cecilia Frosinini (Milan: 5 Continents Editions, 2001), 29-39.

¹⁶⁵ Ibid, 12-15; Broecke's decisions are informed by taking into account the context of the materials being discussed as well the complicating matter that the original manuscript no longer exists (there is a copy dated to around 1437 as well as a later copy dating to the sixteenth century). While Broecke discusses the complexity behind words such as "colore," she does not refer to the term "tempera" in particular; however, close comparison of Broecke's version with Daniel V. Thompson's 1933/56 versions relating to key passages demonstrates Broecke's different approach regarding the translation of the word. See also Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte'*, trans. Daniel V. Thompson, Jr. (1933; repr., New York: Dover Publications, 1954).

portions of the treatise are meant to un-objectively promote Tuscan painting practices, Broecke has noted that the text is written in a Paduan (or a northern Italian) dialect and includes descriptions of techniques that were more commonly encountered and/or practiced in northern Italy rather than Siena or Florence.¹⁶⁶ Broecke further postulates that during his time at the Carrara court in Padua, Cennini may have been inspired to generate a manuscript to bolster his own reputation as well as his profession.¹⁶⁷ Cennini would have been familiar with the writings of another attendee of the Carrara court, a scholar known as Giovanni Conversini whose 1399 treatise recommended that members of the royalty populate their court with doctors, lawyers, and philosophers rather than painters.¹⁶⁸ *Il Libro dell'Arte* was likely a concerted effort by Cennini to collect an impressive body of information rather than have the manual be used as a guide for the workshop; this may account for the handful of recipes in the

¹⁶⁶ Ibid; Lisa Monnas, *Merchants, Princes, and Painters: Silk Fabrics in Italian and Northern Paintings, 1300-1550* (New Haven & London: Yale University Press, 2008), 97, 108-10; Clarke, *Mediaeval Painters' Materials and Techniques: The Montpelier Liber diversarum arcium (c.1200-1400)*, 91. See also Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell'Arte'*, trans. Daniel V. Thompson, Jr. (1933; repr., New York: Dover, 1954). Refer to Chapter 4 for more information regarding the discrepancies noted between Cennino's recommended painting methods and the technical analysis of early fifteenth-century panel paintings. Broecke states that the reference to ducats, a currency only used in northern Italy, as well as other "northern" terms attests to the fact that Cennino did not conceive *Il Libro dell'Arte* in his native Tuscan town of Colle di Val d'Elsa. Broecke cites Cennino's descriptions relating to reverse glass gilded reliquaries, punching gold foil into relief, and the use of canvas strips to cover defects in wooden panels, a technique that was commonly used in the Veneto by this period but was not used in Florence until 1429.

¹⁶⁷ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 2-8; Diana Norman, *Siena, Florence, and Padua: Case Studies* (New Haven: Yale University Press, 1995), 18-22. See also Benjamin G. Kohl, *Padua Under the Carrara, 1318-1405* (Baltimore: Johns Hopkins University Press, 1998).

¹⁶⁸ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 2-8.

text that are unusable and impractical.¹⁶⁹ In light of this new contextual information, Broecke re-assesses Cennini's references to materials and methods (such as the preparation of drying oils and the use of linden and willow panels) that reflect northern practices, passages that may be connected to the technical findings associated with paintings originating in and around the Veneto (particularly those emerging from the Paduan workshop of Francisco Squarcione and the Bellini and Vivarini families).¹⁷⁰ Cennini's introduction of the oil technique is most poignant, for he infers that by this period much remained to be learned from the "Germans" regarding this particular medium; the decision to include this instruction suggests that the oil technique was already in practice in northern Italy by the late fourteenth-century and methods involving pre-treating drying oils using heat (as opposed to siccatives) were in fact known. Broecke proposes the possible scenario of Cennini being first introduced to the oil medium by French and German artists who were working in Padua at the time of his residence; in his text

¹⁶⁹ Ibid. As examples of recipes that can be classified as "unusable," Broecke includes several references to the preparation of pigments, making shell gold by grinding gold leaf with egg white, and the recommendation to throw oneself into a bed of wet plaster to create a full figural cast. Furthermore, Broecke states that while many of the recipes do contain practical information, Cennini repeatedly stresses the importance of completing an apprenticeship under the tutelage of a master painter, supporting the theory that the manual was not originally intended to be used as a workshop manual.

¹⁷⁰ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 6, 125; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 47-8. Ames-Lewis cites a contract dated 1437 in which a Giovanni da Ulma (likely Giovanni d'Alemagna of Germany) is asked to use oil paint to decorate the Chapel of S. Massimo in the palace of the Bishop of Padua. Broecke states that there were French and German artists working in Padua that may have introduced the oil technique to Cennini but that oil was not the default medium for Italian paintings even by the beginning of the sixteenth century. I disagree with the latter statement only since it is based on the scientific analysis of binding media obtained in years past, many of which require revisitation as technology has continued to evolve. See Chapter 4, Sections 4.3.1 and 4.3.2 for more information regarding technical studies of paintings associated with Padua, Venice, and the surrounding territories.

Cennini writes that he has been able to “find” oil that is perfectly suitable in Florence (implying that this was available for purchase ready-made), suggesting that the medium was available in and around Tuscany but still considered quite novel:

Chapter 89 – The way in which you work in oil on walls, on panel, on iron and wherever you like - Before I go any farther I want to teach you to work with oil on wall or panel, as the Germans are much given to do; and likewise on iron and stone. But we will discuss the walls first.

Chapter 91 – How you should make oil good for a binder and also for mordants, boiled over a fire – You ought to know how to make this oil because it is one of the useful things that you need to know, since it is used for both mordants and for lots of the other things. And so take 1 pound, or two or 3 or 4, of linseed oil and put it in a new pan; and if it is glazed, so much the better. Make a little oven and make a round hole that this pan fits into precisely so that the fire cannot come up over it, because the fire would love to come over, and you would risk the oil and even burning the house down. When you have made your oven, [light] a moderate fire, because the slower you bring it to the boil the better and more perfect it will be. And let it boil down to a half. And that is it. But to make mordants, when it has become half add an ounce of liquid varnish, which should be lovely and clear, for each pound of oil. And this same oil is good for mordants.

Chapter 92 – How you make a good and perfect oil cooked in the sun – When you have made this oil, which can be also cooked another way (and it is more perfect for painting, whereas for mordants the oil should only be from fire, that is, cooked): take your linseed oil and, in the summer, put it into a bronze or copper basin or a tub and when there is a Leo sun keep it in the sun; and if you keep it there until it becomes half it is absolutely perfect for painting. And know that in Florence I have found it as good and refined as it can be.

Chapter 94 - How you should work in oil on iron, on panel, or on stone - And work in the same way on iron, any stone, any panel, always sizing first; and likewise on glass, or wherever you want to work.¹⁷¹

¹⁷¹ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 3-10, 125-8; Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 47-8. Broecke indicates that Cennini likely left Padua by 1403 in response to the escalating political tension between the Carrara regime and Venetian officials. This again supports the notion that the text likely reflects painting techniques that were practiced by Italian painters during the latter half of the fourteenth century rather than the fifteenth century; however, many of the techniques presented in *Il Libro dell'Arte* do continue to be used by Italian painters throughout the Quattrocento. In addition, Cennini’s reference to

Eastlake may have been correct in his supposition that most early Quattrocento Italian painters, like Theophilus, were unaware of siccatives; Cennini's recipe makes no mention of adding lead or copper-based additives during the preparation of oil.¹⁷² On the other hand, remnants of an original oil-resin varnish on Jacopo di Cione's *San Pier Maggiore Altarpiece* (c. 1370-31) at the National Gallery London were found to contain trace amounts of red lead, presumably used as a drier.¹⁷³ Whether Jacopo was aware of red lead siccativ properties is unknown as pre-made oil-resin varnishes and mordants were likely available for purchase by this date. In Cennini's text, however, driers are mentioned in considerable detail in the recipe outlining the procedure for preparing mordants for gilding in which he describes a direct relationship between the amount of siccativ added to the number of days one should expect the mordant to dry.¹⁷⁴ Verdigris (a copper-based green) is also recommended as an oil glaze

“liquid varnish” infers that this particular material was probably available to him ready-made as he never provides a recipe for it in the text; Broecke points out that the Bolognese Manuscript includes a recipe that is based on a mixture of linseed oil and sandarac while another recipe calls for the addition of vermilion and red lead, likely to act as driers. This dismisses Eastlake's theory that it may possibly imply a “clear” and/or “light” state of the medium. In this instance it is unclear whether or not Cennino was unconsciously adding driers to his heat-bodied oil or not. Finally, Cennini's Chapter 92 was apparently left unfinished; Broecke considers this entire chapter to be somewhat grammatically awkward while his concluding statement relating to Florence is quite the opposite. See also Sir Charles Lock Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I (1847; repr., New York: Dover Publications, 2001), 228.

¹⁷² Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 70-1.

¹⁷³ David Bomford, et al., *Art in the Making: Italian Painting before 1400* (London: National Gallery London Publications, 1989), 182-5.

¹⁷⁴ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 197.

for metal leaf as well as red lake, a technique that had been used by artists in the north (and possibly parts of Italy) for over a century; these passages, however, are the only sections where Cennini specifically describes the process of mixing a pigment with drying oil.¹⁷⁵ Cennini also alludes to a “liquid varnish” as the most durable of all media; it is possible that this material is composed of hard resins combined with oils prepared using heat and/or siccatives, although Cennini fails to provide specific information regarding its exact nature.¹⁷⁶ In reviewing these specific recipes collected from *Il Libro*, it seems that Cennini wrote his treatise before most Italian artists had begun to incorporate oils prepared with siccatives into their painting process; these faster-drying oils would have been more attractive to a painter trained to use the quick-drying egg tempera medium:

Chapter 147 – ‘Item. Gild the ground; draw’ - Likewise, gild the ground, draw the design that you want on it. Lay in the grounds with verdigris in oil, shading some folds twice. Then apply it everywhere, evenly all over the ground and over the design.

Chapter 148 – ‘Item. Lay the drapery’ - Likewise, silver the clothing. Draw your drapery when you have burnished, which is always understood to be the way. Lay in the ground or motifs with vermilion bound in pure egg yolk. Then apply one or two layers of good quality lacca in oil over each design...

Chapter 164 – ‘A short section’ – A mordant is made which is perfect on walls, on panel, on glass, on iron and anywhere at all, which is made in the following way; you will take your oil which has been cooked on the fire or in the sun (cooked by the method that I showed you earlier) and mull a little lead white and verdigris with this oil. And when you have mulled it so that it is like water, add a little varnish to it and leave it to boil a little with everything together...

Chapter 165 – ‘How to control’ – If you want the mordant mentioned above to last for eight days before it is ready for gilding, do not add verdigris to it. If you want it to last 4 days, add a little verdigris to it. If you want the mordant to be good from one evening to the next, add a lot of verdigris to it

¹⁷⁵ Ibid, 180-81. See also Cyriel Stroo, “Tooled and painted gilding in pre-Eyckian panel painting,” *Zeitschrift für Kunsttechnologie and Konservierung* 26 (2001): 220-9.

¹⁷⁶ See Note 143.

and also a smidgeon of bole. And if you find that anyone censures you for the verdigris because it might end up tainting the gold, just say that, in my experience, the gold stays in good condition.

Chapter 233 - How to clean off the paint after you have made up a face – In the exercise of the profession, you will sometimes have to stain or paint on flesh, chiefly to paint the face of a man or woman. You may have your colours tempered with egg; or, for making up, with oil, or with liquid varnish, which is the strongest tempera of all.¹⁷⁷

Cennini's passage in Chapter 233 implies that painting in oils or oil-based media was more commonly practiced in certain circles, a statement that may have been influenced by his time in northern Italy. Aside from the chapters quoted above, the only instance where Cennini guides the reader in applying oil-bound paints can be found in his instructions for preparing *a secco* paints.¹⁷⁸ In comparison to the *Liber diversarum artium*, Cennini's *Il Libro* does not limit wall painters to pigmented lime washes and other aqueous-based *a secco* paints (such as egg tempera) indicating that by the late fourteenth century artists were using both drying oils and aqueous-based *a secco* paints (e.g. glue, egg) for murals, an observation that has been corroborated by technical studies of wall paintings dating to the fourteenth and fifteenth centuries:

Chapter 90 – In what way you should begin to work on walls in oil the wall in the way that you use for fresco except that, where you plaster little by little, here you should plaster everywhere, over all the area to be worked. Then draw your scene with charcoal and fix it either with ink or with verdaccio in a binder. Then get a little well-diluted glue. A still better binder is whole egg, beaten up in a bowl with fig milk and add a drinking glass of clear water to the egg. Then, either with a sponge or with a soft and quite blunt brush, whichever

¹⁷⁷ Broecke, *Cennino Cennini's 'Il Libro dell'Arte': A new English translation and commentary with Italian translation*, 180-1, 195-7, 248. There have been a handful of early Italian panel paintings that have been found to contain drying oil in glazes applied over metal leaf; see Chapter 4.2.1, Note 261.

¹⁷⁸ *Ibid*, 112-24, 126-130.

you prefer, apply one layer of it over the whole ground that you need to work on and leave it to dry for at least a day.

Chapter 93 – How you should mull pigments in oil and use them on walls – Go back to working up or grinding, colour by colour, as you did for work in fresco; except that where you worked them up with water you now work them up with this oil. And when you have got them worked up, that is, some of every colour, for all the colors will stand oil except lime white, get little lead or tin dishes into which to put these colours. And if you cannot find those, get glazed ones. And put in these ground-up colours; and put them into a little box to keep them clean. Then when you wish to make a drapery in three values, as I have told you, mark them out and set them in their places with minever brushes, working one color well into another, keeping the colours quite stiff. Then wait a day or so, and go back, and see how they are covered, and lay them in again as necessary. And do the same for flesh painting, and for doing any sort of work which you may care to carry out; and mountains, trees, and every other subject in the same way. Then have a plate of tin or lead which is one finger deep all around, like a lamp; and keep it half full of oil, and keep your brushes in it when idle, so that they will not dry up.¹⁷⁹

¹⁷⁹ Ibid, 126, 129-30; Clarke, *Mediaeval Painters' Materials and Techniques: The Montpellier Liber diversarum arcium (c.1200-1400)*, 143; Francesca Benetti, Guido Perra, Damiano Damiani, Andrea Atrei, and Nadia Marchettini, "ToF-SIMS characterization of proteinaceous binders in the wall painting 'Madonna and Child enthroned with Saints' by Ambrogio Lorenzetti in the St. Augustine Church (Siena, Italy), *International Journal of Mass Spectrometry* 392 (2015): 111-7, doi: 10.1016/j.ijms.2015.09.018; Gwenaëlle Gautier. "A Reliable Analytical Procedure for the Characterization and Identification of Proteinaceous Binding Media in Wall Paintings" (PhD diss., University of Pisa, 2006); Giovani Bottirolì, Antonietta Gallone, and Barbara Masala, "Analisi Microspettrofluorimetrica di Leganti Organici," in *GiOTTO nella Cappella Degli Scrovegni: Materiali per la Tecnica Pittorica. Studi e Ricerche dell'Istituto Centrale per il Restauro*, ed. Giuseppe Basile (Rome: Istituto poligrafico e Zecca dello Stato, 2005): 83-102; Maria Perla Colombini, Francesca Modugno, Marina Giacomelli, and Sandro Francesconi, "Characterisation of proteinaceous binders and drying oils in wall painting samples by gas chromatography-mass spectrometry," *Journal of Chromatography A* 846 (1999): 113-24, doi: 10.1002/jssc.200301625; Maria Perla Colombini, Alessio Ceccarini, and Alessia Carmignani, "Ion Chromatography Characterization of Polysaccharides in Ancient Wall Paintings," *Journal of Chromatography A* 968 (2002): 79-88, doi: S0021-9673(02)00950-0. See also Palazzo Medici-Riccardi, *Chapel of the Magi: Benozzo Gozzoli's Frescoes in the Palazzo Medici-Riccardi Florence*, Cristina Acidini Luchinat, ed. (London: Thames & Hudson, 1994) and Anna Maria Maetzke et al., "Progetto Piero della Francesca: il restauro della 'Leggenda della Vera Croce,'" *Kermes: la rivista del restauro* 14, (2001 Jan-Mar): 19-42. Recipes for a *secco* paints in the *Liber diversarum arcium* call for the use of glair (egg white), egg yolk, and fish glue. While some of the publications included above cite various scientific methods used to characterize the organic

Leon Battista Alberti's (1404-1472) writings dating to the mid-fifteenth century also suggest that painting in oil on walls was perhaps more common in Italy than painting in oil on panels.¹⁸⁰ Like Cennini, Alberti spent time in northern Italy, spending time as a schoolboy in Padua, continuing on to Bologna and eventually accompanying the papal court of Eugenius IV to Florence and Ferrara; by the time Alberti completed his first treatise on painting in 1435 (probably a few years following Cennini's death), he would have been familiar with oil paintings from the north.¹⁸¹ Alberti was well-traveled and educated, keeping close company with artists, humanists, and patrons of northern art such as the Este family and Pope Eugenius IV.¹⁸² While Alberti encouraged artists to use paint to depict golden objects rather than gold leaf in his *Della pittura* (a northern practice), he refrained from including details regarding particular techniques or materials; however, there is a brief passage on oil painting in Chapter Nine of his treatise on architecture (*Re De Aedificatoria*) completed in 1452.¹⁸³ Whether or

binders present on wall paintings, the precision of some of these methods is now being questioned and to some extent revisited; see Chapter 5.

¹⁸⁰ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48.

¹⁸¹ Ames-Lewis, 53; Leon Battista Alberti, *On Painting*, trans. John R. Spencer (New Haven: Yale University Press, 1966), 13-6; Monnas, *Merchants, Princes, and Painters: Silk Fabrics in Italian and Northern Paintings, 1300-1550*, 110. Alberti is also suspected to have accompanied Cardinal Niccolo Albergati to the Burgundian court in 1431. Note that the original version of Alberti's treatise was published as *De Pictura* in 1435 while the vulgate edition *Della Pittura* became available the following year.

¹⁸² Ames-Lewis, *Ibid.* Alberti is also suspected to have accompanied Cardinal Niccolo Albergati to the Burgundian court in 1431.

¹⁸³ *Ibid.*; Monnas, *Merchants, Princes, and Painters: Silk Fabrics in Italian and Northern Paintings, 1300-1550*, 110; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. II, 63-4. See also Leon Battista Alberti, *On the Art of Building in Ten Books*, trans. Joseph Rykwert, Neil Leach, and Robert Tavernor (Cambridge: MIT Press, 1991). Alberti states the following in his *Della pittura*: "There are painters who use too much

not Alberti was aware of Cennini's *Il Libro* is unknown, yet both texts confirm that by the mid-fifteenth century, it was not uncommon for Italian painters to use oil-based paints for the decoration of walls. Interestingly, Alberti describes the method as something novel, a technique that Cennino had already recorded after or during his time in Padua:

There is a new invention, in which all kinds of colors applied with linseed oil are proof against all effects of the atmosphere; provided the wall on which they are spread be dry and perfectly free of moisture [within]... ¹⁸⁴

Nearly a decade following Alberti's treatise on painting, Florentine artist Lorenzo Ghiberti (1378-1455) again mentioned the oil medium in his *Commentarii* (an incomplete manuscript begun around 1447) but in an entirely different context.¹⁸⁵ In the second book of his treatise, Ghiberti traced the evolution of Tuscan painting in the thirteenth and fourteenth centuries, crediting Giotto as one of the first great masters of painting.¹⁸⁶ To date none of Giotto's panel paintings have been found to contain oil; however, analysis of the *a secco* paints in the Scrovegni chapel suggest the possible presence of an oil-based medium in addition to aqueous-based paints.¹⁸⁷ By the latter half of the fifteenth century, the oil

gold in their pictures because they think it gives them majesty: I do not praise this...to represent the glitter of gold with plain colors brings the craftsman more admiration and praise.”

¹⁸⁴ Ibid. Note that there exist numerous renditions of the English translation which vary slight from one version to the next. The excerpt here is taken from Eastlake's own interpretation of the Latin text published in 1512.

¹⁸⁵ Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 48-9.

¹⁸⁶ Ritter von Julius Schlosser, trans., *Lorenzo Ghiberti's 'Denkwürdigkeiten (I commentarii)' zum ersten male nach der handschrift der Biblioteca nazionale in Florenz vollständig hrsg. und erläutert von Julius von Schlosser* (Berlin: Julius Bard, 1912), 35-7; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 46-7.

¹⁸⁷ Giovanni Bottiroli, Antonietta Gallone, and Barbara Masala, “Microspectrofluorometric analysis of organic binders,” in *Bolletino d'Art - The Scrovegni Chapel: Materials used in the*

technique had evidently earned a unique reputation and this technology was suddenly claimed by the Florentines themselves. By associating the oil medium with Giotto, Ghiberti elevated the status of oil painting, alluding to a general acceptance and familiarity of the technique amongst certain circles of Italian painters.

With Alberti and Ghiberti's treatises came the rise of humanism in art criticism, generating an entirely new approach to evaluating, documenting, and criticizing traditional easel painting. Many records from humanist writers of the Renaissance offer anecdotal accounts throughout this transitional period in Italian art, documenting a growing respect for the oil technique among Italian patrons and painters. Remarking on his travels to the city of Ferrara in 1449, the historian Ciriaco d'Ancona (1391- 1453/55) described the Sieneese painter Angelo Maccagnino as "the distinguish imitator" of northern oil paintings.¹⁸⁸ Ciriaco remarked on paintings by Rogier van der Weyden in Ferrara, particularly the painter's ability to "paint gold like real gold" as opposed to using gold leaf, almost paraphrasing Alberti's sentiment on the subject recorded in his *Della pittura* a few years earlier.¹⁸⁹ Ciriaco and the humanist scholar Bartolomeo Facio (c. 1410–1457) were equally impressed with Leonello d'Este's collection of northern works in Ferrara; Facio expressed his admiration in his *De Viris Illustribus* of 1456, declaring Jan van Eyck to be "the leading painter of our time," along

painting technique – Study and Research by the ICR, ed. Giuseppe Basile (Rome: Istituto poligrafico e zecca dello stato, 2005), 83-104.

¹⁸⁸ Lorne Campbell, "Cosmè Tura and Netherlandish Art," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Steven Campbell (Boston: Isabella Stewart Gardner Museum, 2002), 85; Carol M. Richardson, Kim W. Woods, and Michael W. Franklin, eds., *Renaissance Art Reconsidered* (Chicester: John Wiley and Sons, Ltd., 2007), 186; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50, 57. See Chapter 4.3.3 for more information on Ferrarese painters of the Renaissance.

¹⁸⁹ Richardson, Woods, and Franklin, *Renaissance Art Reconsidered*, 186 (note 168).

with Rogier van der Weyden, Gentile da Fabriano, and Pisanello.¹⁹⁰ Ciriaco's letters and Facio's treatise mark a significant turning point for Italian patrons and painters: the oil technique was no longer assigned to a group of nameless "Germans" but to notable northern artists with established and successful workshops. Further promoting his humanist virtues, Facio attributed van Eyck's skill as a painter to his knowledge of classical literature and mathematics:

Jan of Gaul has been judged the leading painter of our time. He was not unlettered, particularly in geometry and such arts as contribute to the enrichment of painting, and he is thought for this reason to have discovered many things about the properties of colors recorded by the ancients and learned by him from reading of Pliny and other authors.¹⁹¹

Although these written accounts by Ciriaco and Facio are considered to be the earliest Italian descriptions of Netherlandish paintings, they do not include direct references to the oil medium.¹⁹² A Florentine architect by the name of Antonio Averlino or "Filarete" (c. 1400-1469), has been credited as the first Italian to record a detailed description of painting in

¹⁹⁰ Ibid., 186-9; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 49-50, 53, 55-7; Michael Baxandall, "Bartholomaeus Facius on Painting: A Fifteenth-century Manuscript of *De viris illustribus*," *Journal of the Warburg & Courtauld Institutes* 27 (1964): 90-107, doi: 10.2307/750513; Oskar Batschmann, *Giovanni Bellini* (London: Reaktion Books, 2008), 55.

¹⁹¹ Richardson, Woods, and Franklin, *Renaissance Art Reconsidered*, 188; Baxandall, "Bartholomaeus Facius on Painting: A Fifteenth-century Manuscript of *De viris illustribus*," 102. Bartolomeo Facio writes of Jan van Eyck's paintings in the collection of the Duke Alfonso of Aragon in Naples as well as paintings owned by the Lomellini family in Genoa. See Chapter 2.3 for more information regarding northern paintings in Italian collections during the Quattrocento.

¹⁹² Richardson, Woods, and Franklin, *Renaissance Art Reconsidered*, 186-96; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 49-50, 53, 55-7. While Ciriaco and Facio do not mention the oil technique, the medium is used as a descriptor for northern paintings in the early sixteenth-century writings of Marcantonio Michiel and Pietro Summonte.

oil on panel (as opposed to walls); Eastlake has pointed out that this particular passage in Filarete's *Trattato di architettura* (completed sometime around 1464) is the first of its kind to be written in Italy, a passage that surpasses Alberti's description of the oil medium that had been published just a few years prior:

You can mix all these colors in oil but this is another practice and another mode; it is beautiful for anyone who knows how to do it [...].

Tell me how one works in oil. What oil is it?

It is linseed oil.

Isn't it very dark?

Yes, but it can be lightened. I do not know how except that it is put in an amoretto. Let it stand for a good time and it will clarify. It is true that they say there is another way to do it quicker. Let us leave this.

How one works. First [one works] on the gessoed panel or better the wall where the lime must be well dried. First the wood [should be] gessoed and well polished and then you give it a coat of glue. Then [give it] a coat of color ground in oil if it is white [biacca: lead white in oil] and good or if it is any other color. It is not important what color it is [...]. When you have given a coat of white to the forms of all the things you want to do on this [panel], [go over it] with the colors that you want to use for shadows and then with a light coat of the color that you want to clothe them in. When your shadows are dry, you can return, heightening them with white and other colors that go well with what you have given your figures. You will do this with everything you paint. This same method should be observed on the [panel] and also the wall.

If you have to do a thing that should appear to be of gold, silver, or other metal, choose suitable colors that will appear like [metal] even though they are not.¹⁹³

¹⁹³ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48-50, 54; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vol. I, 64-5; Wolfgang Stechow, *Northern Renaissance Art, 1400-1600: Sources and Documents* (New Jersey: Prentice-Hall, Inc., 1966), 145; See also Filarete (Antonio Averlino), *Trattato d'architettura*, vols. I & II, trans. Anna Maria Finoli and Liliana Grassi (Milan: Edizioni Il Polifilo, 1972). This passage can only be found in the Magliabechian copy (completed in 1464) of Filarete's treatise and not in the Palatine copy. Filarete's *Trattato di architettura* was the first treatise on architecture in the Renaissance that was written in Italian instead of Latin.

In this single passage Filarete revealed that Italian artists were not only well aware of oil painting by the mid-fifteenth century but also continued to view the technique as one that was worthy of mastering. Filarete stated that the sun is instrumental in the preparation of the oil medium, a procedure that he associated only with clarification; however, his description reveals that he was unaware (as was Cennini) that the heat from the sun would also create an oil that dries slightly faster than if it were simply cold-pressed.¹⁹⁴ Filarete admitted that there was “another way to do it quicker,” and it is entirely possible that he was unknowingly referencing the process of heating the oil in the presence of siccatives. While technical studies have shown that Italian painters were using the oil medium by the early fifteenth century, it seems that the “secret” of the oil medium had as much to do with its preparation as it did its application, further adding to the rarified and exotic appeal of northern oil paintings.¹⁹⁵ In his writings to the Duke Francesco Sforza of Milan, Filarete recommended two northern artists whom he considered worthy of decorating the ducal palace (Rogier van der Weyden and a Frenchman named “Grachetto” who has been identified by some as Jean Fouquet) a recommendation that likely compelled the Duke to send his court painter Zanetto Bugatto to train directly under Rogier himself.¹⁹⁶ Filarete’s account of Grachetto’s portraits reveals his

¹⁹⁴ Joyce Townsend and Erma Hermens, “Binding Media,” in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 209-11. A number of technical studies and reconstructions have found that ultraviolet light from the sun effectively bleaches out the yellowed components of the oil medium both during preparation and after initial curing.

¹⁹⁵ See Chapter 4 for an overview of technical studies focusing on Quattrocento paintings.

¹⁹⁶ Stechow, *Northern Renaissance Art, 1400-1600: Sources and Documents*, 145-6; Luke Syson, “Zanetto Bugatto, Court Portraitist in Sforza Milan,” *The Burlington Magazine* 138 (1996): 300, accessed November 12, 2015, <http://www.jstor.org/stable/886901>; Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 48-50; Marina Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe* (Cambridge: Cambridge University Press, 2012), 194-5. Filarete does mention Jan van Eyck and praises him for his

admiration for oil paintings and their naturalistic appearance, describing the sitters as appearing “to be really alive,” a sentiment that is again echoed in the humanist’s statement regarding northern painters and their ability to paint with colors:

In Germany they work well in this method, especially Master Giovanni of Bruges and Master Rogier who employed these oil colors excellently.¹⁹⁷

By the second half of the fifteenth century, writers became increasingly entranced with the artistic ability to render objects and figures in a realistic manner. From 1450 on, the term *colore* (or *colorito*, *colorire*) was often used to describe the application of colors and the depiction of objects in their natural form, a skill that the Italians closely associated with the Netherlandish technique of oil painting.¹⁹⁸ Art historian Paula Nuttal has identified this term in the writings of Filarete, Facio, Vespasiano da Bisticci (1421–1498), and Giovanni Santi (c. 1435–1494), a term that she argues was considered of equal importance to the notion of *disegno*, the ability to create a composition in both the intellectual and artistic sense.¹⁹⁹ This

mastery of the medium but as van Eyck had died in 1441, Filarete is not able include him in his recommendation to the Duke. During his service in Milan between 1461 and 1464, Filarete writes the following regarding the ducal palace: If you would like, we could look beyond the Alps to see if there are any good ones. There was a very good master called Giovanni da Bruggia. He too is dead. I think there is a master Ruggieri who is very good. There is also a Frenchman called Grachetto; if he is alive he is a good master, especially for doing portraits from life. He did a portrait of Pope Eugene and two of his retainers that seemed to be really alive. He painted this on linen and it was placed in the sacristy of the Minerva. I say this because he painted it in my time.

¹⁹⁷ Ibid.; Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Art Press, 2004), 34; Filarete (Antonio Averlino), *Trattato d’architettura*, vol. II, 668.

¹⁹⁸ Nuttal, *From Flanders to Florence*, 35.

¹⁹⁹ Ibid. Nuttal further states that this quickly changed with the arrival of the sixteenth century as the terms were considered “antithetical” to one another.

concept is echoed in Vespasiano's text dating to 1473, which was conceived in a court that had already managed to recruit a northern artist:

[Frederico da Montefeltro] was most knowledgeable about painting, and not finding masters to his taste in Italy, who knew how to paint in oil on panel, he sent to Flanders to find a distinguished master, and had him brought to Urbino.²⁰⁰

By 1472 Justus of Ghent was recorded working for Frederico, decorating the interior of the Duke's studiolo with a series of portraits depicting a series of *Uomini Illustri* or Illustrious Men.²⁰¹ Frederico's attraction to the northern aesthetic may have also impacted his court painter, Giovanni Santi, who made a distinct connection between northern painters and the concept of *colorire* in his *Cronaca rimata* of 1480:

At Bruges, among the others most praised
The great Jan, also his pupil Roger,
And many gifted with great excellence,
So that in this high art and mystery
They have been so excellent in coloring
That often they have even outdone the life.²⁰²

²⁰⁰ Ibid., 34; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50; Vespasiano da Bisticci, *Vite di uomini illustri del secolo XV*, trans. Paolo d'Ancona and Erhard Aeschliman (Milan: Hoepli, 1951), 209.

²⁰¹ Michel Menu et al. "Examination of the Uomini Illustri: Looking for the Origins of the portraits in the Studiolo of the Ducal Palace of Urbino. Part 1," in *Studying Old Master Paintings: Technology and Practice*, ed. Marika Spring (London: Archetype Publications and the National Gallery, 2011), 37-43; June Osborne, *Urbino: The Story of a Renaissance City*, (Chicago: University of Chicago Press, 2003), 104-8; Sir William Martin Conway, *The Van Eycks and their Followers* (London: E.P. Dutton, 1921), 174. Justus of Ghent became a recognized master painter by the Antwerp Guild of St. Luke in 1460 and eventually relocated to the city of Ghent some four years later.

²⁰² Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 56; Nuttal, *From Flanders to Florence*, 34; Paolo Torresan, *Il Dipingere di Fiandra: La pittura neerlandese nella letteratura artistica italiana del Quattro e Cinquecento* (Modena: S.T.E.M. Mucchi, 1981), 29.

It is evident from Santi's writings and those of his contemporaries that Netherlandish paintings were highly praised for their realistic portrayal of landscapes, objects, and figures, an aesthetic achieved through the masterful preparation and handling of the oil medium. These written accounts reflect the challenges that faced fifteenth-century Italian painters, particularly for those who were less willing to deviate from the traditional tempera technique. In reviewing these texts and treatises, a major component behind the "secret" of oil painting seems to have been tied to preparation methods involving siccatives as well as the successful application of heat. If Quattrocento painters had been more familiar with such processes, it is possible that the oil medium would have been adopted more rapidly by painters working south of the Alps. Written sources suggest a general unfamiliarity with the properties of siccatives, a technology that would have allowed artists to exercise more control over the long drying time associated with the oil medium, a skill that was undoubtedly mastered by the sixteenth century.

3.3. Leonardo, Vasari, and Beyond

The challenges associated with the oil medium continued to generate legendary tales and myths well beyond the 1400s, although written accounts from the fifteenth and sixteenth centuries offer occasional insight into the evolution of oil painting in Quattrocento Italy. Scarcely any workshop "secrets" relating to the oil technique have been located (or translated) in records dating to the height of the Italian Renaissance and the years that followed. It is possible that as Italian painters became increasingly familiar with the medium, daily workshop practices involving drying oils may have been considered too practical to warrant extensive documentation. By the mid-sixteenth century, Italian painters had fully transitioned

away from the traditional egg tempera technique and seem to have been less inclined to record or even summarize their daily experiences with binding media. Conversely, the years following the Renaissance produced written accounts that contain important social viewpoints regarding the evolution of Quattrocento painting, with anecdotal information that can occasionally shed light on workshop practice.

Leonardo da Vinci's records are perhaps the most explicit in their detail relating to the preparation of oil, providing a glimpse of the technology that may have been practiced in Italy by the end of the fifteenth century. The survival of Leonardo da Vinci's *Codex Atlanticus* (c. 1478-1519) has provided scholars with some insight into the preparation of drying (and non-drying) oils that may have been used by Leonardo's immediate predecessors.²⁰³ Of particular interest is Leonardo's lengthy description concerning walnut oil, a material that has since been identified in Leonardo's *Madonna of the Carnation* (1478-80; Figure 4.26) in Munich as well as *The Virgin of the Rocks* (1491/2 and 1506/8; Figure 4.27) at the National Gallery in London:

Since walnuts are enveloped in a thin rind, which partakes of the nature of . . . , if you do not remove it when you make the oil from them, this skin tinges the oil and rises to the surface of the painting, and this is what makes it change.²⁰⁴

²⁰³ Jean Paul Richter, *The Literary Works of Leonardo da Vinci*, vol. 1 (London: Sampson Low, Marston, Searle & Rivington, 1883), 319-22, <http://warburg.sas.ac.uk/pdf/cnm22b2242052v1.pdf>; Leonardo writes about the preparation of other non-drying oils like mustard seed oil; it is possible that Leonardo may have inadvertently incorporated small amounts of non-drying oil into his linseed oil medium, particularly if he was using the same press that he refers to in his notes.

²⁰⁴ Ibid, 320; Larry Keith, Ashok Roy, Rachel Morrison, and Peter Scade, "Leonardo da Vinci's *Virgin of the Rocks*: Technique and the Context of Restoration," *National Gallery Technical Bulletin* 32 (2011): 48; Johann Koller and Ursula Baumer, "'Er [...] erprobte die seltsamsten methoden, um öle zum malen [...] zu finden.' Leonardos rolle in der frühen italienschen ölemaleri" in *Leonardo da Vinci, Die Madonna mit der Nelke*, eds. Cornelia Syre, Jan Schmidt, and Heike Stege (Munich: Alte Pinakothek and Schirmer/Mosel, 2006), 155-74.

This may be one of the first references to walnut oil by an Italian painter as earlier recipes cite the use of linseed oil or fail to specify the source of the oil altogether. Leonardo undoubtedly used linseed as well; he mentioned the oil on several occasions in his *Codex Atlanticus* and traces of linseed oil were identified in both London's *The Virgin of the Rocks* and *Madonna of the Carnation*.²⁰⁵ Like Cennini and Filarete before him, Leonardo referenced the use of heat in the preparation of his oils; however, it is not entirely clear whether Leonardo fully comprehended the reason behind using heat to prepare walnut and/or linseed oil. He recommended heating walnut oil in the presence of camphor if one wanted an "oil that is good and not too thick (sic)" emphasizing that this would create an oil that "will never harden," an unlikely outcome based on what is now known regarding the oil medium; technical studies and reconstructions have shown that intense amounts of heat typically impart a certain amount of viscosity to cold-pressed oils in addition to creating a faster drying medium.²⁰⁶ Leonardo also cited the use of boiled oil in another passage describing the preparation of panels for oil painting:

Note that linseed oil was also identified in the *Virgin of the Rocks*. See Chapter 4 for a more in-depth discussion of these analytical findings and Chapter 5 for more information relating to the problems associated with the characterization of drying oils.

²⁰⁵ Ibid; Richter, *The Literary Works of Leonardo da Vinci*, vol. 1, 319-22. Some of Leonardo's works possess disfiguring wrinkles and cracks; technical studies have now found that defects in an oil-based paint film can be caused by several factors including the use of certain pigments, the purity of the oil, film thickness, and/or insufficient dry-time between successive paint layers. Interestingly, Keith et al. have identified a Cassel earth-type pigment in the underlayers of the *Virgin of the Rocks*, a pigment that dramatically slows the drying rate of oils which can lead to pronounced drying cracks.

²⁰⁶ Richter, *The Literary Works of Leonardo da Vinci*, vol. 1, 321. Further research is needed to confirm whether camphor would prevent walnut oil from drying; however, the chemical nature of camphor suggests that it would volatilize almost immediately in the presence of heat. It is impossible to know how frequently Leonardo would administer heat in his preparation of walnut and/or linseed oil, yet he intimates some concern over this process with his statement that "fire or heat by its nature has the power to make them [oils] acquire color."

The panel should be cypress or pear or service-tree or walnut. You must coat it over with mastic and turpentine twice distilled and white or, if you like, lime, and put it in a frame so that it may expand and shrink according to its moisture and dryness. Then give it [a coat] of aqua vitae in which you have dissolved arsenic or [corrosive] sublimate, 2 or 3 times. Then apply boiled linseed oil in such a way as that it may penetrate every part, and before it is cold rub it well with a cloth to dry it. Over this apply liquid varnish and white with a stick, then wash it with urine when it is dry, and dry it again. Then pounce and outline your drawing finely and over it lay a priming of 30 parts of verdigris with one of verdigris with two of yellow.²⁰⁷

In surprising contrast to his detailed recipes found in other sections of the *Codex*, Leonardo did not include a description relating to the preparation of linseed oil using heat or the sun, suggesting that this process may have been considered standard practice by the mid to late-fifteenth century. Leonardo also specified the use of verdigris, a pigment that would have undoubtedly helped to quicken the drying time of the priming layer; however, the painter failed to disclose the reason behind this sudden stipulation for the incorporation of the copper-green pigment.²⁰⁸ This omission seems to suggest that Leonardo was unaware of its siccativ properties, simply repeating a technique based on knowledge that he may have acquired during his time in northern Italy (this section of the *Codex* was likely written after his arrival in Milan in 1482). Furthermore, while Leonardo's ambiguous reference to the use of "white" could be interpreted to mean a number of pigments, technical studies of Leonardo's paintings have identified the presence of a lead white-containing *imprimatura* (oil-bound) atop a gesso

²⁰⁷ Ibid., 319.

²⁰⁸ Keith et al., "Leonardo da Vinci's *Virgin of the Rocks*: Technique and the Context of Restoration," 43-7; Koller and Baumer, "'Er [...] erprobte die seltsamsten methoden, um öle zum malen [...] zu finden.' Leonardos rolle in der frühen italienschen ölemaleri," 162-7. Cross-sectional samples taken from both the *The Virgin of the Rocks* in London and the *Madonna of the Carnation* have identified a dark, translucent brown layer atop a lead-white containing *imprimatura* layer(s) rather than a copper-containing layer.

ground (calcium sulphate and animal glue).²⁰⁹ Both Filarete and Leonardo mentioned the application of glue or oil to gessoed panels (presumably to cut the absorbency) as well as the use of pigmented *imprimaturas*. Unpigmented isolation layers containing either glue or oil/oil-resin in addition to pigmented *imprimaturas* have been found on Italian paintings dating from the fourteenth to the sixteenth centuries, a technique that was likely learned from northern oil painters who had been applying such preparatory layers to their panels since the 1200s.²¹⁰ Similar to Filarete's experience in Milan, Leonardo would have immediately learned of his Milanese patron's interest in painters who were capable of emulating Netherlandish oil paintings and may have even encountered foreign artisans working in the Sforza court.²¹¹ Early written sources indicate that northern painters were more familiar with the technologies behind heat-treating oils as well as the incorporation of siccatives by the beginning of the fifteenth-century, technologies that were likely to have reached artists working in northern Italy before spreading to Florence, Rome, and the southern territories.²¹² Although Cennini described the drying capabilities of verdigris relating to oil mordants, Leonardo's recipe appears to be one of the earliest Italian references that outlines the

²⁰⁹ Ibid. The unfinished *Adoration of the Magi*, the *The Virgin of the Rocks* in London, and the *Madonna of the Carnation*, and all have gesso grounds, while the latter two contain lead-white-containing *imprimatura* layers.

²¹⁰ Maartje Stols-Witlox, "Grounds, 1400-1900," in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 164-5. See also Rolf E. Straub, "Tafel und Tuchleinmaleri des Mittelalters" in *Reclam's Handbuch der kunstlerischen Techniken*, vol. 1, eds. Hermann Kühn, Hein Roosen-Runge, Rolf E. Straub and Manfred Koller (Stuttgart: Philipp Reclam, 1984), 166-8.

²¹¹ See Chapter 2, section 2.3.

²¹² The works of Colantonio and Antonello da Messina are clearly exceptions in this case; see Chapter 4, section 4.1.

incorporation of driers in oil painting. While Leonardo and his contemporaries may not have understood the chemical properties of these materials or even the reason behind using heat-treated oils, excerpts from the *Codex Atlanticus* suggest that such practices were in place by the latter half of the fifteenth-century, particularly throughout the northern Italian territories.

Leonardo did not mention any northern painters such as Jan van Eyck or Rogier van der Weyden in his passages relating to the preparation of drying oils and oil-varnishes, a curious omission that is not repeated in later written accounts of the sixteenth century. Leonardo's acquaintance, the artist and writer Giovanni Paolo Lomazzo (1538-1592), even mentioned Jan van Eyck in his *Trattato dell' arte della pittura, scultura et architettura* of 1584 that likely contains a reference to Leonardo's use of solvents (with his reference to alembics):

Leonardo has colored almost all his works in oil, a manner of coloring discovered first by Jan van Eyck, since the ancients certainly did not know about it. However, we read that the great Protogenes of Caunus covered one of his paintings four times, so that if one layer fell off, there would still be another. Apelles did the same thing with his very famous *Venus*, which lasted until the time of Augustus and was then conserved by Nero, worm-eaten as it was. Leaving aside the ancients and speaking of the modern period, there was, similarly, paintings at the time of Leonardo colored in tempera. And I had two paintings colored like this, one by Mantegna and the other by Bramante; they were covered with a kind of viscous liquid that I cleaned off, restoring them to look as if they had just been painted. Now was the one who abandoned the use of tempera and turned to oils, usually distilling them with alembics. This was the reason why almost all his works became detached from the wall, as can be seen, among others, in the marvelous *Battle* for the Council Hall of Florence and in *The Last Supper* for Santa Maria della Grazie of Milan; both were ruined because of the preparation he applied underneath.²¹³

²¹³ Giovanni Paolo Lomazzo, *Idea of the Temple of Painting*, trans. Jean Julia Chai (Pittsburgh: Pennsylvania State University Press, 2013), 84; Theophilus Presbyter, *An Essay Upon Various Arts in Three Books by Theophilus called also Rugerus Forming an Encyclopedia of Christian Art of the Eleventh Century*, trans. Robert Hendrie (London: John Murray, Albemarle Street, 1847), xxxi. It should be noted that Lomazzo conflated the use of alembics or stills with the preparation of drying oils; in fact, only solvents were refined using these instruments. On the other hand, his reference to alembics is a strong indication that solvents

Throughout the first half of Leonardo's career, Italian writers continued to associate the "secret" of the oil medium with Netherlandish painting techniques so Leonardo's failure to acknowledge the origin of the technology may reflect a shift in attitude towards the northern aesthetic. Lomazzo praised fresco painting above all other techniques, stating the oil painting was "really suited for effeminate youths."²¹⁴ Michelangelo's statement, found in Francisco de Hollanda's *Da pintura antiga* (c. 1541-8), underhandedly dismissed these early oil painters, describing northern paintings as objects that attracted those with "no sense of true harmony:"

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Flemish painting [...] will, generally speaking, Signora, please the devout better than any painting of Italy, which will never cause him to shed a tear, whereas that of Flanders will cause him to shed many; and this not owing to the vigor and quality of the painting but because of the goodness of the devout person. It will appeal to the women, especially the very old and the very young, and also to monks and nuns and to certain noblemen who have no true sense of harmony.²¹⁶

It is difficult to confirm whether Hollanda's treatise accurately reflects Michelangelo's sentiments regarding northern works.²¹⁷ Some scholars believe that this statement is a fair representation of the artist's disdain for art produced outside of Italy; however, others have

were being used by oil painters during the age of Leonardo if not before. In addition, the "viscous liquid" which Lomazzo removed from his tempera paintings was most likely an oil-resin varnish, again an testament to the early use of oil as a surface coating in fifteenth-century Italy.

²¹⁴ Lomazzo, *Idea of the Temple of Painting*, 104.

²¹⁵ Laura Camille Agoston, "Male/Female, Italy/Flanders, Michelangelo/Vittoria Colonna," *Renaissance Quarterly* 58 (2005): 1175-1219.

²¹⁶ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 56.

²¹⁷ Agoston, "Male/Female, Italy/Flanders, Michelangelo/Vittoria Colonna," 1188.

postulated that Hollanda used Michelangelo (along with other notable scholars, artists, and poets) as a mouthpiece to elevate the status of his text as well as Hollanda's own Italian training.²¹⁸ Michelangelo's denigration of Flemish painting is based on its emotional appeal, the same characteristic that he later describes as an essential component of idealized sacred painting, artwork that is required to "move mortals to tears and devotion."²¹⁹ Scholar Laura Camille Agoston has also revealed curious discrepancies regarding Michelangelo's supposed rejection of Flemish painting, including his inspired and faithful copy of Martin Schongauer's *Temptation of St. Anthony* and his relationship with Flemish patrons.²²⁰ Hollanda's treatise was written with the intention of appealing to his own patrons upon his return to Portugal, so the dialogues summarized in *Da pintura antiga* may not accurately reflect the demands of the Italian marketplace or even workshop practice.

Throughout the course of Michelangelo's career, it is possible that the artist eventually came to feel that his own paintings (of which only a handful survive) surpassed those generated by northern painters, a sentiment that was further intimated in Giorgio Vasari's biography of the artist in *The Lives of the Painters, Sculptors and Architects*.²²¹ Michelangelo and Vasari shared a biased preference for Italian art. Vasari credited northern painters for their "beautiful invention" in the introduction to his *Lives* (1550); however, he quickly followed this historical milestone with subsequent descriptions of Italian painters who he felt had superseded the abilities of early proponents of the oil technique:

²¹⁸ Ibid; Robert J. Clements, "The Authenticity of de Hollanda's Dialogos em Roma," *PMLA* 61 (1946): 1018-28.

²¹⁹ Agoston, "Male/Female, Italy/Flanders, Michelangelo/Vittoria Colonna," 1192.

²²⁰ Ibid, 1195, 1198.

²²¹ See Giorgio Vasari, *The Lives of the Painters, Sculptors and Architects*, ed. William Gaunt (London & New York: Everyman's Library, J. M. Dent and E. P. Dutton, 1963).

This art was afterwards brought into Italy by Antonello da Messina, who spent many years in Flanders, and when he returned to this side of the mountains, he took up his abode in Venice, and there taught the art to some friends. One of these was Domenico Veneziano, who brought it afterwards to Florence, where he painted in oil the chapel of the Portinari in Santa Maria Nuova. Here Andrea del Castagno learned the art and taught it to other masters, among whom it was amplified and went on gaining its importance till the time of Piero Perugino, of Leonardo da Vinci and of Raffaello da Urbino, so much so that it has now attained to that beauty which thanks to these masters our artists have achieved. This manner of painting kindles the pigments and nothing else is needed save diligence and devotion, because the oil in itself softens and sweetens the colors and renders them more delicate and more easily blended than do the other mediums. While the work is wet the colors readily mix and unite one with the other; in short, by this method the artists impart wonderful grace and vivacity and vigor to their figures, so much so that these often seem to us in relief and ready to issue forth from the panel, especially when they are carried out in good drawing with invention and a beautiful style.²²²

The only non-Florentine painter mentioned in connection with the early use of the oil medium is the Neapolitan painter Antonello da Messina; Vasari credits Antonello for being solely responsible for the dissemination of the oil medium in Italy. Vasari's account detailing the spread of the oil technique was questioned as early as 1563 by another Florentine, the Italian monk, philosopher, and art collector Vincenzo Borghini. As Borghini apparently

²²² Giorgio Vasari, *On Technique*, trans. Louisa S. Maclehorse, ed. G. Baldwin Brown (New York: Dover Publications, 1960), 228-30. In his Chapter VII entitled "Oil Painting, its Discovery and Early History," Vasari introduces this section with the following: A most beautiful invention and a great convenience to the art of Painting, was the discovery of coloring in oil. The first inventor of it was Jan of Bruges in Flanders, who sent the panel to Naples to King Alfonso, and to the Duke of Urbino, Frederico II, the paintings for his bathroom. He made also a San Geronimo, that Lorenzo de Medici possessed, and many other estimable things. Then Roger of Bruges his disciple followed him; and Ausse (Hans) disciple of Roger, who painted for the Portinari at Santa maria Nuova in Florence a small picture which is to-day in Duke Cosimo's possession. From his hand also comes the picture at Careggi, a villa outside of Florence belonging to the most illustrious house of the Medici. There were likewise among the first painters in oil Lodovico da Luano and Pietro Crista, and master Martin and Justus of Ghent who painted the panel of the communion of the Duke of Urbino and other pictures; and Hugo of Antwerp who was the author of the picture at Santa Maria Nuova in Florence.

owned a copy of Cennini's *Il Libro dell'Arte*, his reaction to Vasari's first edition of the treatise (written in 1550) included a suggestion to review Cennini's description of the oil technique:

I draw your attention to the fact that he [Cennini] mentions oil painting, and that, since it is so early as far as chronology goes, it must have appeared before Antonello da Messina.²²³

Vasari did not heed his colleague's advice; subsequent to his correspondence with Borghini he produced a revised edition of his treatise in 1568 and made no corrections to his passages relating to the evolution of oil painting in Italy. Rather than depicting van Eyck as a man well versed in classical studies, mathematics, and other popular humanistic subjects, Vasari focused instead on Jan van Eyck's familiarity with alchemy and his reticence to share the "secret" behind his discoveries purposefully omitting any reference to Cennini's earlier writings:

Now, while matters stood thus, it came to pass that, while working in Flanders, Johann of Bruges, a painter much esteemed in those parts by reason of the great mastery that he had acquired in his profession, set himself to make trial of various sorts of colors, and, as one who took delight in alchemy, to prepare many kinds of oil for making varnishes and other things dear to men of inventive brain, as he was. Now, on one occasion, having taken very great pains with the painting of a panel, and having brought it to completion with much diligence, he gave it the varnish and put it to dry in the sun, as was the custom. But, either because the heat was too violent, or perchance because the wood was badly joined together or not seasoned well enough, the said panel opened out at the joinings in a ruinous fashion. Whereupon Johann, seeing the harm that the heat of the sun had done to it, determined to bring it about that the sun should never again do such great damage to his works. And so, being disgusted no less with his varnish than with working in distemper, he began to

²²³ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 53; Lara Broecke, e-mail message to author, 4 January, 2016. Frances Ames-Lewis suggests that Borghini may have received a copy of Cennini's manuscript directly from Cennini but Lara Broecke feels that this information is in need of further research and confirmation.

look for a method of making a varnish that should dry in the shade, without putting his pictures in the sun. Wherefore, after he had made many experiments with substances both pure and mixed together, he found at length that linseed oil and oil of nuts dried more readily than all the others that he had tried. These, then, boiled together with other mixtures of his, gave him that varnish that he--nay, all the painters of the world--had long desired. Afterwards, having made experiments with many other substances, he saw that mixing the colors with those oils gave them a very solid consistency, not only securing the work, when dried, from all danger from water, but also making the color so brilliant as to give it lustre by itself without varnish; and what appeared most marvelous to him was this, that it could be blended infinitely better than distemper. Rejoicing greatly over such a discovery, as was only reasonable, Johann made a beginning with many works and filled all those parts with them, with incredible pleasure for others and very great profit for himself; and, assisted by experience from day to day, he kept on ever making greater and better works. The fame of this invention soon spread not only through Flanders, but to Italy and many other parts of the world, and great desire was aroused in other artists to know how he brought his works to such perfection. And seeing his pictures, and not knowing how they were done, finally they were obliged to give him great praise, while at the same time they envied him with a virtuous envy, especially because for a time he would not let any one see him work, or teach any one his secret.²²⁴

Vasari's description can be considered a commentary on the primary challenge that faced fifteenth and sixteenth-century Italian painters who attempted to master the oil technique, namely the incredibly long drying time of the medium itself. It seems more likely that this passage refers to technology learned by Vasari's predecessors or even pre-conceived notions relating to the medium that had evolved over various generations of Italian scholars and artisans.²²⁵ In addition, since Vasari portrayed van Eyck as an enviable painter who guarded his "secret" from his competitors, it can be deduced that this knowledge continued to be highly sought by Italian painters and collectors even in Vasari's lifetime. In his section on

²²⁴ Vasari, *On Technique*, 226-30.

²²⁵ Nuttal, *From Flanders to Florence*, 161. Refer to sections 3.1 and 3.2 of this chapter for earlier recipes and documents relating to this evolution of the oil technology in Italy.

egg tempera painting Vasari stated that most Italian painters had transitioned away from the traditional medium, a conversion that appears to have been facilitated through newly acquired knowledge that allowed for more control over the slow-drying medium.²²⁶ By Vasari's time the technology associated with siccatives as well as the issue of yellowing was understood by most Italian painters; both topics are mentioned in his subsequent section entitled "How to Prime the Panel or Canvas":

When the artist wishes to begin, that is, after he has laid the gesso on the panels or framed canvases and smoothed it, he spreads over this with a sponge four or five coats of the smoothest size, and proceeds to grind the colors with walnut or linseed oil, though walnut oil is better because it yellows less with time. When they are ground with these oils, which is their tempera (medium), nothing else is needed so far as the colors are concerned, but to lay them on with a brush. But first these must be made a composition of pigments which possess seccative (sic) qualities as white lead, dryers, and earth such as is used for bells, all thoroughly well mixed together and of one tint, and when the size is dry this must be plastered over the panel and then beaten with the palm of the hand so that it becomes evenly united and spread all over, and this many call the 'imprimatura' (priming).²²⁷

Vasari's statements appear to corroborate what earlier written sources suggest; Italian painters were long familiar with the preparation of heat-bodied oils, using heat to prepare oils for oil-based varnishes (and mordants), eventually incorporating the medium as a binder for painting. Furthermore, Vasari's description of siccatives also indicates that by the mid-1500s this technology was known to Tuscan and Roman painters, knowledge that was likely

²²⁶ Vasari, *On Technique*, 224-5.

²²⁷ Ibid, 230-1. Maclehorse freely substitutes "dryers" for *giallolino* in Vasari's original text. In this instance the term likely refers to the use of massicot (lead-tin yellow) as this pigment is known to accelerate the drying time of oils. It is also unclear what Vasari meant by "bell earths" or *terre da campane*. While Maclehorse suspected it may refer to a material derived from the casts used to make bell, it is possible that this earth may have been rich in manganese or lead ores, both of which are effective driers when added to oil.

disseminated from artists working in the northern Italian territories. Despite Vasari's predisposition for Florentine art, his writings offer invaluable commentary relating to the technical and historical implications generated by van Eyck's "invention" and its subsequent adoption by Italian painters.

Vasari's northern counterpart, Karel van Mander (1548-1606), traced the evolution of oil painting in his *Het Schilderboeck* from a northern perspective, re-introducing the early development of the medium and its subsequent impact on Italian art. Published in 1604, van Mander's treatise may seem far removed from Italian Renaissance painting technique; however, portions of the text are translated (albeit sometimes loosely) from *The Lives of the Painters, Sculptors and Architects* with additional sections that appear to have been written in response to Vasari's viewpoints. For example, in van Mander's passage that outlines the evolution of oil paintings, Jan van Eyck's achievements are described in far greater detail than in Vasari's *Lives*. Van Mander also portrayed Jan van Eyck as a learned individual whose skill surpassed those of Apelles and Zeuxis (the legendary Greek painters who were celebrated for their ability to emulate their natural surroundings), an achievement that van Mander attributed to van Eyck's use of the oil medium:

He succeeded in coating his egg- and glue-based colors with a varnish made from oils, which very much pleased his viewers, for it gave his works a beautiful, gleaming luster. Many had sought this secret in Italy, but to no avail... Now after he had investigated many oils and other things of nature, he found that linseed and walnut oil dried almost thoroughly... He researched ever further, aspiring to perfection, and found after much investigation that pigments mixed with such oils became malleable and dried hard, and having dried became impermeable, and that the oil made colors livelier, and that they themselves became lustrous without varnishing. And what most astonished and pleased him was his discovery that colors mixed with oil could be applied and

worked better than those mixed with wet egg or glue, and that they did not need to be hatched.²²⁸

Van Mander's specific reference to the fact that artists were no longer forced to use "hatched" brushstrokes reveals his training as a painter; to van Mander the hatched appearance of egg tempera paintings prevented such works from obscuring the boundary between nature and art. Art historian Walter S. Melion observed that Van Eyck's invention was triumphantly claimed by van Mander as one of the greatest achievements of the north, aside from the movable type and gunpowder, and one that generated permanent and luminous works that eventually disrupted "the historical continuum of Italian art."²²⁹ Melion also stated that *Het Schilderboeck* was organized to portray Italian artists as masters of fresco and egg tempera while the Northerners are instead associated with oil painting; van Mander added sections on Venetian painters, praising artists such as Titian and Bassano for deviating from their Italian tradition and embracing the oil medium.²³⁰ Van Mander must have been aware of Michelangelo's dismissive attitude toward the oil technique as Melion describes van Mander's defensive response in chapter twelve entitled "On Painting and Coloring Well":

...van Mander recounts Michelangelo's gendered distinction between oil-painting, stigmatized as a woman's work, and fresco, praised as manly effort, only to conclude by arguing the impossibility of such criteria in the Netherlands, where neither climate nor the local plaster allow fresco.²³¹

²²⁸ Walter S. Melion, *Shaping the Netherlandish Canon: Karel van Mander's 'Schilder-Boeck'* (Chicago: University of Chicago, 1992), 54-55.

²²⁹ Melion, *Shaping the Netherlandish Canon: Karel van Mander's 'Schilder-Boeck,'* 19-22, 54-55, 141.

²³⁰ *Ibid*, 82.

²³¹ *Ibid*.

In comparison to *Het Schilderboeck*, Vasari's texts offer more information on practical methods of painting; however, van Mander's treatise appears to serve as a respectful reminder to painters everywhere, a reminder of where the oil technique was born and how it impacted the art world south of the Alps. *Het Schilderboeck* may be considered an improvement over Vasari's *Lives* as it categorizes artists using a more objective, regional approach, commending the Romans for their excellent draftsmanship, the Florentines for their mastery of fresco and tempera, and the Venetians for their adoption of the northern medium.

From a technical standpoint, only a handful of written accounts dating from the fourteenth to the sixteenth centuries contain information regarding the oil technique, although it is entirely possible that additional manuscripts from this period still await publication and/or re-examination.²³² Early manuscripts focused predominantly on pigments, gilding and other topics, with only an occasional reference to the preparation of binders such as egg tempera and drying oils. Cennino Cennini, Filarete, and Leonardo da Vinci are exceptions; piecing together excerpts from these manuscripts together with recent codicological research provides a tentative regional timeline for the spread of oil painting in Italy, likely beginning with artists in the north who were more familiar with preparatory methods involving heat and/or siccatives. Of all the texts that have been surveyed in this chapter there are no recipes that cite the use of egg yolk combined with oil; while a few recipes cite specific layering systems involving both media, it seems more likely that artists would choose one over the other given the specific project at hand. Nonetheless, the lack of emulsion recipes is intriguing and should be kept in mind when presented with the technical studies of Quattrocento paintings that are outlined in the following chapters. By the beginning of the fifteenth century, fewer and fewer

²³² Clarke, "Codicological indicators or practical medieval artists' recipes," 8. Clarke states that "over 400 medieval manuscript volumes containing artists' technical instructions and recipes have been identified."

written sources include descriptive information relating to binding media, a shift that is possibly explained by the fact that apothecaries had been stocked with pre-made oils, resins, and other materials throughout the 1300s. Most Quattrocento artists appear to have been relatively silent on the topic of oil painting until the age of Vasari; if any of these workshop “secrets” relating to the oil technique were recorded it is possible that they have yet to be published or were considered too practical to be scrupulously documented in newly bound volumes. Giorgio Vasari’s seminal *Lives of the Painters, Sculptors and Architects* reveals that by the sixteenth century, Italian painters were well aware of the role that heat, solvents, and siccatives played in the preparation and application of drying oils, while van Mander’s *Het Schilderboeck* emphasized the importance of contextualizing artists and art technology from a regional standpoint. As scholars continue to examine and re-examine the hundreds of extant texts that have found to contain artists’ recipes, more information may come to light regarding the evolution of oil painting both before and during the Italian Renaissance.

Chapter 4

EARLY EVIDENCE OF OIL PAINTING IN THE QUATTROCENTO

The transition from egg to oil appears to have been a gradual process that involved multiple artists and numerous territories. As we continue to learn more about Quattrocento painting techniques it becomes evident that cultural developments throughout the peninsula must be treated as regional occurrences and not as events representative of the country as a whole. Since 1762, Giorgio Vasari's account describing the sudden introduction of oil has been successfully refuted, compelling subsequent generations of scholars to revisit this complex artistic evolution through historical and technical research.²³³ Subsequent attempts to

²³³ Jill Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery* (New Haven and London: Yale University Press and National Gallery Publications, 1991), 197-9; Elise Effman, "Theories about the Eyckian painting medium from the late-eighteenth to the mid-twentieth centuries," *Reviews in Conservation* 7 (2006):17-26, accessed November 1, 2015, <http://deyoung.famsf.org/files/vanEyck.pdf>; Joanne Wright, "Antonello da Messina The origins of his Style and Technique," *Art History* 3 (1980): 1-53; Frances Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," in *Cultural Exchange Between the Low Countries and Italy, 1440-1600*, ed. Ingrid Alexander-Skipnes (New York: Brepols Publishers, 2007), 53; Carol M. Richardson, Kim W. Woods, and Michael W. Franklin, eds., *Renaissance Art Reconsidered* (Chicester: John Wiley and Sons, Ltd., 2007), 193-6. Sir Horace Walpole is considered to be the first scholar to question Vasari's notion that the van Eyck brother's invented the oil technique in his 1762 publication *Anecdotes of Painting in England* followed soon after by Gotthold Ephriam Lessing's *Vom Alter der Ölmahlery*, a 1774 technical study of Eyckian paintings. Joanne Wright also points towards Fausto Nicolini's 1923 publication of Pietro Summonte's letter to Marcantonio Michiel (1524) as the first document to contest Antonello da Messina's suggested association with Jan van Eyck. Ames-Lewis has also discussed a letter written by Vasari's acquaintance Vincenzo Borghini in 1563, contesting Vasari's story that Messina had introduced the oil medium (by then Borghini had read a copy of Cennino Cennini's *Il Libro dell'Arte* that discusses the material). Antonello da Messina is also thought to have completed his apprenticeship by the early 1450s and subsequently introduced the oil technique to Venetian painters by 1475/76.

summarize this shift in traditional Italian painting practice have also condensed this topic into one specific event, further perpetuating unrealistic and over-simplistic interpretations of the egg-oil transition. Italy was a disjointed country during the Medieval and Renaissance periods: the north was populated by a number of rival city states, the central peninsula was under the direct rule of the Papacy, and the south was in a perpetual state of war between the Spanish and the French. The prosperity witnessed by an ever-growing number of stately courts throughout Italy (and much of Western Europe) also played an essential part in fostering cross-cultural exchanges throughout artistic circles, one that will be further explored in this chapter from a regional perspective. The transition from egg to oil appears to have been a gradual process that involved multiple artists and numerous territories. Therefore, this dissertation will offer an alternative summary outlining the evolution of oil painting in Italy by connecting relevant historic events to technical findings that have helped to shed new light on regional artistic trends. While future scholarship relating to Quattrocento painting practice will continue to benefit from collaborative research among art historians, scientists, and conservators, scholars should be encouraged to re-consider some of the technical findings described in this chapter relating to Italian paintings in light of new advancements in analytical techniques.

4.1 Spain, Aragon, and Southern Italy

Studies that focus on painting practices associated with the *Mezzogiorno* region (territories lying to south of Rome) are still surprisingly lacking; however, relatively recent research suggests that this area offers potentially rich information relating to the introduction

and recognition of the oil medium throughout the Italian Renaissance.²³⁴ As discussed in the previous chapters, only a handful of fourteenth and fifteenth-century paintings and historical documents from the southern territories have managed to survive, perhaps as a result of the continual warfare that plagued the region for over two centuries.²³⁵ The *Mezzogiorno* includes nearly half of the entire Italian peninsula with several international port cities that were essential for trade within the Mediterranean and beyond (see Figure 4.1). It is entirely plausible then to assume the south likely played a critical role in the introduction of artistic traditions and techniques that originated from lands beyond the Italian territories.

From a militaristic and economic standpoint, Sicily and Naples were considered by major European powers (including the Spanish and French) to be geographically advantageous, ultimately leading to the development of a rather culturally diverse environment.²³⁶ By the late 1300s, the South was divided into two kingdoms: the Kingdom of Sicily, ruled by the House of Aragon, and the Kingdom of Naples, ruled by the House of Anjou. During the fourteenth and fifteenth centuries, the *Mezzogiorno* continued to experience

²³⁴ Ibid; Carl Brandon Strehlke, "Review: Naples - Quattrocento Aragonese," *Burlington Magazine* 140 (1998), 144-45, accessed October 22, 2015, <http://www.jstor.org/stable/887721>; Joanne Wright, "Antonello in formazione: un riesame della Crocifissione di Bucharest," *Arte Veneta: Rivista di Storia dell'Arte* 45 (1993): 20-31; Keith Christiansen, "The View from Italy," in *From Van Eyck to Brueghel*, eds. Maryan W. Ainsworth and Keith Christiansen (New York City: Metropolitan Museum of Art, 1998), 40-1. See also Marco Lucco, Dominique Thiebault, and Marco Collareta, *Antonello da Messina. L'opera completa* (Milano: Silvana Editoriale S.p.A., 2006).

²³⁵ Steven Runciman, *The Sicilian Vespers: A History of the Mediterranean World in the Later Thirteenth Century* (Cambridge: Cambridge University Press, 1992), 214.

²³⁶ Runciman, *The Sicilian Vespers: A History of the Mediterranean World in the Later Thirteenth Century*, 214. After the French lost Sicily to the Spanish during the Vespers Revolt in 1282, the two countries continued to wage war over the southern territories well into the 15th century.

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Figure 4.1: A map of Renaissance Italy showing the expansive southern territories of Naples and Sicily as compared to the Papal States and the City-States in the north.²³⁷

a permanent and ever-changing relationship with its northern neighbors, creating an environment where native artisans were not only exposed to northern art but also to foreign painters who may have accompanied the French and Spanish courts. Extant paintings from this period display a very different aesthetic as compared to contemporary works associated with northern cultural centers such as Florence and Venice. The *Mezzogiorno* offered an ideal

²³⁷ “The Transformation of the West, 1450-1750,” accessed November 3, 2015, <http://crossenhistory.weebly.com/chapter-17-the-transformation-of-the-west-1450-1750.html>.

setting for international cultural exchange, which is perhaps why Vasari chose a painter trained in the south as the primary protagonist in his account detailing the introduction of oil painting in Italy.

Very little technical analysis has been conducted on the artworks from the *Mezzogiorno* region; however paintings, dating as early as the mid-fourteenth century already began to demonstrate compositional homage to northern styles, a characteristic not commonly encountered in easel paintings from the same period associated with the central and northern territories.²³⁸ Simone Martini's *Saint Louis of Toulouse Crowning Robert of Anjou* is a perfect example of an Italian artist deviating from the traditional norm in response to northern influences (see Figures 4.2 and 4.3).²³⁹ Although technical analysis has not been carried out on the *Saint Louis* painting, it contains compositional features more commonly found in German and French works of art dating to the twelfth and thirteenth centuries.²⁴⁰ It is still unclear why King Robert of Anjou selected a Siennese painter for this commission; nonetheless Simone Martini incorporated northern elements into his composition in an attempt to please his patron. Soon after the panel was completed, Simone Martini followed in the footsteps of Giotto, traveling north to Avignon to work under Cardinal Giacomo Stefaneschi and

²³⁸ It may be argued that works attributed to Gentile da Fabriano are an exception.

²³⁹ With the relocation of the papal court from Rome to Avignon in 1309, a number of artisans including Italian painters travelled to the city to obtain work through commissions, indicating that there may have already been a north-south cultural dialogue in place between the French and the *Mezzogiorno* prior to the arrival of the Avignon dignitaries in Naples.

²⁴⁰ Julian Gardner, "Saint Louis of Toulouse, Robert of Anjou and Simone Martini," *Zeitschrift für Kunstgeschichte*, 39 (1976): 12-33, accessed October 2, 2015, <http://www.jstor.org/stable/1481915>. Such motifs include the fleur-de-lis shaped punchmarks and pattern painted on the backside of the panel as well as the depiction of an enthroned ecclesiastic. To date no technical analysis has been performed on the panel; it would be interesting to characterize the binder of the paint applied to the backside of the panel and to assess whether a ground layer is also present.

ultimately residing in France from 1340 to 1344 (the same patron who commissioned Giotto to create the *Navicella* a few years earlier).²⁴¹ As evidenced by Simone Martini's panel, the French occupation of Naples did not deter Italian artists from pursuing patronage from these new Angevin rulers, thus paving the way for future relationships between native artisans and foreign patrons even after arrival of the Spanish armies.

Concrete evidence of artistic cultural exchange in the Neapolitan region does not surface again until the reign of Rene of Anjou in 1438. Upon claiming the throne of Naples, King Rene subsequently recruited the local Italian painter Niccolo Colantonio (mentioned in the previous chapter) to serve as his court painter. Little is known regarding Colantonio's career; he may have received training from the painter Francesco Simone but, according to the humanist writer Summonte, became known for his ability to produce copies of Netherlandish paintings.²⁴² Whether or not Colantonio reproduced northern paintings from Rene's collection is not known, although his exposure to Flemish works likely continued even after Rene's expulsion from Naples in 1442 by Duke Alfonso of Aragon. As previously discussed, Alfonso's collection contained a wide variety of northern masterpieces while his court was populated with foreign artists who were well versed in Flemish painting techniques.²⁴³ During

²⁴¹ Diana Norman, *Painting in late medieval and renaissance Siena, 1260-1555* (New Haven: Yale University Press, 2003), 43; Claire Guinomet, "Italian Influences," in *The Road to Van Eyck*, eds. Stephan Kemperdick and Friso Lammertse (Rotterdam: Museum Boijmans Van Beuningen, 2012), 52.

²⁴² Christiansen, "The View from Italy, 40-1; Richardson, Woods, and Franklin, eds., *Renaissance Art Reconsidered*, 193-6; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50-1, 56.

²⁴³ See Chapter 2.3 for more information regarding northern paintings in Italian collections during the Quattrocento.

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Figure 4.2 (left) and 4.3 (right): Simone Martini, *Saint Louis of Toulouse Crowning Robert of Anjou* (c. 1317, Museo di Capodimonte, Naples), front view (left) and verso (right).

his tenure as court painter, Colantonio is thought to have produced a series of works including the *St. Jerome in His Study*, a composition that is visibly influenced by the northern aesthetic (see Figure 4.4).

While Colantonio's works have yet to undergo technical investigation, extant works by the painter's most renowned pupil, Antonello da Messina, have been subjected to comprehensive scientific analysis in conjunction with recent exhibitions occurring over



Figure 4.4: Niccolo Colantonio, *Saint Jerome in His Study* (c. 1420-60, Museo di Capodimonte, Naples).

the last 25 years.²⁴⁴ Born around 1430 in the Sicilian port city of Messina, Antonello eventually traveled to Naples where his interest in the northern aesthetic was likely cultivated. Most scholars agree that Antonello initially trained in Naples sometime between 1445 and

²⁴⁴ Wright, "Antonello da Messina, the Origins of His Style and Technique," 47; Although Wright claims that Colantonio painted in oils, this has yet to be confirmed through technical analysis. See also *Antonello da Messina: Sicily's Renaissance Master*, ed. Gioacchino Barbera (New York: Metropolitan Museum of Art, 2005) and *Antonello da Messina: L'opera completa*, ed. Mauro Lucco (Milano: Silvana Editoriale S.p.A., 2006).

1455, presumably under the tutelage of Colantonio during Alfonso's reign.²⁴⁵ Antonello painted the Bucharest *Crucifixion* (c. 1450-55; see Figure 4.5), which is generally considered to be one of his earliest surviving works, not long after completing his apprenticeship, a composition.²⁴⁶ The striking similarity to other compositions by northern painters (particularly to those of Jan van Eyck) suggests that Antonello almost certainly encountered northern paintings in Alfonso's collection before he eventually returned to Messina in the mid-1450s to establish his own workshop (see Figure 4.6).²⁴⁷

There are considerable periods of time in Antonello's career when his whereabouts remain unknown (1457-1460; 1467-1471); however, recent scholarship has attempted to chronologically trace Antonello's development as an artist by identifying trends in the use of his certain artistic materials and techniques. Consequently technical studies performed over the last twenty-five years have unearthed a considerable amount of information relating to the materiality of his paintings, revealing several types of wooden supports (beyond the typical poplar that was commonly used by his contemporaries), the eventual adoption of a lead white priming layer, and the implementation of several binders, from egg tempera to drying oil to

²⁴⁵ Gioacchino Barbera and Andrea Bayer, "Biographical Note," in *Antonello da Messina: Sicily's Renaissance Master*, ed. Gioacchino Barbera (New York: Metropolitan Museum of Art, 2005), 51.

²⁴⁶ Joanne Wright, "Antonello's Lost 'St. Augustine': A Painting in its Landscape," *Apollo* 165 (2007): 78-84; —, "Antonello in formazione: un riesame della Crocifissione di Bucharest," 20-31; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50, 55-7; Borchert, Till-Holger, "Antonello da Messina e la pittura fiamminga," in *Antonello da Messina: L'opera completa*, ed. Mauro Lucco, (Milano: Silvana Editoriale S.p.A., 2006), 27-42; Luke Syson, "Antonello da Messina," *The Burlington Magazine* 148 (2006): 541-4, accessed October 3, 2015, <http://www.jstor.org/stable/20074525>. Joanne Wright has noted that the background landscapes depicted in Antonello's early compositions are strongly suggestive of the coastline in Messina.

²⁴⁷ Joanne Wright, "Antonello da Messina, the Origins of His Style and Technique," 47.

mixtures of the two.²⁴⁸ Art historian Maria Clelia Galassi uses the term “artistic schizophrenia” when describing Antonello’s career, particularly the artist’s ever-evolving selection of materials.²⁴⁹ Galassi points out that Antonello’s eclectic style seems to have been more popular among the aristocracy in Venice and Milan while his Sicilian commissions tended to stipulate the use of sound materials and traditional imagery. This scenario is also echoed in the writings of contemporary historians; Francesco Maurolico (1494-1575), who was born in Messina, merely mentions Antonello as someone “who lived for some years in Venice, publicly well known, and he was very famous in Milan too” while Pietro Summonte’s letter of 1524 to the Venetian Marcantonio Michael acknowledges the artist’s birthplace and subsequent training in Naples.²⁵⁰ We can assume then that Antonello had to satisfy traditional tastes at home while catering to the ever-growing fascination with the northern aesthetic amongst the Italian elite. Galassi suggests that Antonello’s Sicilian clients must have been aware of his experimental techniques as a 1472 commission for a *gonfalone* (a decorated cloth banner intended for religious purposes) issued by the confraternity of the Spirito Santo in Noto dictated a six-year guarantee lest the banner begin to show signs of deterioration

²⁴⁸ Maria Clelia Galassi, “Aspects of Antonello da Messina’s Technique and Working Method in the 1470s: Between Italian and Flemish Tradition,” in *Cultural Exchange between the Low Countries and Italy (1400-1600)*, ed. Ingrid Alexander-Skipnes (Turnhout, Belgium: Brepols Pub, 2007), 63-85. See also *Antonello da Messina: Sicily’s Renaissance Master*, ed. Gioacchino Barbera (New York: Metropolitan Museum of Art, 2005), *Antonello da Messina: L’opera completa*, eds. Dominique Thiebault, and Marco Collareta (Milano: Silvana Editoriale S.p.A., 2006), and *Around Antonello da Messina: Reintegrating Quattrocento Culture*, eds. Michael Kwakkelstein and Bette Talvacchia (Firenze: Centro Di, 2014).

²⁴⁹ Galassi, “Aspects of Antonello da Messina’s Technique and Working Method in the 1470s: Between Italian and Flemish Tradition,” 64.

²⁵⁰ *Ibid*, 63-5.

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Figure 4.5 (left) and Figure 4.6 (right): Antonello da Messina, *Crucifixion* (c. 1440-50, Brukenthal National Museum, Sibiu, Romania; left) and a detail of Jan van Eyck and Workshop Assistant, *Crucifixion* (c. 1435-40, Metropolitan Museum of Art, New York; right).

“because of ever faults or imperfections attributable to the Master Antonello himself.”²⁵¹ The inherent fragility of these religious banners, however, may have been reason enough for these confraternities to exercise caution rather than a conscious awareness of Antonello’s interest in experimenting with various painting techniques. None of the artist’s *gonfalones* have survived

²⁵¹ Ibid, 65.

and the Bucharest *Crucifixion* has yet to be analyzed for the presence of oil so it is impossible to know how early the artist began to adopt the oil medium into his daily practice.

Subsequent works by Antonello da Messina have been characterized as having been painted either partially or completely in oil.²⁵² Based on scientific analysis, linseed oil has been identified in the Virgin's blue robe in the Uffizi's *Saint John the Evangelist* (1465-70), in Christ's flesh in the Louvre's *Christ at the Column* (c. 1475-78?), in Venice's *Pietà* (1475-77?), in Antwerp's *Crucifixion* (c. 1475), and in the Philadelphia Museum of Art's *Portrait of a Young Man* (1474), while walnut oil has been found in the National Gallery, London's *Salvator Mundi* (1465) and *Saint Jerome in his Study* (early 1460s; see Figure 4.7).²⁵³

²⁵² Wright, "Antonello in formazione: un riesame della Crocifissione di Bucharest," 25-6.

²⁵³ Fabio Talarico, "Risultati delle analisi chimiche sulle due tavole," in *Antonello agli Uffizi. Un acquisto della Stato per il riscatto dell'eredità Bardini*, eds. Cristina Acidini and Antonio Paolucci (Firenze: Giunti Editore, 2002), 82-4; Elisabeth Martin, "Le Christ à la colonne. Étude matérielle. Contribution à l'étude technique," in *Le Christ à la colonne d'Antonello da Messina*, ed. Dominique Thiébaud (Paris: Musée du Louvre, 1993), 59; R&C Scientifica, "Sezioni stratigrafiche e riconoscimento dei pigmenti e dei leganti," in *Carpaccio, Bellini, Tura, Antonello: e altri restauri quattrocenteschi della Pinacoteca del Museo Correr*, ed. Attila Dorigato (Milan: Electa, 1993), 218; Jill Dunkerton, "Antonello da Messina and oil painting in the 15th century," in *Around Antonello da Messina: Reintegrating Quattrocento Culture*, eds. Michael W. Kwakkelstein and Bette Talvacchia (Firenze: Centro Di, 2014), 46-7; Carl Brandon Strehlke, Ken Sutherland, and Mark Tucker, "The 'Portrait of a Young Man' by Antonello da Messina in the Philadelphia Museum of Art," in *Around Antonello da Messina: Reintegrating Quattrocento Culture*, eds. Michael W. Kwakkelstein and Bette Talvacchia (Firenze: Centro Di, 2014), 70; Raymond White and Jennifer Pilc, "Analyses of the Paint Media," *National Gallery Technical Bulletin* 14 (1993): 87. It should be noted that only a few of these publications provide details regarding analysis performed with gas chromatography-mass spectrometry (GC-MS) and/or Attenuated Total Reflectance-Fourier-Transform Infrared Spectroscopy (ATR-FTIR). It is the author's opinion that analysis performed using Fourier-Transform Infrared Spectroscopy (FTIR), staining of cross-sectional samples, and gas chromatography not equipped with a mass spectrometer does not provide conclusive information relating to the presence of organic binders within discrete layers or even definitive characterization of individual binders. A general overview of Antonello's materials and techniques can be found in Gianluca Poldi and Giovanni C. F. Villa's "Cuius

Figure removed due to copyrighting

Figure 4.7: Antonello da Messina, *St. Jerome in his Study* (c. 1474-75, National Gallery, London).

Considerable attention has been directed to the latter work, as the London *St Jerome* is undeniably influenced by the northern aesthetic. Marcantonio Michiel praised the painting for

pictura est intuenda admirationi'. Contributo alla comprensione della tecnica di Antonello," in *Antonello da Messina: L'opera completa*, ed. Mauro Lucco (Milano: Silvana Editoriale S.p.A., 2006), 91-114.

its beauty and “alla ponentina” or Flemish style, even suggesting that the painting belonged to the hand of Jan van Eyck or Hans Memling rather than Antonello.²⁵⁴ Michiel’s misattribution is unsurprising as this particular composition is considered by many to be one of the first successful oil paintings attempted by an Italian Renaissance artist.²⁵⁵

Antonello may not have abandoned the traditional tempera technique altogether, a notion supported by scientific analysis performed on other works attributed to the artist and his workshop. In conjunction with the 2006 exhibition “Antonello da Messina” at the Scuderie del Quirinale in Rome, a team of scientists from the Doerner Institut analyzed four samples collected from Antonello’s *Saint Sebastian* (1475-76; Figure 4.8) in Dresden, likely created during the artist’s sojourn in Venice. The results are indeed curious and seem to present conflicting results with analysis performed on other paintings that date to this same period in Antonello’s career.²⁵⁶ The authors should be commended for presenting the analytical information in great detail; however, there are a few discrepancies that warrant further discussion and interpretation, much of which will be presented in subsequent chapters. In summary, initial results performed with Fourier-Transform Infrared Spectroscopy (FTIR) pointed towards the presence of an oil-based medium; however, subsequent analysis performed using more sophisticated chromatography methods suggested the presence of egg

²⁵⁴ Galassi, “Aspects of Antonello da Messina’s Technique and Working Method in the 1470s: Between Italian and Flemish Tradition,” 63; Christiansen, “The View from Italy,” 39-61, 65; Wolfgang Stechow, *Northern Renaissance Art, 1400-1600: Sources and Documents* (New Jersey: Prentice-Hall, Inc., 1966), 29-31.

²⁵⁵ Dunkerton, “Antonello da Messina and oil painting in the 15th century,” 46-7; Penny Howell Jolly, “Antonello da Messina’s ‘Saint Jerome in His Study’: An Iconographic Analysis,” *The Art Bulletin* 65 (1983): 238-53, accessed October 15, 2015, <http://www.jstor.org/stable/3050320>.

²⁵⁶ Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197.

yolk and/or whole egg and even egg white in three paint samples, with a fourth sample testing positive for animal glue.²⁵⁷ It is worth noting that the conservator Andreas Henning, who carried out the restoration of the painting, states that the problematic interpretation may be due to where the team was allowed to collect samples, shedding light on some of the realistic challenges often facing conservation scientists.²⁵⁸ Henning concludes that since all four samples were collected from the edge may not provide an accurate representation of the entire picture it is possible the artist employed drying oils in other sections of the composition.²⁵⁹

The Dresden *Saint Sebastian* is not the only painting that has tested positive for the presence of proteinaceous binders. *The Portrait of a Man* in the Borghese Gallery (c. 1475-76), as well as the two paintings attributed to Antonello in Washington, have all been found to contain markers associated with egg tempera.²⁶⁰ The Borghese portrait was found to contain egg tempera “residues” using micro-chemical tests, FTIR, and chromatography

²⁵⁷ Andreas Henning, “Il ‘San Sebastiano’ di Antonello da Messina a Dresda. Iconografia e restauro,” in *Antonello da Messina: L’opera completa*, ed. Mauro Lucco (Milano: Silvana Editoriale S.p.A., 2006), 85-7; Andreas Henning and Gunter Ohlhoff, *Antonello da Messina: Der Heilige Sebastian* (Dresden: Staatliche Kunstmuseen, 2005), 61-7. The suggestive use of egg white as a primary binding medium is highly unlikely in this case based on what has been deduced from the analysis of hundreds of Italian Renaissance panel paintings.

²⁵⁸ Henning, “Il ‘San Sebastiano’ di Antonello da Messina a Dresda. Iconografia e restauro,” 87.

²⁵⁹ *Ibid.*

²⁶⁰ Elisabetta Zatti, “The Restoration of Antonello da Messina’s ‘Portrait of a Man,’” in *Incontri/Encounters*, ed. Alba Costamagna (Rome: Galleria Borghese, 2002/2003), 74; Maurizio Seracini, “Digital Clinical Charts of the Galleria Borghese’s Paintings,” in *Incontri/Encounters*, ed. Alba Costamagna (Rome: Galleria Borghese, 2002/2003), 109-11; Miklos Boskovits and David Alan Brown, eds., *Italian Paintings of the Fifteenth Century* (Washington DC: Oxford University Press and the National Gallery of Art, 2003), 36-45; Gianluco Poldi, “Antonello da Messina between Sicily and Venice: the San Cassiano altarpiece,” *Technologische Studien: Konservierung, Restaurierung, Forschung, Technologie/Kunsthistorisches Museum* 6 (2009): 94.

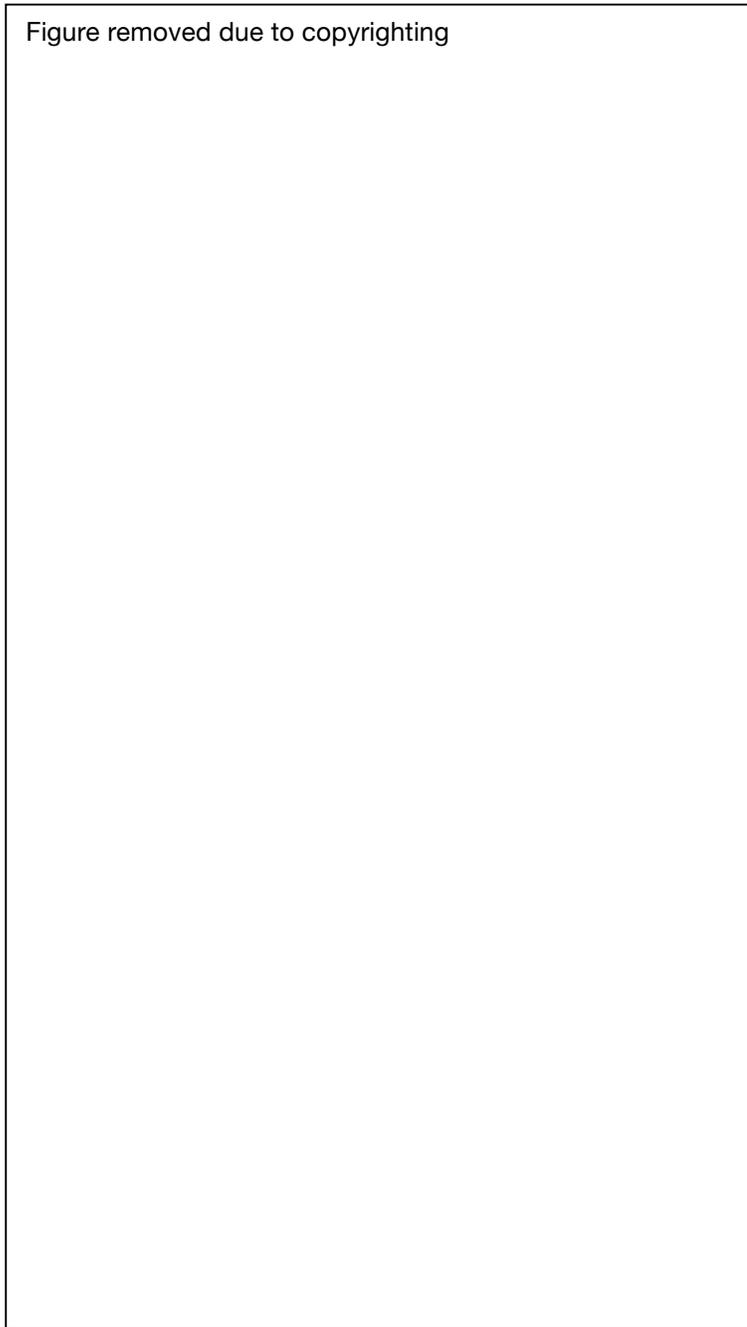


Figure 4.8: Antonello da Messina, *St. Sebastian* (c. 1476-77, Gemäldegalerie Alte Meister, Dresden).

methods (GC-MS) but the visual examination of the picture suggests “the presence of an oily binding agent” due to prominent brushstrokes encountered in certain parts of the composition.²⁶¹ Both the *Madonna and Child* (c. 1475, Figure 4.9) and the *Portrait of a Young Man* (c. 1475/80, Figure 4.10) were subjected to scientific analysis in 1988 using a range of techniques although there seems to be conflicting information between the scientific reports and the technical notes published in the 2003 Systematic Catalogue.²⁶² In summary, the *Portrait of a Young Man* was found to have been painted predominantly in egg tempera while the *Madonna and Child* yielded results that were far more perplexing: cross-sectional staining did not identify egg tempera in the paint (although glue was confirmed in the ground); however, chromatography methods were able to confirm the presence of amino acids that presumably indicated the use of egg. In addition, the technical notes indicate that chromatography methods identified drying oil in the green cushion yet there is no mention of this in the analytical report.²⁶³ A possible explanation for the conflicting analytical results could be related to *The Madonna and Child*'s troubled restoration history as the painting was completely transferred from its original wooden support in 1936.²⁶⁴ It is likely that during this

²⁶¹ Zatti, “The Restoration of Antonello da Messina’s ‘Portrait of a Man,’” 74-80; Seracini “Digital Clinical Charts of the Galleria Borghese’s Paintings,” 111.

²⁶² Boskovits and Brown, eds., *Italian Paintings of the Fifteenth Century*, 36-45; “Antonello da Messina – ‘Madonna and Child,’” (conservation file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC); “Antonello da Messina – ‘Portrait of a Young Man,’” (conservation file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC).

²⁶³ Ibid. Cross-sectional staining on a sample collected from the green cushion did suggest the presence of drying oil in the upper paint layers so it is likely that the author of the technical notes made an understandable mistake (although this unfortunately conflates the application of a less sophisticated technique with a technique that is far more sensitive and precise).

²⁶⁴ Boskovits and Brown, eds., *Italian Paintings of the Fifteenth Century*, 36.

same restoration campaign, large sections of the composition were overpainted, namely the sky, the background, and the green cushion, the same cushion that was identified as having been painted in oil by the original artist.²⁶⁵ The confusion surrounding the nature of the binding medium prompted scientists and conservators to revisit the *Madonna and Child* during a recent conservation treatment in 2011, the results of which will be discussed in Chapter 6.



Figure 4.9 (left) and Figure 4.10 (right): Antonello da Messina, *Madonna and Child* (c. 1475, The National Gallery of Art, Washington DC; left) and *Portrait of a Young Man* (c. 1475/80, The National Gallery of Art, Washington DC; right).

²⁶⁵ These results also reveal the difficulty in differentiating between fatty acid markers associated with the original paint layers vs. restoration paints.

With a career that extended from Southern Italy to Venice, Antonello's path as an artist is one that continues to warrant closer inspection. An overview of the scientific findings seem to provide some merit to Vasari's fictional tale, crediting the young artist with spreading the knowledge of oil painting throughout the Italian peninsula. While many of Antonello's works point toward a somewhat early adoption and mastery of the oil medium, there still seems to remain several outstanding questions as whether or not the artist and his workshop abandoned egg tempera altogether.

4.2 Central Italy

While much remains to be learned regarding Renaissance painting traditions in the south, a significant amount of scholarship has been devoted to painters working throughout central Italy. Throughout the fifteenth century, this region consisted of several city-states, nearly all of which were able to remain autonomous and free from foreign occupation. Consequently, cities like Florence and Siena were able to encourage civic involvement, fostering growth within their respective artistic communities. Many of these city-states became obvious destinations for artisans hoping to establish or enter successful workshops in order to meet the rising demands of the market. While some cities imposed only a few restrictions on practicing artisans, others were less lenient, examples of which will be provided below; by the early Renaissance, city-states like Florence and Siena had established guild systems, organizations that in turn affected cross-cultural exchanges between artists and possibly the adoption of the oil technique.

4.2.1 Florence

Technical studies suggest that most artists working in the cultural epicenter of Tuscany did not fully embrace the oil technique until the second half of fifteenth century. It is surprising that flourishing artistic centers such as Florence have not produced earlier examples of oil painting, a phenomenon that may be explained by the history and development of the guilds.²⁶⁶ Florence possessed one of the most complex and elaborate guild systems as the

²⁶⁶ It is likely that several paintings dating to the fourteenth and early fifteenth century were partially executed using oil; however, most of these early examples tend to be more commonly associated with glazes applied over metal leaf or used for specific pigment. This includes: 1) the Master of St. Francis's *Crucifix* (c. 1260s/70s) 2) two panels attributed to a Master of the Venezia Madonna (*Saint Corona* and *Saint Vittorio of Siena*, 1340-60) in Copenhagen where the use of oil is applied as a glaze over metal leaf while the rest of the panels are done using a tempera medium 3) Jacopo di Cione's *Crucifix* (c. 1370) in which GC-MS was used to identify an egg and oil in a darkened green-brown glaze atop the gold lining of the Virgin's mantle 4) Sassetta's *Sansepolcro Altarpiece* (1437-44) and 5) Bernardo Daddi's *Coronation of the Virgin* (c. 1430). In a 1996 publication, Dunkerton states that the earliest possible use of oil as a paint medium is in London's *Crucifix* (c.1260s/70s) by the Master of St. Francis. However, the analyses of the copper-green glaze was performed using FTIR alone and Dunkerton describes the condition of the work to be "complicated: many old restorations were left in place when it was cleaned on acquisition in 1965 and so we do not see any of this original green paint on the surface of the picture." As the condition of the picture is compromised, the analytical results of the picture are problematic and still open to interpretation, especially in light of recent technological advancements in analytical imaging of paint-cross-sections that can now be used to help differentiate between restoration and original materials. In the same 1996 publication, Dunkerton discusses the possible presence of a discolored green oil-containing glaze on Jacopo di Cione's *Crucifix* but states that "an insufficient sample was available for detailed analysis. Curiously the problematic size of the sample was not disclosed in a later publication in 2002, in which the authors confirm that oil is used as a glaze atop the mordant lining. In regards to the Sassetta panels, cross-sectional analysis revealed the presence of a translucent yellow glaze in *The Funeral of Saint Francis*; however, as this layer auto-fluoresces under ultraviolet light it is possible that it is leftover from an original resinous glaze or varnish. While FTIR analysis did point towards the presence of a drying oil with smaller amounts of protein, Rachael Billinge stipulates that more scientific analysis would be needed to confirm the presence of oil. For Daddi's *Coronation*, FTIR and GC-MS identified an oil glaze over silver leaf while the principal paint media was determined to be egg tempera. For information on the Master of the Palazzo Venezia Madonna panels in Copenhagen (the analytical techniques are not listed) see Catherine Higgitt and Raymond White, "Analyses of Paint Media: New Studies of the Fifteenth and Sixteenth Centuries," *National Gallery Technical Bulletin* 26 (2005): 88. For information on Jacopo di

seven distinct groups or *Arti* can be traced back as early as the thirteenth century; however, it was not until 1303 that artists became officially incorporated into the *Art de Medici e Speciali*, or Guild of Physicians and Apothecaries/Pharmacists.²⁶⁷ Artisans relied heavily on these local *speciali* or apothecaries as they were routinely stocked with basic painting materials and colorants ready for use; early Florentine guild statutes of the *Medici e Speciali* dating to the 1300s indicate that linseed oil, ragia (pine resin), and trementina (likely oil of turpentine) were readily available for purchase in apothecaries although it is unclear to what extent these materials impacted painting practice.²⁶⁸ By the late fourteenth century, painters had established themselves as a separate group with more restrictive entrance fees, eventually leading to the *Ciompi* revolt of 1378.²⁶⁹ Partially in response to civil unrest, officials sought to

Cione's *Crucifix* see Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 14 (1993): 86-91. For information regarding Sassetta's altarpiece see Rachel Billinge, "Some Panels from Sassetta's Sansepolcro Altarpiece revisited," *National Gallery Technical Bulletin* 30 (2009): 8-25. For information regarding Bernardo Daddi's *Coronation*, the Master of St. Francis's *Crucifix*, and Jacopo di Cione's *Crucifix* see Jill Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, ed. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997), 29-30 and Ashok Roy and Jill Dunkerton, "Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London," in *Early Italian Paintings: Approaches to Conservation*, ed. Patricia Sherwin Garland (New Haven: Yale University Art Gallery, 2002), 125-6.

²⁶⁷ John Edgcumbe Staley, *The Guilds of Florence* (London: Methuen, 1906), 269.

²⁶⁸ Alan Phenix, *Some Instances in the History of Distilled Oil of Turpentine, the Disappearing Painters' Material* (Los Angeles: Alan Phenix, 2015), 12. See also Raffaella Ciasca, *L'arte dei medici e speciali nella storia e nel commercio fiorentino dal secolo XII al XV* (Florence: L.S. Olschki, 1927).

²⁶⁹ *Ibid.*, 169-170; Roberto Bellucci and Cecilia Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," in *The Panel Paintings of Masaccio and Masolino: The Role of Technique*, eds. Carl Brandon Strehlke and Cecilia Frosinini

exercise tight control over guild statutes in the years leading up to the Renaissance. Statutes issued during this period suggests that the guild was intricately involved in controlling legal and administrative issues as well as monitoring the quality of materials and techniques artists were using.²⁷⁰ Resident Florentines working under the umbrella of the guild system were therefore subjected to a strict set of rules and regulations, a system that simultaneously implemented further restrictions for foreign painters hoping to participate in the city's flourishing art market.

The number of northerners residing in Florence was considerably less than the number of Italians residing in Bruges; however, despite the regulations imposed by the guild there is still evidence of northern artisans working within the city during the fourteenth and fifteenth centuries. Individuals were not formally recognized as practicing painters in Florence unless they belonged to the *Art de Medici e Speciali*. But perhaps more relevant to the adoption of oil were the rules that applied to foreign artisans; the guild required an additional fee from artists who were not native Florentines as well as references from at least two patrons.²⁷¹ While most of the artists that belonged to resident *tedeschi* or "German" population were weavers, a considerable number of them were also registered painters and traders involved with the

(Milan: 5 Continents Editions, 2001), 29-31. By November of 1339, painters established themselves as a separate group (the *L'Arte de' Pittori*) eventually assuming more of a socio-religious role by becoming the *Compagnia e Fraternita di San Luca* in 1354. The guild established a set of statutes and instigated a matriculation fee of 5 lire, however membership to the *Art de Medici e Speciali* was required before one could join the confraternity. This last stipulation prohibited most lower class artisans from being able to join, generating unrest that would eventually lead to the *Ciompi* revolt of 1378

²⁷⁰ Ibid; David Bomford et al., *Italian Painting Before 1400: Art in the Making* (London: National Gallery London Publications, 1989), 6.

²⁷¹ Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 29.

importation of the pigment azurite.²⁷² Some foreign residents eventually formed their own brotherhoods or confraternities, the most unique of which was the St. Barbara confraternity at SS. Annunziata founded in 1448.²⁷³ The group was mostly comprised of individuals who hailed from the Low Countries as well as from Germany; however, several Florentines were also recorded as active members, especially wealthy Florentine women and even painters' wives (e.g. the wives of Pietro Perugino and Antonio da Sangallo). Art historian Paula Nuttal notes that the patronage of this confraternity seems to be largely Florentine, an indication that the northern aesthetic had already become popular among the upper classes by the mid-1400s. Despite the stipulations exercised by the guild, the system appears to have evolved into more fluid organization as the market flourished, one that grew to encourage "the expansion of an artisan's activity into multiple occupations" and offer an environment that fostered cross-cultural exchange.²⁷⁴

By the late fourteenth century, as Florence began to experience a period of cultural growth and prosperity, it is perhaps unsurprising that the earliest known Italian oil painting was produced by a Florentine artist.²⁷⁵ Technical studies show that Masolino da Panicale (c.1383 - c.1447) may have been one of the first artists to introduce oil painting techniques to

²⁷² Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Art Press, 2004), 95.

²⁷³ *Ibid*, 93.

²⁷⁴ Jean Cadogan, *Domenico Ghirlandaio: Artist and Artisan* (New Haven and London: Yale University Press, 2000), 27.

²⁷⁵ It is the author's opinion that there are likely earlier examples of the use of oil as a paint medium in Italy (see Note 143).

Italy, and more specifically, to Rome and Florence.²⁷⁶ After registering with the *Arte dei Medici e Speziali* in 1423, the artist embarked on a two-year trip to Hungary eventually returning to Rome to collaborate with Masaccio (1401-1428) to produce the Santa Maria Maggiore altarpiece for one of the four papal basilicas (see Figure 1.3).²⁷⁷ The two artists began the project together in 1427, with Masolino completing the altarpiece alone after Masaccio's untimely death in 1428. At present, the two exterior panels from the altarpiece are the earliest known Italian paintings to have been partially painted using drying oils. Extensive analysis performed by at least three separate institutions found the lateral and central panels of the altarpiece (suspected as having been painted by Masolino) to contain drying oil and/or egg while areas attributed to Masaccio revealed the use of the traditional egg tempera binding medium.²⁷⁸ Painting conservators Roberto Bellucci and Cecilia Frosinini point out that Masolino's probable use of oil (a technique likely learned during his time in Hungary) may also relate to the artist's adoption of other "northern" techniques, specifically his adoption of a lead-white underlayer (or *imprimatura*) instead of the traditional green-colored paint that

²⁷⁶ Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 34-40.

²⁷⁷ Carl Brandon Strehlke, "The Case for Studying Masolino's and Masaccio's Panel Paintings in the Laboratory," in *The Panel Paintings of Masaccio and Masolino: The Role of Technique*, eds. Carl Brandon Strehlke and Cecilia Frosinini (Milan: 5 Continents Editions, 2001), 23-4; Masolino was not the first Tuscan painter to embark on such a trip as the Florentine painter Gherardo Starnina is recorded as moving to Spain in 1380 to work under Juan I of Castile. There is even evidence that both Duccio and Simone traveled extensively during their careers, well before Masolino and Starnina.

²⁷⁸ Ibid; Ashok Roy and Jill Dunkerton, "Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London," in *Early Italian Paintings: Approaches to Conservation*, ed Patricia Sherwin Garland (New Haven: Yale University Art Gallery, 2002), 125-6; "Masaccio and Masolino," (conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art).

often was used to model flesh tones.²⁷⁹ While Masolino's collaborator may have stuck to egg tempera as his primary binder, examination of earlier works by Masaccio also hint at the use of non-traditional methods; Masaccio used up to three different techniques for painting flesh tones and utilized large amounts of calcium carbonate (a white, transparent pigment that is normally found in northern paintings).²⁸⁰ While Cennini does mention this pigment in his *Il Libro dell'Arte*, he specifically instructs painters only to use this pigment as a colorant on wall paintings, emphasizing a strict step-by-step approach to the painting of flesh tones.²⁸¹

While both Masaccio and Masolino appear to have embraced non-traditional painting practices, of greater interest is the unique use of both egg and oil-based paints. As mentioned in Chapter 1, the Santa Maggiore altarpiece is one of the most extensively studied in terms of medium analysis. Visual examination of the panels, particularly in the flesh tones, reveals a distinctive range of optical properties throughout the painted passages that is not typically encountered in traditional tempera paintings. The contributing authors in *The Panel Paintings of Masolino and Masaccio* present the reader with a thorough description of the various analytical techniques that were used to painstakingly unravel the compositional evolution of the altarpiece and Table 4.1 has been included to show a summary of the organic analysis

²⁷⁹ Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 29.

²⁸⁰ Ibid. It should be noted that calcium carbonate is also used in the production of frescoes (lime); it may have been more common for Italian artists who specialized in frescoes as well as easel paintings (like Masaccio) to occasionally use the transparent, white pigment in their painting practice. More research is needed to confirm this observation.

²⁸¹ Ibid. In chpt LXVII of Cennini's treatise he disparages all methods of flesh painting recommending only verdaccio. While Bellucci and Frosinini postulate that Cennini's *Il Libro dell'Arte* was possibly commissioned by the Florentine guild in an attempt to exercise tighter control over artists, further restricting experimentation with new techniques and materials. See Chapter 3.2 for a different assessment of Cennini's *Il Libro*.

results obtained between approximately 1993 to 2003. There appears to be discrepancies when comparing the results generated from different laboratories and even various techniques. For example, GC-MS results in 1993 suggested that egg tempera was the dominant medium present in St. Peter's face, while subsequent analysis performed using GC-MS as well as microspectrofluorometric techniques on cross-sections (to measure UV-visible fluorescence) revealed drying oil to be the primary binder.²⁸² A sample from St. Peter's foot was also examined using cross-sectional staining (Amido Black series) which suggested the absence of protein while subsequent analysis carried out in 1993 and 2002 determined that egg tempera was present.²⁸³ As some of the most capable and well-equipped museum laboratories were involved in the Masaccio-Masolino project, these discrepancies reveal unforeseen challenges when interpreting organic analysis in fifteenth-century Italian paintings: different laboratories may employ different methods of preparation and/or interpretation while advancements in technology are likely to occur, even over a ten-year period.²⁸⁴ Certainly visual examination of

²⁸² "Masaccio and Masolino," (conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art).

²⁸³ Refer to Chapter 5 (sections 5.2 and 5.3) for additional information the various analytical techniques used in this case study. UV-vis microspectrofluorometric analysis of cross-sections, FTIR, and GC-MS performed in 2001-3 produced similar findings it should be noted that amino acid analysis was not performed to confirm the presence of proteins; regarding GC-MS, the presence of egg tempera and/or oil was based on fatty acid ratios (as was done in the 1993 GC-MS analysis).

²⁸⁴ Marika Spring, Rachel Morrison, and David Pegg, personal communication with the author, 21 September, 2009. Discussions with staff at the National Gallery in London in 2009 confirmed that scientists working in the cultural heritage sector are often well aware of these issues. It is evident that many of the early conclusions surrounding the presence of protein were formed based on fatty acid ratios and occasionally peaks present in FTIR spectra, scientific evidence that is no longer felt to be conclusive regarding the characterization of egg tempera. Furthermore, the National Gallery scientists also pointed out that pigments can interfere with these results, specifically red lakes and carbonates that can give false positives for the presence of proteins.

	St. Peter (PMA)	St. Paul (PMA)	St. John the Evangelist (PMA)	St. Martin (PMA)	St. John the Baptist (NGL)	St. Liberius/Gregory (NGL)	St. Matthias (NGL)	Founding of Santa Maria Maggiore (Naples)
GC-MS (1993-5/NGL)	Tempera (mid-tone flesh from face); Walnut oil with possible addition of egg tempera (orange drapery)	Tempera with possible trace Walnut oil (flesh from foot); Tempera and Oil (mid-tone in red drapery)	Tempera with trace Oil (flesh from shoulder; also in red cloak); Tempera and Oil? (red foreground; mid-tone in red drapery; highlight in green drapery)	Tempera and Oil? (red foreground)	Tempera with possible trace oil (flesh from foot; red cloak);	Linseed Oil (pink drapery)	Tempera and Oil (flesh from neck; perhaps from separate layers?); Linseed oil and possibly tempera (green drapery)	Drying Oil (Probably Linseed) and possibly egg tempera (white paint from snow)
FT-IR (1993/4-NGL)	<i>Not Reported</i>	Carboxylate bands indicate presence of drying oil (flesh from face)	No protein but oil detected (red foreground; oil is likely from Pb White underlayer); Oil (mid-tone in red drapery; highlight in green drapery)	No protein but oil detected (red foreground; oil is likely from Pb White underlayer)	<i>Not Reported</i>	2002 publication states that FTIR was performed but these results were not found in the PMA files	2002 publication states that FTIR was performed but these results were not found in the PMA files	<i>Not Reported</i>
Staining/Spot tests (1993/4-NGL)	No protein detected with Amido Black series (flesh from foot)	<i>Not Reported</i>	Oil shown with Ninhydrin test (green drapery)	Protein detected in all paint layers with Amino Black series (mid-tone from flesh in face)	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>
UV-Vis (2001/2-Gallone)	Egg Tempera in upper layers with underdrawing containing egg and trace oil (flesh from foot); Oil in three layers (flesh from forehead)	Egg in upper layers with underdrawing containing egg with trace oil, intermediate layer contained vermilion mixed with glue (proper right hand); oil three layers (flesh from forehead)	Oil in all upper layers (flesh from proper-left hand)	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>
GC-MS (2002-PMA)	Tempera (flesh from foot); Linseed Oil (flesh from face)	Tempera (flesh from foot); Linseed Oil (flesh from face)	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>
FT-IR (2002-PMA)	Protein detected (flesh from foot); Oil? (flesh from face)	Protein detected (flesh from foot); inconclusive (flesh from face)	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>	<i>Not Reported</i>

Table 4.1: A summary of analytical results obtained between 1993 and 2002 performed on Masolino and Masaccio's Santa Maria Maggiore altarpiece.

the Santa Maggiore altarpiece strongly suggests the use of drying oil as corroborated by most of the reported results; however, caution should be exercised when reviewing earlier published scientific findings associated with works of art.

According to Vasari, Masaccio's frescoes in the Brancacci Chapel of the Carmine had a dramatic impact on the young Fra Filippo (c. 1406-1469) so it is perhaps no accident that his paintings also tend to deviate from the norm.²⁸⁵ A northern influence can also be detected in some of Lippi's earlier works, most notably his *Tarquinia Madonna* (1437, Figure 4.11), one of the first Italian compositions to depict Mary within a realistic setting, a



Figure 4.11: Fra Filippo Lippi, *Madonna and Child (Tarquinia Madonna)* (1437, Galleria Nazionale d'Arte Antica, Rome).

²⁸⁵ Keith Christiansen, *From Filippo Lippi to Piero della Francesca: Fra Carnevale and the Making of a Renaissance Master*, ed. Keith Christiansen (New York: Metropolitan Museum of Art, 2005), 51.

characteristic that was more commonly encountered in Flemish works.²⁸⁶ It is possible that Lippi may have seen northern works in Pope Eugenius's collection as the *Tarquinia Madonna* was painted for Cardinal Vitellschi, a close acquaintance of the Pope. Holmes has also suggested that Lippi may have become familiar with the northern aesthetic working alongside from a German friar (Fra Arrigo d'Arrigo who is recorded as an illuminator) in 1418-37 at the convent in Carmine.²⁸⁷

Lippi's travels to northern Italy during the 1430s may also explain some of the less traditional aspects of his compositions such as the double portrait in New York (c. 1440, Figure 4.12) and his fresco cycles in the Prato Cathedral (c. 1452-66).²⁸⁸ By 1434 Lippi was recorded working in Padua under Francesco Squarcione, a workshop that has been connected to a number of renowned artists such as Cosme Tura and Andrea Mantegna whose works have also been associated with the oil medium.²⁸⁹ In Padua, Lippi may have been exposed to

²⁸⁶ Francis Ames-Lewis, "Filippo Lippi and Flanders," *Zeitschrift für Kunstgeschichte*, 42 (1979): 255-73, accessed October 20, 2015, <http://www.jstor.org/stable/1481985>; Jeffrey Ruda, "Flemish Painting and the Early Renaissance in Florence: Questions of Influence," *Zeitschrift für Kunstgeschichte*, 47 (1979): 210-36, accessed October 20, 2015, <http://www.jstor.org/stable/1482190>. To date no scientific analysis relating to the painting has been published.

²⁸⁷ Megan Holmes, *Fra Filippo Lippi: The Carmelite Painter* (New Haven: Yale University Press, 1999), 16-18.

²⁸⁸ *Ibid.*, 269. No scientific analysis of the double portrait has been published. Lippi's frescoes in the Prato Cathedral (excuted between 1452 and 1465) suggest that the artist was no longer employing the use of a verdaccio layer in his flesh tones. This was revealed in several abraded areas such as the feet of St. Gerolamo when the cycle was cleaned in 1995. See Maria Pia Mannini, *'La Nativita' di Filippo Lippi: Restauro, saggi e ricerche* (Pisa & Comune di Prato: Pacini Editore, 1995).

²⁸⁹ Holmes, *Fra Filippo Lippi: The Carmelite Painter*, 113; Liliana Leopardi, "Aesthetic Hybrids: Interpreting Carlo Crivelli's Ornamental Style" (PhD diss., New York University, 2007), 50-69; Steven Campbell, "Cosme Tura and Court Culture," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Steven Campbell (Boston: Isabella Stewart Gardner

northern painting practices as well as foreign artists, an experience that may account for the artist's willingness to accept foreign assistants into his workshop several years later.²⁹⁰ While scarcely any of Lippi's works have been subjected to a thorough technical investigation, art historian Frances Ames-Lewis suggests that several attributes in paintings dating to the late 1430s and 40s may be linked to Lippi's use of oil, such as the jewels depicted in the *Tarquinta Madonna* and the glass carafe in the *St. Lorenzo Annunciation* (c. 1440, Figure 4.13).²⁹¹ Analysis performed on Lippi's *St. Bernard's Vision of the Virgin* (1447) in London appears to confirm this theory, as samples collected from the grey robe of the Saint as well as the dark background were found to contain egg with traces of oil, although this particular painting appears to have a complex restoration history.²⁹² Examination of Lippi's lesser known *Nativity* (c. 1456) in the Museo Civico in Prato, indicates that by this date the artist began to abandon the use of the green verdaccio; transparent glazes present throughout the painting were observed during the restoration of the painting, leading scholars to believe that oil was

Museum, 2002), 11; Creighton E. Gilbert, *Italian Art 1400-1500* (Evanston, IL: Northwestern University Press, 1992), 34. See section 4.3 for more information on Squarcione's workshop.

²⁹⁰ Eliot W. Rowlands, "Filippo Lippi and his experience of painting in the Veneto region," *Artibus et Historiae* 10 (1989): 53-83, accessed October 25, 2015, <http://www.jstor.org/stable/1483284>; Christiansen, "Florence: Filippo Lippi and Fra Carnevale," 56. Christiansen cites a Spanish assistant and several other possible painters working with Lippi from 1442-45.

²⁹¹ Ames-Lewis, "Filippo Lippi and Flanders," 269.

²⁹² John Mills and Raymond White, "Organic Analysis in the Arts: Some Further Paint Medium Analyses," *National Gallery Technical Bulletin* 2 (1979): 74-5; Note that the authors performed cross-sectional staining and Gas Liquid Chromatography (GLC or GC) and intimate their hesitance at pronouncing definitive assignments as the painting was found to have been overpainted in previous restoration campaigns.

Figure removed due to copyrighting

Figure 4.12 (left) and Figure 4.13 (right): Fra Filippo Lippi, *Double Portrait at a Casement* (c. 1440, Metropolitan Museum of Art, New York; left) and a detail from Filippo Lippi's *Annunciation* (c. 1440, Basilica di San Lorenzo, Florence; right).

likely used by the artist.²⁹³ Lippi's famed *Barbadori* altarpiece (Figure 4.14) has also been linked to Flemish works, a masterpiece prompted Domenico Veneziano to send a letter to Piero di Cosimo in 1438 extolling the artist's abilities as a painter.²⁹⁴

²⁹³ Maria Pia Mannini, *'La Nativita' di Filippo Lippi: Restauro, saggi e ricerche* (Pisa & Comune di Prato: Pacini Editore, 1995), 50-1.

²⁹⁴ Ibid, 267; David S. Chambers, ed., *Patrons and Artists in the Italian Renaissance* (London: MacMillan and Co., Ltd., 1970), 91-5; Jeffery Ruda, *Fra Filippo Lippi* (New York: Phaidon Press, 1999), 132; —, "Flemish Painting and the Early Renaissance in Florence: Questions of Influence," 226-7; Edward C. Strut, *Fra Filippo Lippi* (London: George Bell & Sons, 1906), 57-8.

Figure removed due to copyrighting

Figure 4.14: Fra Filippo Lippi, *Barbadori Altarpiece* (1438, Musée du Louvre, Paris).

Unlike the technical study of Masaccio and Masolino's Santa Maria Maggiore altarpiece, scientific analysis has not been able to concretely assign sections of *Trinity Altarpiece* (also known as *The Trinity with Saints*, Figure 4.15) produced by both Fra Filippo Lippi and Pesellino (c. 1422-1457). Pesellino died soon after he began work on the project (commissioned in 1455), leaving Filippo Lippi to complete the altarpiece over the next five

Figure removed due to copyrighting

Figure 4.15: Fra Filippo Lippi and Pesellino, *Trinity Altarpiece* (1455-60, National Gallery, London).

years.²⁹⁵ A complicating factor when discussing the evolution and attribution of the altarpiece concerns Pesellino's training as it is generally thought that Pesellino was working in Lippi's workshop during this period.²⁹⁶ The analytical results were first performed in 1988/89 and

²⁹⁵ Ibid.

²⁹⁶ Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 17 (1996): 92.

then repeated again in 1995, identifying *tempera grassa* or a mixture of egg and oil in the green trees along the horizon, the yellow of the cloak on the leftmost saint, and in the red robe of St. Jerome. Other locations on the other hand tested positive for only egg, such as the blue sky and the white highlights of the rocks within the scenes of the predella.²⁹⁷ As it is nearly impossible to know the state of this painting soon after Pesellino's death these results do not help in assigning areas to each individual artist; however, technical evidence suggests that these artists may have been exploiting the oil medium to help impart a richer, translucent quality to certain colors, namely dark greens, reds, and yellows. Pure egg tempera was reserved for lighter colors such as whites and blues perhaps to avoid the inevitable yellowing that is eventually caused by drying oils. If Pesellino was incorporating oil into his paints, he may have first encountered the medium during his time as a pupil in Filippo Lippi's workshop.

Like Masolino and Fra Filippo Lippi, Domenico Veneziano (c. 1410-1461) seems to have also occasionally been influenced by the northern aesthetic and may have also been an early adopter of the oil medium. Vasari included Domenico in his tale relating to the spread of oil painting in Italy, alleging that the artist was brutally murdered by a jealous Andrea del Castagno (1423-1457) over his mastery of the oil technique.²⁹⁸ Little is known about Domenico's training; he was born in Venice and moved to Florence around 1422-23 to work under Gentile da Fabriano (c. 1370-1427). The young artist would have witnessed Gentile's

²⁹⁷ Ibid; Marika Spring, David Peggie, and Rachel Morrison, personal communication with the author, 21 September, 2009. The first analysis was performed in 1988/89 on the sky, rocks, and robe of St. Jerome using FTIR. Later analysis done with GC-MS yielded an A/P ratio of .45 for the green trees while FTIR did not identify protein.

²⁹⁸ Nuttal, *From Flanders to Florence*, 35; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48, 53. Note that Castagno's death is recorded to be around 1457, four years prior to the death of Domenico Veneziano.

work on a polyptych depicting *The Intercession* (c. 1423) for the church of San Niccolò Oltrarno in Florence, a painting that was identified as partially painted in oil (and egg tempera) using FTIR in during the restoration of the painting in 2006.²⁹⁹ It may have been under Gentile's tutelage that Domenico first became familiar with the oil medium; in 1439 the artist was documented ordering a large quantity of drying oil for a collaborative fresco project together with Andrea del Castagno, Piero della Francesca (c. 1416/17-1492), and Alessandro Baldinovetti (1447-1510) in the church of Sant'Egidio in Florence (home to the Portinari chapel).³⁰⁰ While the frescoes have not survived, Jill Dunkerton suggests this large quantity of oil could have been used for lavish decorations including mordant gilding and, more importantly, *a secco* paints, colors applied over the pictorial fresco once the lime had completely oxidized (the *intonnaco* layer).³⁰¹ For unknown reasons Domenico halted work on

²⁹⁹ Marco Ciatti, Cecilica Frosinini, and Roberto Bellucci, *Il Gentile Risorto; Il politico dell'Intercessione di Gentile da Fabriano: studi e restauro* (Firenze: Edizioni Firenze, 2006), 144, 194; Note that the authors only cite the use of cross-sectional analysis, FTIR, and solvent extraction using a 2:1 pentane/methylene chloride mixture. While it is unclear whether the latter generated an FTIR spectrum or a GC spectrum, the authors deduced the presence of drying oil from the solvent extraction process. Other samples showed the presence of proteinaceous materials (which in some instances was determined to be glue) combined with traces of fatty acids. A cross-section collected from Gentile's *Madonna and Child* (c. 1425) of the Quaratesi altarpiece also suggested the presence of oil; however, it is unclear whether analytical testing was conducted on the cross-section or whether this conclusion was based on visual examination alone. See Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 39, 64 (Note 54).

³⁰⁰ Nuttal, *From Flanders to Florence*, 162, 183; Helmut Wohl, "Domenico Veneziano Studies: The Sant'Egidio and Parenti Documents," *The Burlington Magazine* 113 (1971): 635-41, accessed November 4, 2015, <http://www.jstor.org/stable/876783>; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48-9, 54.

³⁰¹ *Ibid*; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197. Dunkerton describes traces of gilding on Domenico's damaged *Virgin and Child* painted for the Carnesecchi tabernacle, indicating that his earlier fresco cycles may have been highly decorated.

the cycle in 1445, and with Andrea del Castagno completed the cycle between 1451 and 1453. If Domenico had been using oil to execute portions of the frescoes it is possible that he began experiencing difficulties related to drying within the cool confines of the church. What is more probable is that he received a commission from the Church of Santa Lucia dei Magnoli for his second surviving signed work, the *St. Lucy Altarpiece* (c. 1445, Figure 4.16), a masterpiece in which Domenico pushed the tempera medium to its absolute limit, emulating intricate golden threads without the use of metal leaf and jewels with definitive strokes of paint. The northern influence in the *St. Lucy* altarpiece is abundantly evident, a testament to Domenico's reputed skill as an oil painter, or at least his familiarity with the northern technique; this masterpiece may account for a panel painting "colorita a olio" listed in the 1492 inventory of the Medici collection that is attributed to Veneziano.³⁰² This may explain why the artist was called to formally consult on Lippi and Pesellino's *Trinity* altarpiece in 1457, a masterpiece created using both egg and oil.³⁰³

One of Domenico's first assistants was Piero della Francesca (c. 1415-1427), another painter who likely embraced the oil medium during his career. After assisting Domenico with the Sant'Edigio frescoes, Piero returned to San Sepolcro where he had spent much of his early years training alongside several artists. By 1445 he received a commission from the Compagnia della Misericordia, a confraternity of Borgo Sansopolcro, to paint a polyptych within three years time although Piero did not complete the altarpiece until seventeen years

³⁰² Nuttal, 162; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48-9.

³⁰³ Dillian Gordon, "The missing predella panel of Pesellino's *Trinity* altarpiece," *Burlington Magazine* 138 (1996): 87, accessed November 22, 2015, <http://www.jstor.org/stable/886733>; Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 30-1; — et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 201.

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Figure 4.16: Domenico Veneziano, *St. Lucy Altarpiece* (c. 1445, Uffizi Gallery, Florence).

later. It is presumed that Piero must have begun to work on the central panel for the polyptych, the *Madonna della Misericordia* (Figure 4.17), at least before leaving for Ferrara to paint a series of frescoes. Based on the examination of the painting, scholars have concluded that Piero may have become familiar with the oil technique during his time in Ferrara and Arrezzo before his return to Sansopolcro in 1462; some portions of the *Madonna*

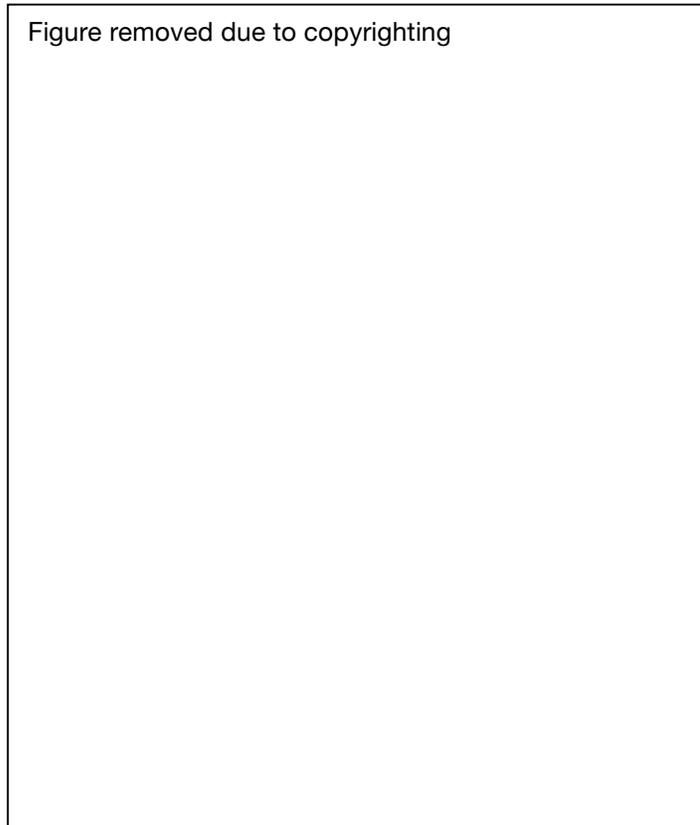


Figure 4.17: Piero della Francesca, *Madonna della Misericordia* (1445-62, Pinacoteca Comunale, Sansepolcro).

della Misericordia appears to have been were executed in oil or in *tempera grassa* based on the presence of large drying cracks that are more characteristic of oil films rather than egg tempera.³⁰⁴

³⁰⁴ Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 30-1; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 51; Roberto Bellucci and Cecilia Frosinini, "Piero della Francesca's Process: Panel Painting Technique," in *Painting techniques history, materials and studio practice: contributions to the Dublin Congress, 7-11 September 1998*, eds. Ashok Roy and Perry Smith, (London: International Institute for Conservation of Historic and Artistic Works, 1998), 89-93.

The *Madonna della Misericordia* has not been subjected to medium analysis, but paint cross-sections collected from the central panel revealed the presence of a medium-rich layer atop the gesso ground that may contain oil.³⁰⁵ This technique, presumably intended to reduce the absorbency of the gesso ground, is more commonly encountered in northern works during the fifteenth century; examination of works created after Piero's departure from Sansopolcro confirms that he continued to apply this medium-rich layer over his prepared panels.³⁰⁶ Art historian Ames-Lewis cites a *Portrait of Sigismondo Malatesta* (c. 1451) that has been identified as partially painted in tempera grassa and oil as well as a now lost double-sided *gonfalone* for the Borgo in 1466, a banner that was stipulated to be 'lavorato a oglio.'³⁰⁷ Piero may have first become familiar with northern painting techniques during his time in Arezzo, Urbino, and Ferrara; technical studies of paintings by artists known to have frequented cities and courts throughout northern Italy such as Carlo Crivelli (c. 1430-1495) and Cosme Tura (c.

³⁰⁵ Frosinini and Bellucci, "Piero della Francesca's Process: Panel Painting Technique," 91.

³⁰⁶ Ibid; Cross-sectional samples collected from the *Polyptych of Saint Augustine*, the *Polyptych of Sant'Antonio*, the *Flagellation* and the *Pala di San Bernardino* revealed the presence of medium-rich layer atop the ground although no medium analysis was performed. On northern painting techniques see the following: Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 193-6; Rachel Billinge et al., "The Materials and Techniques of Five Paintings by Rogier van der Weyden and his Workshop," *National Gallery Technical Bulletin* 18 (1997): 68-86; Cathy Metzger and Griet Steyaert, "Painting, A Distinct Profession," in *Rogier van der Weyden: Master of Passions*, eds. Lorne Campbell and Jan Van der Stock (Zwolle and Leuven: Waanders Publishers and Davidsfonds, 2009), 167.

³⁰⁷ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 51; Michel Laclotte, "Le portrait de Sigismond Malatesta par Piero della Francesca," *Revue du Louvre* 28 (1978): 255-66. No specific analytical technique is mentioned in the Laclotte's publication so it is likely this conclusion is based on earlier forms of analysis (e.g. solubility/heat tests) and/or visual examination.

1430-1495) have indicated that these artists also adopted the use of the oil medium (at least partially), a topic that will be discussed in the following section.³⁰⁸

Examination of Piero's frescoes done in the main choir chapel for the church of San Francesco has confirmed the presence of egg- and oil-based paints. Samples collected from the *Legend of the True Cross* frescoes (1452-66, Figure 4.18) were analyzed during the restoration of the cycle from 1993 to 1996 and suggested the presence of *a secco* additions done in tempera and *tempera grassa*.³⁰⁹ These additional layers were applied directly atop the *buon fresco* layer and were mixed with pigments that are typically not stable in the fresco medium such as lead white, copper greens, and vermilion.³¹⁰ During his time in Arezzo, Piero received several commissions including requests for painted banners, specifically one that

³⁰⁸ Keith Christiansen, "Saint Jerome in the Wilderness," in *Piero della Francesca: Personal Encounters*, ed. Keith Christiansen (New York: Metropolitan Museum of Art, 2014), 27; Christiansen, *From Filippo Lippi to Piero della Francesca: Fra Carnevale and the Making of a Renaissance Master*, 46; Frosinini and Bellucci, "Piero della Francesca's Process: Panel Painting Technique," 91. Frosinini and Bellucci postulate that since Piero is known to have handed over all of his legal possessions to his brother Marco in 1458 it is very possible that the artist ventured north of the Alps not unlike Zanetto Bugatto's apprenticeship under Rogier van der Weyden from 1460 to 1463; however, no evidence has since been discovered that can concretely support this theory.

³⁰⁹ Maria Perla Colombini, Francesca Modugno, Marina Giacomelli, and Sandro Francesconi, "Characterisation of proteinaceous binders and drying oils in wall painting samples by gas chromatography-mass spectrometry," *Journal of Chromatography A* 846 (1999): 113-24, doi:10.1016/S0021-9673(99)00344-1; Anna Maria Maetzke et al., "Progetto Piero della Francesca: il restauro della 'Leggenda della Vera Croce,'" *Kermes: la rivista del restauro* 14 (2001 Jan-Mar): 30. Maetzke et al. state that Piero "also used tempera and *tempera grassa*, which allowed him to use a wide variety of pigments such as white lead, malachite, verdigris, azurite the resin-coated copper, vermilion, red lead, the madder lake, lead-tin yellow..." GC-MS was performed to characterize the organic binders present in superficial layers of paint above the pigmented *buon fresco*.

³¹⁰ Maetzke et al., "Progetto Piero della Francesca: il restauro della 'Leggenda della Vera Croce,'" 30-1.

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Figure 4.18: Piero della Francesca, *Exaltation of the Cross* (detail from *The Legend of the True Cross* cycle) (1452-66, San Francesco, Arezzo).

documents describe as having been executed painted in oil in 1466.³¹¹ Recent analysis performed on a painting dating to this period, *St. Jerome and a Supplicant* (c. 1460-64?), has revealed the use of mixed techniques, supporting the notion that Piero was routinely incorporating drying oils by the time he had returned to Sansopolcro.³¹² Dunkerton

³¹¹ Gaetano Milanesi, *Nuovi documenti per la storia dell'arte Toscana dal XII a XV secolo* (Firenze: Dotti, 1901), 299-301; Carlo Bertrelli and Antonio Paolucci, *Piero della Francesca e le corti italiane* (Milano: Skira, 2001), 48-9.

³¹² Roberto Bellucci, Cecilia Frosinini, and Chiara Rossi Scarzanella, "The Restoration and Technical Examination of 'Saint Jerome and a Supplicant,'" in *Piero della Francesca: Personal Encounters*, ed. Keith Christiansen (New York: Metropolitan Museum of Art, 2014), 80. Note that the authors do not disclose what specific types of analyses were carried out on the painting to characterize the binding media.

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Figure 4.19 and Figure 4.20: Piero della Francesca's *Nativity* (c. 1470-75, National Gallery, London; left) and a detail of the shepherd's faces (right).

has summarized analytical findings from samples collected from another altarpiece dating to this period, the *Saint Augustine Altarpiece* (1460-70); certain passages in the *St. Michael* panel were found to have been painted using walnut oil as the principal medium.³¹³

Dunkerton points out that the *St. Michael* also possesses a curious layer of brown under-

³¹³ John Mills and Raymond White, "The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 72-7; Ashok Roy, "Perugino's 'Certosa di Pavia Altarpiece': New Technical Perspectives," in *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS TechWorkshop, Quaderni di Kermes*, eds. Brunetto Brunetti, Claudio Seccaroni, and Antonio Sgamellotti (Florence: Nardini Editore, 2003), 15; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197; Note that GC was performed on samples from the blue sky, the white wing, and a brownish, unpigmented layer.

modeling in the flesh tones as opposed to the typical verdaccio green that was normally employed, a similar layer that is also visible in the unfinished or damaged heads of the shepherds in the *Nativity* (c. 1470-75, Figures 4.19 and 4.20) in London.³¹⁴ Both of these works possess areas where the paint layer shows signs of drying defects, suggesting a general unfamiliarity with the working properties of the oil medium but also a willingness to employ non-traditional techniques.

Piero was not the only artist experimenting with oil on wall paintings. Benozzo Gozzoli's (c. 1421-1497) *Chapel of the Magi* underwent a lengthy restoration from 1987-1992, affording conservators and scientists a closer look at the materials used by the artist (Figure 4.21).³¹⁵ Begun in 1459 and completed in 1461, a large portion of the fresco cycle was executed *a secco* similar to Piero's frescoes depicting the *Legend of the Cross*, using layers of colors mixed in tempera and oil to portray clothing, animals, and vegetation. One of the red robes worn by an angel was painted with a red lake ground in oil that had been brushed atop a lead white layer also containing drying oil. In another area depicting a pomegranate tree, Benozzo first laid down a layer of black tempera paint and built up layers of green malachite mixed with verdigris in oil. A letter written in 1459 by Benozzo to his patron Piero di Cosimo de Medici supports the technical findings, as the artist states "I would have to come talk to you, but this morning I began to apply the azure, and it cant be left; its very hot, and the glue could go bad at any moment."³¹⁶ An earlier work by Benozzo,

³¹⁴ Ibid.

³¹⁵ Palazzo Medici-Riccardi, *Chapel of the Magi: Benozzo Gozzoli's Frescoes in the Palazzo Medici-Riccardi Florence*, ed. Cristina Acidini Luchinat (London: Thames & Hudson, 1994), 375. Note that the author does not describe the particular type of analyses used for characterization of the binding medium.

³¹⁶ Ibid, 8.

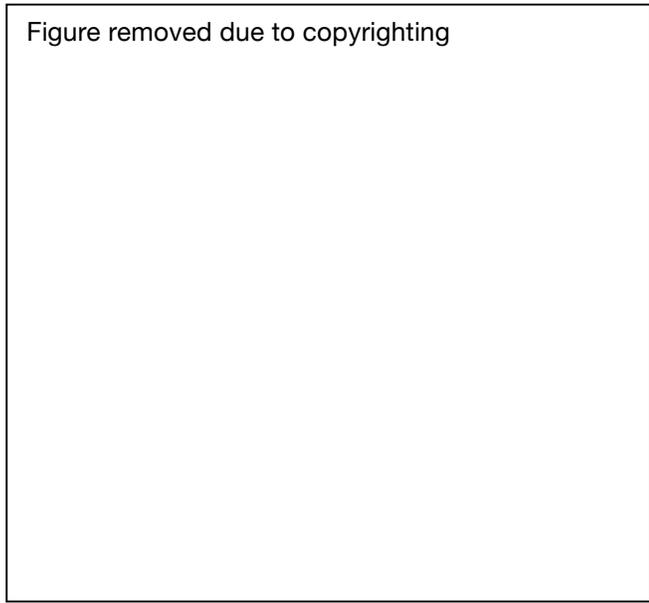


Figure 4.21: Benozzo Gozzoli, *The Procession of the Youngest King* (detail from *The Chapel of the Magi*) (1459-60, Palazzo Medici Riccardi, Florence).



Figure 4.22: Benozzo Gozzoli, *The Sapienza Nuova Altarpiece* (1456, Umbria National Gallery, Perugia).

The Sapienza Nuova Altarpiece (1456, Figure 4.22), has also been found to contain gum, protein, and drying oil (although past restoration campaigns may have left traces of these materials behind).³¹⁷ The yellow mantle of St. Peter was determined to have been painted first in a protein-containing medium, followed by an additional yellow layer bound in protein, gum, and drying oil. Both San Paolo's red robe and the Virgin's blue mantle were also painted using a combination of different media, while the latter contained a lower layer consisting of egg tempera and what appears to be calcium carbonate (a white pigment that is more commonly encountered in northern paintings). Recent analysis conducted on a canvas painting (*The Raising of Lazarus*, c. 1492) at the National Gallery of Art in Washington also revealed the presence of a drying oil while samples from a closely related painting (*The Descent from the Cross*, c. 1491/2) at the Horne Museum were found to contain only protein; however, the analytical results associated with both paintings were not completely conclusive due in part to previous restoration campaigns.³¹⁸ Though only a few of his paintings have

³¹⁷ Assja Landau and Giovanni Martellotti, "Il restauro della pala della Sapienza Nuova di Benozzo Gozzoli," in *Beato Angelico e Benozzo Gozzoli: Artisti del Rinascimento a Perugia*, ed. Vittoria Garibaldi and Tiziana Biganti (Milan: Silvana Editoriale, 1998), 142-7. Only cross-sectional analysis was performed in conjunction with FTIR to identify the presence of organic components. The authors do state the difficulty of differentiating between original materials and restoration but do not explain how they were able to assign certain oil-containing glazes to Gozzoli.

³¹⁸ "Benozzo Gozzoli – 'The Raising of Lazarus,'" Conservation file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC. Both paintings were analyzed in 1991 using High Performance-Liquid Chromatography (HPLC) for the detection of proteins while GC-MS was performed to detect the presence of fatty acids. Samples from *The Descent from the Cross* revealed only proteins (a small amount of hydroxyproline suggested the possible presence of a ground layer) while curiously GC-MS failed to detect any fatty acids (suggesting that the binder may be glue-based). Samples from *The Raising of Lazarus* produced fatty acids related to drying oil as well as amino acids (including hydroxyproline). Additional analysis performed in 2004 on the *The Raising of Lazarus* utilizing FT-IR and GC-MS identified similar markers. As this painting has undergone two lining campaigns (one of which was performed using lead white oil paint) and

been thoroughly examined, it seems likely that Benozzo continued to use different types of media, utilizing oils for *a secco* additions and certain passages in his easel paintings.

Fra Filippo Lippi's thriving workshop may have been integral to the early adoption of oil paint in central Italy, but two additional Florentine workshops likely played a greater role in solidifying the technique's popularity among artists. Both Andrea del Verrocchio (c. 1435-1488) and Domenico Ghirlandaio (1449-1494) are credited with training some of Italy's most renowned painters including Sandro Botticelli (c. 1445-1510), Lorenzo di Credi (c. 1459-1537), Michelangelo (1475-1564), Pietro Perugino (c. 1446/145-1523), and Leonardo da Vinci (1452-1519), all of whom have produced paintings that are completely or partially in oil. Verrocchio's early training and familiarity with the oil technique is not clear, although he may have worked under Fra Filippo Lippi in Prato during the 1460's.³¹⁹ To date few paintings attributed to Verrocchio have been subjected to scientific analysis; examination of *The Virgin and Child with Two Angels* (c. 1476-78) suggests that the artist (possibly assisted by a pupil) used predominantly egg tempera although characterization of the medium has been complicated by past retouching campaigns performed in egg tempera/mastic emulsions and drying oils.³²⁰ Like Domenico Veneziano, Flemish paintings impacted Verrocchio's compositional decisions; Dunkerton describes the exquisite manner in which paint has been used instead of gold leaf to render the golden highlights throughout the fabrics in Verrocchio's *The Virgin and Child with Two Angels* painted around c.1467-9 (Figure 4.23),

likely contains oil-resin varnish residues, it is difficult to confirm the original nature of the binding medium.

³¹⁹ David Alan Brown, *Leonardo da Vinci: Origins of a Genius* (New Haven: Yale University Press, 1998), 26.

³²⁰ Jill Dunkerton and Luke Syson, "In Search of Verrocchio the Painter: Cleaning and Examination of 'The Virgin and Child with Two Angels,'" *National Gallery Technical Bulletin* 31 (2010): 4-41.

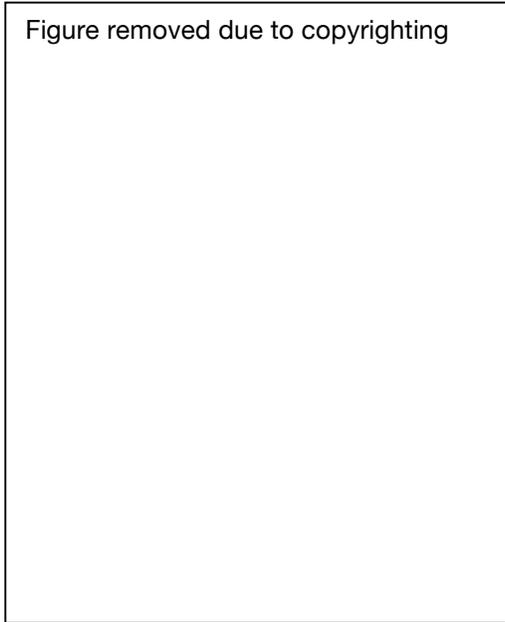


Figure 4.23: Andrea del Verrocchio, *The Virgin and Child with Two Angels* (1467-9, National Gallery, London).

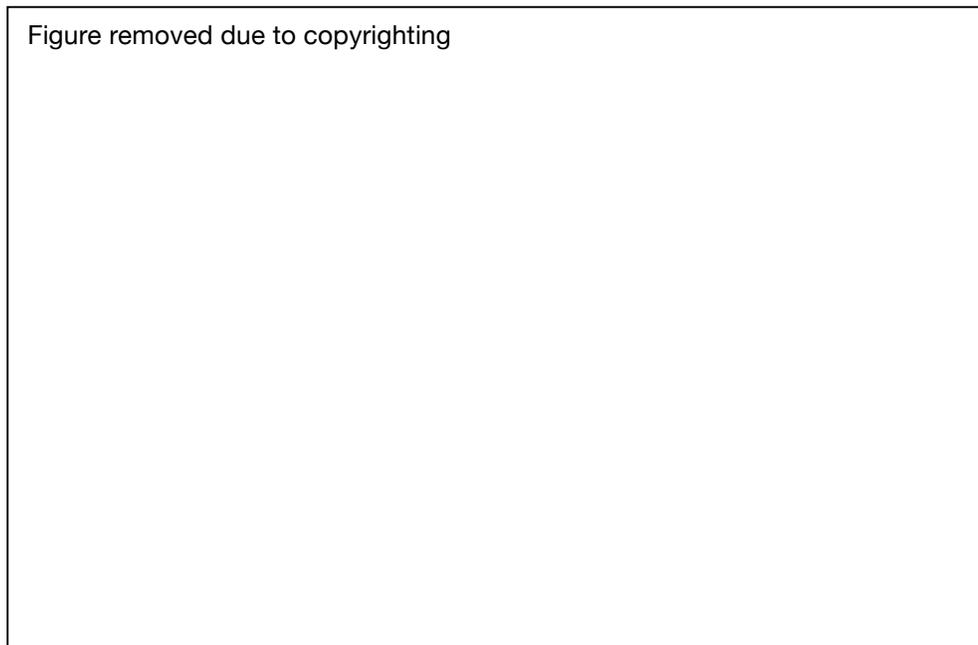


Figure 4.24 (left) and Figure 4.25 (right): Andrea del Verrocchio, *The Baptism of Christ* (1472-5, Uffizi Gallery, Florence; left) and a detail of the rocky cliffs (right).

recalling the delicately applied lead-tin yellow highlights often seen in northern paintings.³²¹ Verrocchio also reincorporated the craggy rocks depicted in Jan van Eyck's St. Francis Receiving the Stigmata (see Figures 2.7 and 2.8) in his Baptism of Christ (c. 1475, Figures 4.24 and 4.25), commissioned around 1468 for the Church of San Salvi.³²² In describing the evolution of the Baptism of Christ, Vasari assigns one of the angels in the painting to the young Leonardo da Vinci, proclaiming the figure to be "so superior to the rest of the work that Andrea resolved he would never take up a brush again."³²³ Verrocchio may have halted work on the painting during the late 1460s due to an increasing number of commissions, leaving Leonardo to complete much of the composition.³²⁴ The painting has undergone multiple restoration campaigns and to date no samples have been collected to characterize the binding media; however, visual examination and analysis has shown that other areas of the painting do appear to have been completely reworked in an oil-containing medium.

Though much has been published regarding Verrocchio's most renowned pupil, scarcely any of Leonardo's paintings have been subjected to comprehensive medium analysis. Leonardo's writings, however, specifically his *Codex Atlanticus* (c. 1478-1519), provide some insight regarding the materials that were both used and developed by the painter throughout

³²¹ Jill Dunkerton, "Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence," *National Gallery Technical Bulletin* 32 (2011): 6.

³²² Ibid; Pietro C. Marani, *Leonardo da Vinci: The Complete Paintings* (New York: Harry N. Abrams, Inc., 2000), 62-6.

³²³ Giorgio Vasari, *Le vite de piu eccellenti pittori, scultori e architettori*, eds. Paolo Barocchi and Rosanna Bettarini, vol. III (Verona: Sansoni-SPES, 1971), 539.

³²⁴ Dunkerton, "Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence," 6.

his career.³²⁵ As an artist, who was presumably trained in tempera, the few surviving paintings that have been firmly linked to Leonardo suggest an early awareness of the oil medium. Furthermore, painting by artists who trained under Leonardo have been found to contain both egg and oil paints; however, only one easel painting attributed to the master painter has been found to contain both types of media.³²⁶

³²⁵ Jean Paul Richter, *The Literary Works of Leonardo da Vinci*, vol. I (London: Sampson Low, Marston, Searle & Rivington, 1883), 319-22, accessed December 10, 2015, <http://warburg.sas.ac.uk/pdf/cnm22b2242052v1.pdf>; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 203-4. See chapter 3, section 3.3 for more information on written accounts relating to Leonardo da Vinci and his technique.

³²⁶ Johann Koller and Ursula Baumer, “‘Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.’ Leonardos Rolle in der frühen italienischen Ölmaleri,” in *Leonardo da Vinci, Die Madonna mit der Nelke*, eds. Cornelia Syre, Jan Schmidt, and Heike Stege (Munich: Alte Pinakothek and Schirmer/Mosel, 2006), 155-74; Dunkerton, “Leonardo in Verrocchio’s Workshop: Re-examining the Technical Evidence,” 4-31; Pietro C. Marani, *Leonardo: catalogo completo dei dipinti* (Firenze: Cantini Editore, 1989), 41-5; Maud Cruttwell, *Verrocchio* (London: Duckworth & Co., 1904), 50; Raymond White and Jennifer Pilc, “Analyses of Paint Media,” *National Gallery Technical Bulletin* 17 (1996): 91-103; Marika Spring, Carol Mazzotta, Ashok Roy, Rachel Billinge, and David Pegg, “Painting Practice in Milan in the 1490s: The Influence of Leonardo,” *National Gallery Technical Bulletin* 32 (2011): 78-112. Giovanni Antonio Boltraffio is known to have studied under Leonardo. Boltraffio’s *The Virgin and Child* (c. 1493-99) was analyzed twice: once in 1996 using FTIR and GC-MS and a second time in 2011 using ATR-FTIR and GC-MS. In 1996, egg tempera (with a trace amount of oil) in the dark underpainting while upper paint layers (the flesh of the Christ child) were found to contain walnut oil. Results from the 2011 study, however, found only traces of oil in the dark underpaint instead of tempera. Boltraffio’s *Portrait of a Man* (c. 1500) was also analyzed in 2011 and found to contain heat-bodied oil (likely walnut) in two samples from the greenish-blue background while two additional paintings attributed to the artist in the National Gallery London were also found to contain oil. Marco d’Oggiono has also been considered to be one of Leonardo’s most important pupils; his *Portrait of a Man Aged 20* (1494) was found to contain walnut oil in the blue doublet and the greenish-blue mantle (using GC). Marco’s *Virgin and Child* (c. 1520) was also found to contain drying oil (walnut) in samples from the sky, the foliage, and Christ’s flesh using GC-MS.

As discussed in the previous chapter, written accounts dating between the twelfth and sixteenth centuries (including Leonardo's own records) do not contain extensive recipes or passages describing the use of egg-oil paint systems with the exception of one manuscript that outlines instructions for the decoration of walls.³²⁷ On the other hand, analysis performed in 2006 on samples collected from Leonardo's *Madonna of the Carnation* (1478-80; Figure 4.26) in Munich suggest that the artist may have used both egg and oil paints early on in his career.³²⁸ Two small samples collected from the edge of the painting were analyzed using chromatographic methods, specifically GC-MS for the characterization of drying oils and ion-exchange chromatography for the identification of proteinaceous components (e.g. glue, egg yolk, etc.): paint and *imprimatura* layers from both the Madonna's blue robe and the brown background revealed the presence of walnut oil, varnish, linseed oil, and egg- and/or glue-based proteins.³²⁹ While Dunkerton suggests that the presence of linseed oil may be due to the

³²⁷ See Chapter 3, section 3.2 for information relating to the recipe outlined in the *Liber diversarum arcium*. It should be noted that while a considerable number of texts have been found to contain information relating to historic artistic practices, only a handful have been translated and/or published; however, to date no references have been unearthed that specify the use of oil glazes over egg-based paints or the use of egg-oil mixtures (*tempera grassa*).

³²⁸ Koller and Baumer, " 'Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.' Leonardos Rolle in der frühen italienischen Ölmaleri," 155-174.

³²⁹ *Ibid*; For the blue sample, the composition of each layer save the glue-gesso ground (from the bottom to the top) is described as the following: 1) yellowish priming consisting of glue with traces of oil towards the top of the layer 2) *imprimatura* consisting of lead white in linseed oil 3) brown intermediate layer containing walnut oil and an unidentified natural resin 4) black paint layer consisting of carbon black and lead white bound in walnut oil (possibly some resin) with additions of linseed oil and egg protein 5) blue paint layer containing lapis lazuli bound in walnut oil, linseed oil, an unidentified natural resin, and traces of egg protein 6) varnish layer (restoration coating) containing dammar. For the brown sample, the composition of each layer save the glue-gesso ground (from the bottom to the top) is described as the following: 1) yellowish priming consisting of glue with traces of oil towards the top of the layer 2) *imprimatura* consisting of lead white in linseed oil 3) brown intermediate layer containing walnut oil and/or an unidentified natural resin with traces of

application of unoriginal oil-containing materials (e.g. paints, varnishes), Johann Koller and Ursula Baumer attribute these additions to Leonardo's desire to speed the drying rate of his walnut oil medium and identify linseed oil as the primary binder in the lower *imprimatura* layer(s).³³⁰ The presence of proteinaceous additions, however, is more perplexing; Koller and Baumer state that while the amount of protein recovered was too small to determine the presence of egg yolk and/or egg white, the additions of protein-based paints was not unusual for the preparation of certain pigments during the Medieval and Renaissance periods.³³¹ Such a suggestion deviates from earlier notions of egg-oil emulsion paints (*tempera grassa*), specifically that the presence of protein and oil markers suggest that artists were intentionally adding oil to their tempera paints in order to achieve certain effects; here the authors instead attribute proteinaceous substances as simple by-products leftover from the preparation of pigments rather than a conscientious addition to oil-based paints made by Leonardo himself.

glue and egg-based proteins 4) varnish layer (restoration coating?) containing dammar, mastic, and walnut oil. For difficulties involved with sampling and accurate identification of drying oils and proteins see chapters 5 and 6.

³³⁰ Ibid. Dunkerton, "Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence," 31 (Note 53). Dunkerton summarizes the analytical results of the *Madonna of the Carnation* as the following: The results of analysis of two small samples from the edge of the painting are complicated. In addition to the walnut oil, which is clearly the principal binder, small amounts of linseed oil were found in the upper blue layer. Leonardo might have added some linseed oil to his paints (and seems to have used linseed oil for the first white *imprimatura* layer) but another possibility is that it is present as a result of contamination by later oil-varnish layers. Traces of egg proteins were also reported, with the suggestion that they might be related to the preparation of the blue pigment.

³³¹ Ibid. The authors state that ox-blood (blood albumin) was routinely added to red colored pigments (such as Turkish Red) to produce a more intense hue while blue and green pigments (such as azurite, malachite, verdigris, etc.) almost always contain a certain amount of protein binder (e.g. egg, glue, etc.). Further research is needed to confirm these generalizations although ancient written sources occasionally mention the use of proteinaceous materials in the preparation of certain pigments.

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Figure 4.26 (left) and Figure 4.27 (right): Leonardo da Vinci, *The Madonna of the Carnation* (1478-80, Alte Pinakotek, Munich; left) and *The Virgin of the Rocks* (1491/2 and 1506-8, National Gallery, London; right).

While Dunkerton questions the origin of the linseed oil found in the samples from the *Madonna of the Carnation*, it should be pointed out that Leonardo does mention the use of boiled linseed oil in his writings in addition to his extensive account of walnut oil.³³² Based on analysis performed in 1995/6, Dunkerton describes walnut oil as the principal medium used in Leonardo's *The Virgin of the Rocks* (1491/2 and 1506-8; Figure 4.27) in London and points to additional unfinished works that reveal preparatory washes of transparent paint

³³² Dunkerton, *Ibid.*; Richter, *The Literary Works of Leonardo da Vinci*, vol. 1, 319-22. See Chapter 3, section 3.3 for more information on Leonardo's written records.

(presumably oil-based) such as his *Adoration of the Magi* (1481); however, recent analysis performed using GC-MS and FTIR in 2011 during the restoration of the *Madonna of the Rocks* identified the use of both linseed and walnut oil.³³³ Though this recent discovery may be attributed to advancements in scientific instrumentation and/or methodology, it should be noted that only FTIR appears to have been used to detect the presence of proteins in the London *Madonna of the Rocks*, an analytical technique that is not especially conclusive for the detection and characterization of proteins.³³⁴ Furthermore Leonardo's experimental

³³³ Dunkerton, 19-20; -- et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 203-4; Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 17 (1996), 96-102; Larry Keith, Ashok Roy, Rachel Morrison, and Peter Scade, "Leonardo da Vinci's *Virgin of the Rocks*: Technique and the Context of Restoration," *National Gallery Technical Bulletin* 32 (2011): 42, 48. Analysis performed in 1995/6 using GC-MS identified walnut oil in five samples collected from the London *The Virgin of the Rocks*: 1) a sample from the right side in the brownish-black paint of the rocks 2) a red-brown *imprimatura* from sample 1 3) blue-black of angel's robe 4) a sample from a green leaf along the lower edge 5) a sample from the pale blue-green sky between the two rocks towards the top. GC-MS and/or FTIR analysis performed in 2011 yielded the following results: 1) partially heat-bodied walnut oil was present in the azurite-underlayer and ultramarine upperlayer of the sky 2) ultramarine paint on the right side of the picture was found to contain heat-bodied linseed oil 3) the grey underpainting of the Virgin's tunic and the red-lake containing underpainting beneath the angel's blue robe contained heat-bodied linseed oil 4) non-heat-bodied walnut oil was found in the uppermost *imprimatura* layer 5) the dark brown, thinly applied paint of the rocks in the foreground contained heat-bodied walnut oil 5) a similar sample collected from the left side of the picture contained heat-bodied linseed oil 6) a flesh sample from the foot of St. John the Baptist was found to contain walnut oil 7) the ultramarine paint from the Virgin's mantle was found to contain predominately oil. The latter sample is described by the authors as being particularly difficult to analyze; FTIR suggested the presence of protein while the GC-MS results yielded surprisingly low amounts of azelaic acid for a normal drying oil (no protein analysis was performed with GC-MS in this instance). These results are partially attributed to the presence of calcium oxalates which the authors state can complicate the characterization of binding media. Furthermore, the sample collected from the flesh of St. John was also complicated by the presence of lead soaps (identified using FTIR), organo-metallic complexes that can alter the ratio of fatty acids. For additional information relating to the challenges associated with the identification of binding media please refer to chapters 5 and 6.

³³⁴ Ibid.

methods, some of which lead to disastrous results, should be taken into account when performing medium analysis of his works; Dunkerton points out that Pope Leo X complained about “Leonardo wasting time on the distillation of herbs and oils before beginning to paint,” materials that may have occasionally found their way into his binders and varnishes.³³⁵ Whether or not the artist may have employed egg-oil paint systems or even different drying oils is a question that may never be adequately answered unless more comprehensive medium analysis is performed on Leonardo’s small but significant body of work.

Ghirlandaio’s studio became extremely productive during the later part of the fourteenth century, generating panel paintings and frescoes that often included direct references to northern works. Like Verrocchio, Ghirlandaio was initially trained in metalworking before he became a painter, perhaps a testament to the artist’s willingness to explore non-traditional artistic techniques including the use of drying oils.³³⁶ The adoption of oil in the Ghirlandaio workshop may have been a familiar affair; David’s painting *The Virgin and Child with Saint John* in London (c. 1480s) was found to contain oil in the red glazes of

³³⁵ Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 203-4; Richter, *The Literary Works of Leonardo da Vinci*, vol. 1, 317-22; Giovanni Paolo Lomazzo, *Idea of the Temple of Painting*, trans. Jean Julia Chai (Pittsburgh: Pennsylvania State University Press, 2013), 84. Leonardo writes about the preparation of other non-drying oils like mustard seed oil; it is possible that Leonardo may have inadvertently incorporated small amounts of non-drying oil into his linseed oil medium, particularly if he was using the same press that he refers to in his notes. The artist’s mention of transparent bituminous browns, descriptions of oil-resin varnishes, and Lamazzo’s reference to Leonardo using “stills” or solvents all suggest that Leonardo’s technique was likely ever-changing and at times problematic, an observation that is further supported by the fragmentary state of *The Last Supper* (c. 1495) in Milan and the disastrous descriptions of his “encaustic” method used to create the now lost *Battle of Anghiari* (1505) in Florence.

³³⁶ Cadogan, *Domenico Ghirlandaio: Artist and Artisan*, 27-30. Ghirlandio’s surname was inherited from his father who worked as a goldsmith, training the young Ghirlandaio in metalworking before the artist eventually started a studio together with his brother David.

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Figure 4.28: Domenico Ghirlandaio, *The Virgin and Child* (c. 1480-90, National Gallery, London).

the rug and the green foliage (other samples tested positive only for egg) while Ghirlandaio's younger brother, Benedetto, is said to have painted an image of the Nativity using a "smoothly blended oil technique" during his tenure as a court painter in the Auvergne from 1486 to 1493.³³⁷ Analysis of Ghirlandaio's *The Virgin and Child* (c. 1480-90; Figure 4.28) reveals the

³³⁷ Nuttal, *From Flanders to Florence*, 98; Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 16 (1995): 85-92; Note that White and Pilc do not explicitly state which analytical technique(s) were used to confirm the presence of oil, however it is assumed in this case that FTIR was used in conjunction with GC-MS. Linseed oil was found in the dark green tress on the left and in a red lake glaze on the carpet over the parapet, but the vermilion underpainting of the carpet is in egg, as are the flesh tints and blue mantle of the Virgin.

use of both mediums as well as *tempera grassa*: the deep red lakes used to depict the rug are bound in egg and oil; oil alone was detected in the Virgin's blue mantle and dark green in the striped cloth, and the flesh tones are in egg tempera.³³⁸ Even without scientific information visual inspection of Ghirlandaio's oeuvre confirms the artist's intimate relationship with Flemish paintings. As discussed in the preceding chapter, northern paintings appear to have periodically found their way to the Ghirlandaio studio (see Figure 2.21); yet another striking example of this cross-cultural occurrence is the Philadelphia *Man of Sorrows* (c. 1490s; Figure 4.29), a direct copy of Memling's composition now in the Palazzo Bianco in

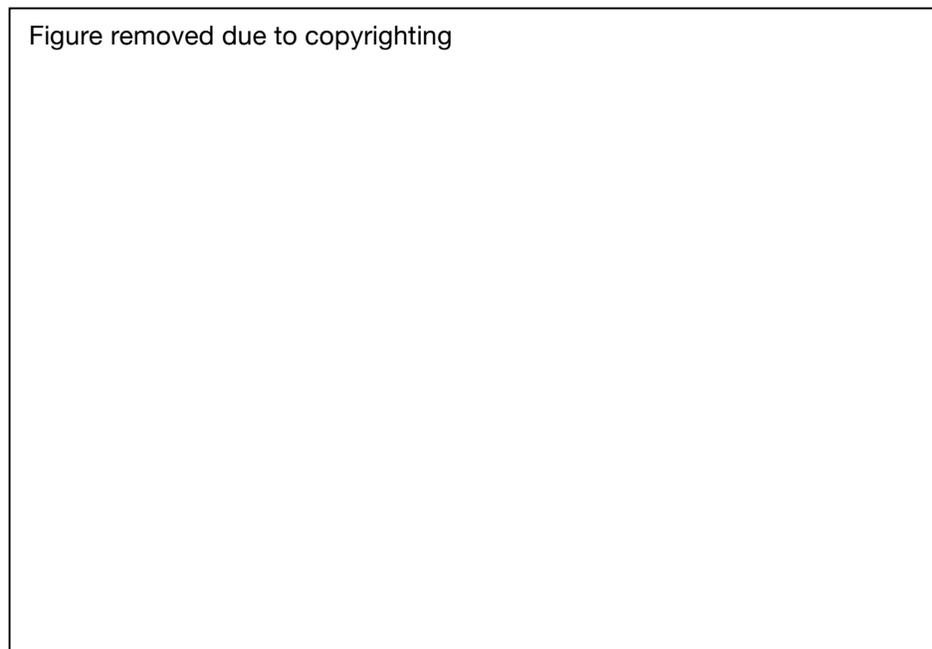


Figure 4.29 (left) and Figure 4.30 (right): Domenico Ghirlandaio's *The Man of Sorrows* (c. 1480-90, Philadelphia Museum of Art; left) and Hans Memling's *The Man of Sorrows* (1480s, Palazzo Bianco, Genoa; right).

³³⁸ White and Pilc, *Ibid*; Both FTIR and GC-MS were used to characterize the binding media.

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Figure 4.31: Domenico Ghirlandaio, *Sasseti Altarpiece* or *The Nativity and Adoration of the Shepherds* (1485, Santa Trinita, Florence).

Genoa (1480s; Figure 4.30). Nuttall has described Ghirlandaio's *Sasseti Altarpiece* (c. 1485; Figure 4.31) as the "best known example of Netherlandish influence on a Florentine artist," attributing several features of the composition to the famed Portinari altarpiece that had recently arrived in Florence.³³⁹ While scientific analysis has not been carried out on the Sasseti altarpiece Ghirlandaio's *Portrait of Giovanna Tornabuoni*, painted just a few years later has recently been analyzed and appears to have been painted with both linseed oil and

³³⁹ Nuttall, *From Flanders to Florence*, 148-9.

egg.³⁴⁰ Like Benozzo Gozzoli and Piero della Francesca, it is also possible that Ghirlandaio's frescoes may contain *a secco* paints bound in oil and/or tempera such as the Tournabuoni frescoes in Santa Maria Novella (1486-90) and his *Pieta* (c. 1470s; Figure 4.32) in the Church of the Ognissanti. The latter pre-dates the Sasseti altarpiece, suggesting the artist's familiarity with northern motifs even before the arrival of the Portinari altarpiece; art historian Keith Christiansen has linked the Medici's painting (the panel attributed to Jan van Eyck; Figure 2.3) to a section of the Ognissanti cycle depicting St. Jerome (Figure 4.33).³⁴¹ Nuttal

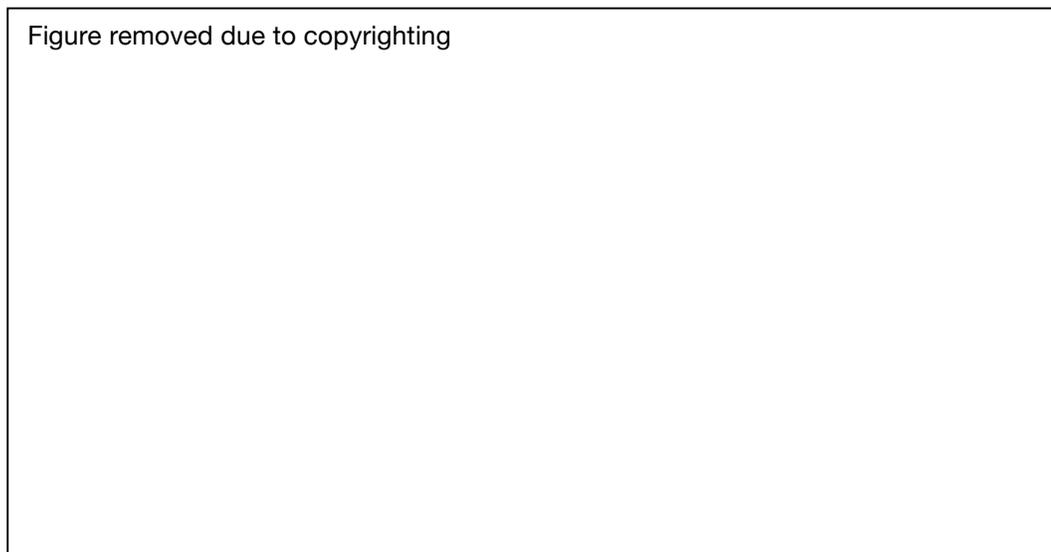


Figure 4.32 (left) and Figure 4.33 (Right): Domenico Ghirlandaio's *Pieta* (left) and *St. Jerome* (right) (1480, Chiesa di Ognissanti, Florence).

³⁴⁰ "Technical Analysis of 'Portrait of Giovanni Tornabuoni,'" accessed October 15, 2015, http://www.museothyssen.org/microsites/ghirlandaio/index_en.html#/chromatography.

³⁴¹ Cadogan, *Domenico Ghirlandaio: Artist and Artisan*, 37; Christiansen, "The View from Italy," 49.

describes a craquelure pattern present in the red and blue glazes throughout the Pieta that do not correspond to typical drying cracks found in frescoes, suggesting the possible use of egg and/or oil containing paints in these regions.³⁴² It is likely that future analysis of works connected to Ghirlandaio's studio will reveal a more consistent use of the oil medium.

It is not entirely clear where Ghirlandaio was first introduced to the art of painting; however, evidence suggests he apprenticed under the mosaicist and painter Alesso Baldovinetti (1425-1499).³⁴³ Baldovinetti worked alongside Domenico Veneziano, Castagno, and Pesellino to create the frescoes at Sant'Egidio in 1438 and although none of his paintings have been subjected to scientific analysis, visual inspection suggests a propensity for deviating from traditional practice.³⁴⁴ Alison Wright discusses the problematic condition of Baldovinetti's frescoes in San Miniato, a project that was carried out in close collaboration with Antonio (c. 1429-1498) and Piero (c. 1443-1496) Pollaiuolo for the Cardinal of Portugal beginning in 1466.³⁴⁵ Cecchi's observation on Baldovinetti's panel painting within the church (*Annunciation*, c. 1466-7; Figure 4.34) is even more curious: both paintings created by the Pollaiuolo brothers and Baldovinetti are on oak panel supports, possibly a stipulation made by

³⁴² Nuttal, *From Flanders to Florence*, 146.

³⁴³ Cadogan, *Domenico Ghirlandaio: Artist and Artisan*, 30; Dunkerton and Syson, "In Search of Verrocchio the Painter: Cleaning and Examination of 'The Virgin with Two Angels,'" 6.

³⁴⁴ Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197; Nuttal, *From Flanders to Florence*, 162.

³⁴⁵ Cadogan, *Domenico Ghirlandaio: Artist and Artisan*, 30; Alison Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome* (New Haven and London: Yale University Press, 2005), 195-6, 204-6; Alessandro Cecchi, Sandra Freschi, and Nicola MacGregor, "The Conservation of Antonio and Piero del Pollaiuolo's Altar-Piece for the Cardinal of Portugal's Chapel," *The Burlington Magazine* 141 (1999): 81-8, accessed December 5, 2015, <http://www.jstor.org/stable/888246>.

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Figure 4.34: Alessandro Baldovinetti, *Annunciation* (c. 1466-7, Galleria degli Uffizi, Florence).

their Portuguese patron that already had a familiarity with northern paintings; however, existing losses in *The Annunciation* panel have been attributed to Baldovinetti's experimental technique using oils, applying his paints atop the oak planks "with no preparation, as can be seen from the wood grain detectable under the paint surface and, still more visible, in the

extensive areas of loss...”³⁴⁶ Regarding the use of oil, more attention has been devoted to Baldovinetti’s partners; Cecchi et al. published a report on the *San Miniato Altarpiece* (Figure 4.35) describing the experimental technique used by the Pollaiuolo brothers in 1466.³⁴⁷ Unfortunately several aspects of the binding media have been deduced from simple cross-sectional analysis, leading the authors to conclude the presence of a thin, lead-white-containing oil priming followed by paint that is bound in egg tempera and/or oil; additional statements in the article claim that the oil priming was a problematic decision made by the brothers since oil primings “do not act as a buffer between the contraction of the wood fibers and the paint layer as the traditional, elastic gesso ground would have done.”³⁴⁸ While this last conclusion has been repeatedly disproven by the conservation community (in fact the proteinaceous glue in traditional gesso has been found to be more responsive to environmental changes than oil films), further analysis is needed to confirm whether the Pollaiuolo brothers employed oil paints in the San Miniato altarpiece.³⁴⁹

³⁴⁶ Wright, *Ibid*; Cecchi, Freschi, and MacGregor, “The Conservation of Antonio and Piero del Pollaiuolo’s Altar-Piece for the Cardinal of Portugal’s Chapel,” 83, 86; Ames-Lewis, “Sources and Documents for the Use of the Oil Medium,” 51.

³⁴⁷ Cecchi, Freschi, and MacGregor, 86-8.

³⁴⁸ *Ibid*; While the characterization of the binding media may be correct, it is impossible to concretely identify proteinaceous and oil based paints based on auto-fluorescent patterns observed during cross-sectional analysis. See Chapter 6 for further discussion on this topic.

³⁴⁹ Stephen Hackney, Joan Reifsnyder, Mireille te Marvelde, and Mikkel Scharff, “Lining Easel Paintings,” in *Conservation of Easel Paintings: Principles and Practice*, ed. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 433-35; Paul Ackroyd, “The Structural Conservation of Paintings on Wooden Panel Supports,” in *Conservation of Easel Paintings: Principles and Practice*, ed. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 472-3.

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Figure 4.35: Piero and Antonio Pollaiuolo, *San Miniato Altarpiece* (1466, San Miniato il Monte, Florence).

Cecchi and Wright's observations are not without cause; Vasari noted that Antonio Pollaiuolo was one of the first Italian artists to generate masterpieces in oil and analysis of London's *St. Sebastian* (c. 1475) has revealed the presence of walnut oil mixed with copper green and

bituminous brown pigments.³⁵⁰ Dunkerton concludes that such a medium would have allowed the brothers to employ a “rapid, more direct method of painting”; visual examination of other related works has also supported the use of the medium (both pigmented and unpigmented).³⁵¹ Wright also discusses the probable use of oil in several of the Mercanzia Virtues (Figures 4.36, 4.37, and 4.38) now in the Uffizi.³⁵² The brothers were commissioned by the Mercanzia in 1469 to create a series of paintings that were intended to be displayed behind their consul seats within their meeting hall; a total of six have been linked to Piero and possibly Antonio, and Wright attributes some of their disparate qualities to the use of varying binding media.³⁵³ While no analysis has been conducted on the series, the medium of the panels has been described as *tempera grassa* while other areas, such as the swirling marble patterns, may have been painted completely in oil; Wright describes their painting method as being “closer to that of orthodox tempera painting but, in contrast to normal tempera effects, use of oil permits the brushstrokes in the flesh and drapery to be fully integrated, creating seamless tonal transitions.”³⁵⁴ Streaky, diaphanous brushstrokes have also been observed in other works by the Pollaiuolos, including *Hercules, Nessus, and Deianira* (now on canvas but originally on a cherry wood panel) while the *Portrait of Galeazzo Maria Sforza* (1471; Figure

³⁵⁰ Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome*, 204; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197; It is unclear what type of analytical testing was carried out to confirm the presence of walnut oil.

³⁵¹ Dunkerton et al., *Ibid.*; George L. Stout, “One Aspect of the So-Called Mixed Technique,” *Technical Studies in the Field of the Fine Arts* 7 (1938): 59-72. Note that while Stout’s publication pre-dates the use of modern analytical methods it does include black and white images of cross-sections from a *Crucifixion* attributed to the Pollaiuolo workshop.

³⁵² Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome*, 242-245.

³⁵³ *Ibid.*

³⁵⁴ *Ibid.*

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Figure 4.36 (left), Figure 4.37 (center), and Figure 4.38 (right): Piero and Antonio Pollaiuolo, *Faith* (left), *Charity* (center), and *Temperance* (right) (1469-70, Galleria degli Uffizi, Florence).

4.39) presents the viewer with dark, saturated tones to depict a three-quarter profile portrait style that was more commonly encountered in the north.³⁵⁵ The Mercanzia panels could have been painted using an emulsion; tempera would have dried fairly quickly, and towards the end of the project the brothers were likely working in haste to meet their deadline. Wright notes that the first three to be completed by the brothers, *Faith*, *Charity*, and *Temperance*, are the

³⁵⁵ Ibid, 98-9, 131-3.

most badly damaged, a characteristic she bases on the [unfounded] observation that the paint layers are applied directly atop the cypress panels without a gesso ground.³⁵⁶ Although Wright claims that many condition issues encountered in works by the Pollaiuolo brothers are likely due to their use of heat-bodied oils, their ability to achieve rich, saturating darks, contrasted with brilliant highlights and flesh tones are likely due to the adoption of oil paint, an aesthetic clearly visible in their monumental San Miniato Altarpiece.³⁵⁷

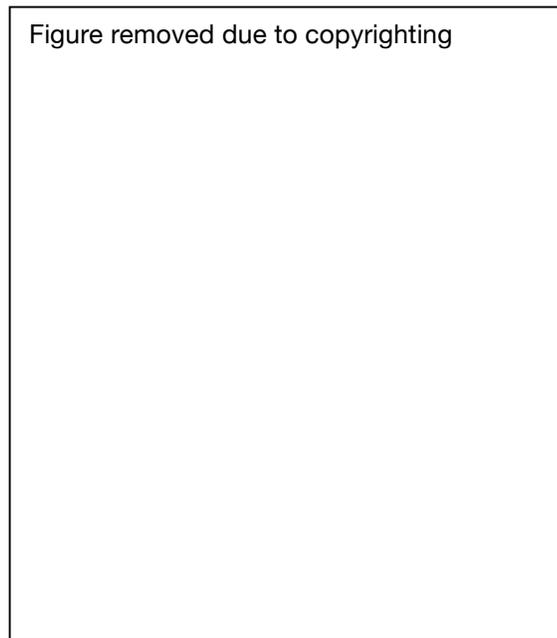


Figure 4.39: Piero and Antonio Pollaiuolo, *Portrait of Galeazzo Maria Sforza* (1471, Galleria degli Uffizi, Florence).

³⁵⁶ Ibid, 131, 204, 245; To date no technical evidence has supported this observation as it would have been unlikely for Italian artists as proficient as the Pollaiuolo brothers to abandon the use of grounds for their panels. Wright also claims the ground layer to be absent in Piero's *Portrait of Galeazzo Maria Sforza* and *David Victorious* (c. 1472) in Berlin, again an observation that is not supported by technical findings.

³⁵⁷ Ibid; To date no evidence has been found to indicate that heat-bodied oils are more likely to lead to poor conditions that are occasionally encountered in panel paintings.

While the Pollaiuolo brothers appear to have embraced the non-traditional oil medium for their panel paintings, they may have applied their oil paints over large-format canvases. As briefly mentioned in the previous chapter, painted cloths created during this period, even if produced using sound techniques, simply may have not survived as compared with paintings on panel.³⁵⁸ Piero Pollaiuolo, along with Paolo Uccello, Pesellino, and Piero della Francesca were all known to have painted elaborate cloth paintings, some which were recorded as having been done in oil.³⁵⁹ In 1460, Pollaiuolo painted three canvases depicting the labors of Hercules for the great hall of the Medici palace in Florence, likely some of the first large-scale mythological decorations produced in Renaissance Italy. The central figures were presumably set against realistic landscapes, much like the naturalistic landscapes seen in the Pollaiuolo's *St. Sebastian* as well as other panel paintings; Nuttall states that this feature is "not unconnected with their interest in oil, which enabled them to imitate with unprecedented skill the atmospheric effects of Netherlandish painting."³⁶⁰ The Medici may have commissioned these large canvases to complement the paintings depicting animals and mythological beasts that adorned the walls of the great hall. Painted by Pesellino and Paolo Uccello (1397-1475), these lost canvas paintings may have been executed in tempera, oil, or a mixed technique; however, Vasari's writings indicate that oil was occasionally used by artists for painting on canvas, describing an oil on canvas made for city of Arezzo by the Pollaiuolo workshop.³⁶¹

³⁵⁸ Christina Young, "History of Fabric Supports," in *Conservation of Easel Paintings: Principles and Practice*, ed. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 116-27; Caroline Villers, "Paintings on Canvas in Fourteenth Century Italy," *Zeitschrift für Kunstgeschichte* 58 (1995): 338-58, doi: 10.2307/1482818.

³⁵⁹ Wright, *The Pollaiuolo Brothers: The Arts of Florence and Rome*, 80.

³⁶⁰ Nuttall, *From Flanders to Florence*, 199.

³⁶¹ *Ibid*; Caroline Villers, "Paintings on Canvas in Fourteenth Century Italy," 349; Villers states that the Medici inventory of 1598 describes the canvas paintings as being in a "torn and

In 1470, the Pollaiuolo brothers likely found themselves unable to meet the deadline imposed by the Sei della Mercanzia, although they were able to complete at least six out of the seven virtues for the Tribunal Hall in Florence. It is generally thought that the tribunal sought the services of the young Sandro Botticelli to complete the project, producing the last and final painting depicting the virtue *Fortitude*.³⁶² While this specific panel has yet to be analyzed, other works associated with the artist and his close associate, Filippino Lippi, have largely been found to contain egg tempera, although oil has been identified in a series of works, used both as a glaze as well as an additive to tempera paints.³⁶³ While analysis has not been performed on Lippi's panels at the Norton Simon Museum (undeniably influenced by Flemish paintings; Figures 4.40 and 4.41) they are most likely painted at least partially in oil as a contemporary portrait in Washington (c. 1485) has been found to contain both egg tempera

tattered" condition although there is no mention of whether they are painted in a specific medium.

³⁶² Barbara Deimling, *Sandro Botticelli* (Koln: Taschen, 2000), 17.

³⁶³ Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 88-96; John Mills and Raymond White, "Organic Analysis in the Arts: Some Further Paint Medium Analysis," *National Gallery Technical Bulletin* 2 (1978): 74-5; Roberto Bellucci et al., "La tecnica pittorica del Botticelli: Un'analisi comparata," in *L'Incoronazione della Virgine' del Botticelli: restauro e ricerche*, ed. Marco Ciatti (exhibition catalogue, Uffizi, Florence, 1990), 97-109, 117-18; Joyce Plesters, "Cross-sections and Chemical Analysis of Paint Samples," *Studies in Conservation* 2 (1956): 118, 121, 126-7, doi: 10.2307/1505000; Helmut Ruhemann, "Technical Analysis of a Painting by Botticelli," *Studies in Conservation* 2 (1955): 17-40, doi: 10.2307/1505031; Note that very little scientific analysis was performed on Botticelli's *Adoration of the Kings* (c. 1470-5) and that the binding media was characterized based on visual assessment of the paint by the Ruhemann.

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Figure 4.40 (left) and Figure 4.41 (right): Filippino Lippi, *Saint Benedict and Apollonia* (left) and *Saints Paul and Frediano* (right) (c. 1483, Norton Simon Museum of Art, Pasadena).

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Figure 4.42: Filippino Lippi, *Virgin and Child with St John* (c. 1493-4, National Gallery, London).

and oil.³⁶⁴ In addition, Lippi's *Virgin and Child with St John* (c. 1493-4; Figure 4.42), possibly produced when the artist was working 1485) has been found to contain egg tempera

³⁶⁴ Suzanne Q. Lomax and Susanna M. Halpine, "Fra Filippino Lippi Scientific Report – 1995," (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC). Samples from the grey architecture and purple drapery were found to contain linseed oil using GC-MS while samples collected from the same areas analyzed using HPLC were found to also contain egg tempera proteins.

tempera in the light-colored paints of the sky, while drying oil was identified as a discrete glaze layer in the red cloak of St. John and in the dark green lining and darker shadows of the Madonna's mantle.³⁶⁵ Similar oil glazes were observed atop egg-containing layers during the analysis of Botticelli's *St. Barnaba* altarpiece at the Uffizi painted in 1488 (Figure 4.43) while oil and egg binders were found present in separate colors in the *Wemyss Madonna* in Scotland (c. 1480-5).³⁶⁶ Interestingly, a tondo dating to the same period, *Madonna and Child with St. John*, was found to contain only egg tempera, suggesting that the Botticelli workshop did not always feel compelled to reach for the slow drying oil medium.³⁶⁷

The use *tempera grassa* has been identified in a handful of works tied to Botticelli and Filippino Lippi as well as to Michelangelo. Two panels belonging to a series that was likely painted by Botticelli (*Scenes from the Early Life of St. Zenobius*, c. 1500; Figure 4.44), were analyzed at the National Gallery in 1995; samples from areas containing red lakes, dark

³⁶⁵ Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 32; Roy and Dunkerton, "Chemistry and Conservation: Changes in Perception and Practice at the National Gallery, London," 126.

³⁶⁶ Nuttal, *From Flanders to Florence*, 186; Roberto Bellucci et al., "La tecnica pittorica del Botticelli: Un'analisi comparata," 89, 97-109; Contrary to Nuttal's statement that scientific analysis was performed to characterize the binding medium, her referral to the former publication (Bellucci et al., 1990) does not elaborate on any scientific analysis performed on paint samples. These suppositions appear to have been based entirely on visual assessment of the paint rather than organic analysis. In one of Lippi's works, Higgitt and White identified egg in lower layers while oil was found in darker tones or used as glazes. See Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 90-95.

³⁶⁷ Danilo Bersani et al. "Pigments and binders in 'Madonna col Bambino e S. Giovannino' by Botticelli investigated by micro-Raman and GC/MS," *Journal of Cultural Heritage* 9 (2008): 97-102, doi:10.1016/j.culher.2007.05.005. Note that this particular study did not detect any fatty acids which is troubling as these markers are also present if egg tempera was used as the primary binder.

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Figure 4.43: Sandro Botticelli, *St. Barnaba Altarpiece* (1488, Galleria degli Uffizi, Florence).

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Figure 4.44: Sandro Botticelli, *Scenes from the Early Life of St. Zenobius* (c. 1500, National Gallery, London).

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Figure 4.45: Sandro Botticelli, *Primavera* (1482, Galleria degli Uffizi, Florence).

greens, as well as a translucent orange-brown paint layer atop the yellow draperies, were found to contain *tempera grassa* while lighter colors (the sky and architecture) were painted using egg alone.³⁶⁸ Botticelli's most intriguing use of *tempera grassa* can be found in his illustrious *Primavera* (1482; Figure 4.45), painted some 8 years before Lippi's St. Zenobius series. Umberto Baldini's 1984 publication discusses the benefits of the medium:

Botticelli and his contemporaries may well have gradually increased the amount of oil in their tempera paints as they found that slower drying allowed them to

³⁶⁸ Jill Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 32; Mills and White, "Organic Analysis in the Arts: Some Further Paint Medium Analysis," 74-5. Note that different passages were also found to contain walnut vs. linseed oil.

produce subtle sfumato effects, which were well suited to the expression of the new subjects and ideas emerging at the time.³⁶⁹

Baldini's take on the painting is rather curious; the restorer seems oddly passionate about *tempera grassa* and claims it to be "better than egg alone, which can be susceptible to the damp beloved by microorganisms, and better than oil alone, which is so sensitive to light that it often causes yellowing and embrittlement of paint," observations that are no longer considered accurate thanks to subsequent technical studies in conservation.³⁷⁰ Baldini did provide the reader with exact details regarding the scientific analysis of the painting, there is a list of analytical techniques included in the final chapter; however, Baldini's suggestion seems based largely on visual examination of the painting, a trend that seems strangely common in other publications that touch upon Botticelli's use of specific binding media.³⁷¹ Yet it is entirely possible that *tempera grassa* was found in the greens of the foliage.³⁷² Visual

³⁶⁹ Umberto Baldini, *Primavera*, trans. Mary Fitton (Sidgwick and Jackson: London, 1984), 48-52.

³⁷⁰ Ibid, 49. Mold can attack oil paintings just as readily as tempera paintings and it is difficult in fact to confirm whether or not the animal glue in the sizing and/or ground layers is more attractive to mold than egg yolk mixed with pigments. Oil films are also less prone to yellowing when exposed to ultraviolet light.

³⁷¹ Bellucci et al., "La tecnica pittorica del Botticelli: Un'analisi comparata," 97-109; Ruhemann, "Technical Analysis of a Painting by Botticelli," 17-40; Alfio del Serra, "Il restauro della Nascita di Venere," *Gli Uffizi: Studi e Ricerche* 4 (1987): 49-57; --, "Il restauro dell'Annunciazione," *Gli Uffizi: Studi e Ricerche* 4 (1987): 58-62; In all four publications, the binding media was characterized based on visual assessment of the paint with little to no scientific testing performed by the authors. It seems that Umberto Baldini, Alfio del Serra, and other Italian restorers commonly drew conclusions regarding the nature of binding media based on visual examination rather than scientific analysis. See also Alfio del Serra, "A Conversation on Painting Techniques," *The Burlington Magazine* 127 (Jan. 1985): 4-16.

³⁷² Ibid. Baldini states that "a fairly comprehensive analysis of the binding agents ... reveals the presence of more fatty substances than would normally occur in egg tempera alone, and chemical tests have in fact shown that Botticelli painted the Primavera in tempera grassa." There is a list of analytical techniques towards the end of the publication but no information is provided to clarify which techniques were able to reveal the presence of *tempera grassa*.

examination of the work shows that the green paint possesses a considerable amount of body, suggesting that other materials such as oils may have been added to the egg medium to create a distinctive textured surface, a technique that has also been identified in the foliage of Paolo Uccello's *The Battle of San Romano* (c. 1438-40).³⁷³ Ashok Roy has pointed out that Botticelli seems to have fully embraced the oil medium by the latter half of his career; analysis and/or visual examination of Berlin's *Bardi Altarpiece* (1484-85) and London's *Mystic Nativity* (c. 1500) reveals that both paintings were likely executed entirely in drying oil (likely walnut) and by the 1490s it seems that Botticelli was already starting to abandon the use of green *verdaccio* underpainting.³⁷⁴

Botticelli's eventual shift in technique may be explained by the artist's involvement in one of the largest collaborative commissioned projects of the fifteenth century. In 1480, Pope Sixtus IV summoned a number of notable painters to decorate the Sistine Chapel in Rome, including Botticelli, Perugino, Domenico Ghirlandaio, and Cosimo Rosselli (1439-1507).³⁷⁵ Many of these artists would have brought with them assistants to help with the execution of

³⁷³ Ashok Roy and Dillian Gordon, "Uccello's 'Battle of San Romano,'" *National Gallery Technical Bulletin* 22 (2001): 8-9. Note that walnut oil mixed with egg was identified using GC-MS and FTIR. *Tempera grassa* was also found in the outer spandrels of the picture and walnut oil mixed with resin was identified in the dark, transparent glazes applied over the silver armor.

³⁷⁴ Roy, "The Painting Technique of Pietro Vannucci, called Il Perugino," 17; Bellucci et al., "La tecnica pittorica del Botticelli: Un'analisi comparata," 99-100, 117-8; Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 91-2. Regarding Botticelli's *Mystic Nativity* the type of analysis used to characterize the binding media is not known although in this instance GC-MS was likely used. Bellucci et al. do not elaborate on any scientific analysis performed on paint samples collected from the *Bardi Altarpiece*.

³⁷⁵ Gretchen A. Hirschauer, "'Building Castles in the Air': The Story of Piero di Cosimo," in *Piero di Cosimo: The Poetry of Painting in Renaissance Florence*, ed. Gretchen A. Hirschauer (Washington DC: The National Gallery of Art, 2015), 7.

these large format frescoes just as Rosselli is documented bringing along the young Piero di Cosimo (1462-1522).³⁷⁶ Over the next few years a significant amount of artistic exchange likely occurred within the walls of the Apostolic Palace, an exchange that may be tied to the fact that oil has been found in works associated with nearly every one of these artists, including Piero di Cosimo.³⁷⁷

Like Verrocchio, Piero di Cosimo grew up in a metalworkers studio, although his father is recorded as a simple blacksmith.³⁷⁸ It is not known when Piero departed from Rosselli's studio; however, art historian Gretchen Hirschauer suggests that the arrival of the Portinari altarpiece in 1483 may have had a profound impact on the young artist upon his return to Florence.³⁷⁹ Scholars have concluded that Piero frequently drew upon motifs that appeared in works by his contemporary Filippino Lippi in addition to Netherlandish themes, both of which prompted the artist to reach beyond the egg tempera medium (see Figure 4.46).³⁸⁰ In conjunction with an exhibition of Piero's work in 2015, a total of eleven paintings

³⁷⁶ Ibid.

³⁷⁷ Refer to additional sections within this chapter regarding works by Botticelli, Ghirlandaio, and Pietro Perugino. To date no comprehensive study has been published in connection to works by Cosimo Rosselli.

³⁷⁸ Hirschauer, " 'Building Castles in the Air': The Story of Piero di Cosimo," 6.

³⁷⁹ Ibid, 8.

³⁸⁰ David Franklin, "Piero and the Painting of His Time," in *Piero di Cosimo: The Poetry of Painting in Renaissance Florence*, ed. Gretchen A. Hirschauer (Washington DC: The National Gallery of Art, 2015), 15-9; Dennis Geronimus, "Plainspoken Piety: Drama and the Poetry of the Everyday in Piero's Devotional Works," in *Piero di Cosimo: The Poetry of Painting in Renaissance Florence*, ed. Gretchen A. Hirschauer (Washington DC: The National Gallery of Art, 2015), 30-2; Serena Padovani, "Piero and Portraiture," in *Piero di Cosimo: The Poetry of Painting in Renaissance Florence*, ed. Gretchen A. Hirschauer (Washington DC: The National Gallery of Art, 2015), 39-45.

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Figure 4.46: Piero di Cosimo, *The Visitation with Saint Nicholas and Saint Anthony Abbot* (c. 1489/90, The National Gallery of Art, Washington DC).

were examined with particular attention paid to the nature of the binding media.³⁸¹ Elizabeth Walmsley's summary of the results warrants much discussion:

Researchers found a range from egg tempera, to linseed oil, to heat-bodied or regular walnut oil (with and without pine resin), as well as mixtures of these various binders, reflecting the transition in Florentine painting from egg tempera to oil paint.³⁸²

There are certainly indications that the artist deviated from the traditional egg tempera medium; examination of London's *spalliera* panels (Figure 4.47) revealed the presence of fingerprints (a characteristic that is more commonly encountered in paintings executed with a slower drying medium such as oil) in the paint and subsequent analysis identified walnut oil in all three panels with some additions of resin.³⁸³ Yet Walmsley appropriately points out the varying conditions of all eleven panels, some of which possess calcium oxalate "crusts" that have been found to potentially interfere with medium analysis.³⁸⁴ Eight out of the eleven panels analyzed were also found to contain a "translucent coating atop the gesso," a technique recommended by Vasari for oil painters as "four or five coats of the smoothest size" can be

³⁸¹ Elizabeth Walmsley, "'A Very Rich and Beautiful Effect': Piero's Painting Technique," in *Piero di Cosimo: The Poetry of Painting in Renaissance Florence* (Washington DC: The National Gallery of Art, 2015), 79-81.

³⁸² *Ibid*, 79-81.

³⁸³ Raymond White, Jennifer Pilc, and Jo Kirby, "Analyses of Paint Media," *National Gallery Technical Bulletin* 19 (1998): 75, 87; White et al. identified pine resin used in the uppermost glazes of the darkened green foliage while heat-bodied walnut oil was found in all panels save for the *Fight Between the Lapiths and Centaurs* which was determined to be cold-pressed. Fingerprints have been found during the examination of modern and contemporary tempera paintings (e.g. Andrew Wyeth) therefore the presence of fingerprints may not be used to confirm the nature of the binding medium.

³⁸⁴ Walmsley, "'A Very Rich and Beautiful Effect': Piero's Painting Technique," 81; Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 93-4.

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Figure 4.47: Piero di Cosimo's *The Fight between the Lapiths and the Centaurs* (c. 1500-15, National Gallery, London).

used to cut the absorbency of the gesso ground.³⁸⁵ Piero seems to have adhered to this practice before applying a lead-white *imprimatura* atop this translucent coating. As with the nature of Piero's binding media, there appear to be conflicting results regarding the composition of this "sizing" layer; just as with analysis of Piero's paints, different laboratories identified different components, ranging from "oil, resin, or both instead of glue."³⁸⁶ Piero's tendency to experiment with stippling and blending of oils and resins is undeniable when presented with his works in person, but the problematic condition of his works combined with a range of analytical approaches left many questions unanswered regarding his technique.

It is impossible that Piero di Cosimo met the young Umbrian painter Pietro Perugino during the decoration of the Sistine Chapel. Perugino's reputation as a skilled oil painter had already been established by the late fifteenth century, a notion that has been corroborated by technical studies of his works as well as paintings attributed to his pupils.³⁸⁷ Using GC-MS,

³⁸⁵ Walmsley, 81.

³⁸⁶ *Ibid.*

³⁸⁷ Ashok Roy, "Perugino's 'Certosa di Pavia Altarpiece': New Technical Perspectives," 13-20; Catherine Higgitt and Raymond White, "Analyses of Paint Media: New Studies of the

walnut oil (and possibly *tempera grassa*) has been identified as the principal medium in samples collected from the *Certosa di Pavia Altarpiece* (c. 1496-1500, Figure 4.48), although the complicated restoration history of the panels appears to have generated some confusion regarding the precise nature of the binding medium.³⁸⁸ Egg tempera and oil have also been identified on separate panels of the *Sant'Agostino Polyptych* (1502-3; Figures 4.49 and 4.50); tempera was identified in the smaller roundels of the polyptych depicting *David* and *Daniel*, suggesting that they may have been painted by one of Perugino's assistants.³⁸⁹

Fifteenth and Sixteenth Centuries,” 88, 95; Elisabeth Martin and Jean Paul Rioux, “Comments on the Technique and the Materials used by Perugino, through the Study of a Few Paintings in French Collections,” in *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS TechWorkshop, Quaderni di Kermes*, eds. Brunetto Brunetti, Claudio Seccaroni, and Antonio Sgamellotti (Florence: Nardini Editore, 2003), 46-56. Works by Raphael have been extensively studied and are typically executed in oil.

³⁸⁸ John Mills and Raymond White, “Analyses of Paint Media,” *National Gallery Technical Bulletin* 3 (1979): 66-7; David Bomford, Janet Brough, and Ashok Roy, “Three Panels from Perugino's ‘Certosa di Pavia Altarpiece,’” *National Gallery Technical Bulletin* 4 (1980): 30-1; Ashok Roy, Marika Spring, and Carol Plazzotta, “Raphael's Early Work in the National Gallery Paintings before Rome,” *National Gallery Technical Bulletin* 25 (2004): 7-8. Roy states that while GC suggested the presence of walnut oil in samples from the *Virgin and Child* and *Sts. Raphael and Michael* (blue sky, blue and red of St. Raphael's robe, blue of Virgin's robe, and green of Tobias's tunic), traces of egg tempera were also detected but “because the panels have had a confused history of treatment and retouching it is not possible to reliably attribute a mixed medium to this work by Perugino” as repaints removed during the restoration were found to consist of tempera. Staining performed on cross-sectional samples from the upper blue layer of St. Raphael's robe, the red of St. Tobias's stockings, and a sample containing a copper-green-containing layer all tested positive for oil alone. Staining tests on both layers found in the blue sky confirmed the presence of both egg tempera and oil while the white underpaint of St. Raphael's blue robe tested positive for egg tempera.

³⁸⁹ Luciana Bordoni, Giovanna Martellotti, Michele Minno, Roberto Saccuman, and Claudio Seccaroni, “Si conclude l'anno del Perugino. Il polittico di Sant'Agostino. Ragionamenti e ipotesi ricostruttive,” *Quaderni di Kermes* 56 (2004): 46-7; Catherine Higgitt, Marika Spring, Anthony Reeve, and Luke Syson, “Working with Perugino: The Technique of an Annunciation attributed to Giannicola di Paolo,” *National Gallery Technical Bulletin* 27 (2006): 106. Neither FTIR nor GC-MS was performed on samples from the Sant'Agostino altarpiece panels in the Galleria Nazionale dell'Umbria. Cross-sectional analysis revealed an

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Figure 4.48: Pietro Perugino, The Certosa di Pavia Altarpiece (c. 1496-1500, National Gallery, London).

Tempera has only rarely been encountered in Perugino's oeuvre, generally associated with earlier works save for a few exceptions; *The Virgin and Child between St. Jerome and St. Augustine* (1505-10), painted in tempera, still possesses the traditional green verdaccio layer while his later paintings are often prepared with an oil-rich *imprimatura* layer, a feature

imprimatura layer in the *St. Jerome and Madeleine* panel while no *imprimatura* layer was found in the *David and Daniel* tondo panels leading the authors to believe that the *imprimatura* was likely oil-containing and that the former was executed in oil while the tondo panels were executed in tempera.

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Figure 4.49: Pietro Perugino, *Sant'Agostino Altarpiece* (1502-3, St. Agostino Church, Perugia) (recto view).

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Figure 4.50: Pietro Perugino, *Sant'Agostino Altarpiece* (1502-3, St. Agostino Church, Perugia) (verso view).

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Figure 4.51: Pietro Perugino, *The Virgin and Child between St. Jerome and St. Augustine* (1505-10, Musée des Beaux Arts, Bordeaux).

typically associated with paintings done in oil.³⁹⁰ Cross-sectional staining performed on *The Marriage of the Virgin* (1504), *Young Saint with a Sword* (1502-5), and two panels from the

³⁹⁰ Martin and Rioux, “Comments on the Technique and the Materials used by Perugino, through the Study of a Few Paintings in French Collections,” 53-6. GC and GC-MS was used to confirm the presence of protein in Perugino’s *The Virgin and Child between St. Jerome and St. Augustine*. Note that Martin et al. state that based on cross-sectional staining (using Amido Black; see Note 254) of the paint cross-sections collected from the *Certosa* altarpiece it seems

Sant'Agostino Polyptych indicated that only the ground contained protein (likely from the gesso-glue ground), suggesting the *imprimatura* and paint layers consisted of mainly oil.³⁹¹ Despite Perugino's early shift towards oil painting, his *Combat between Love and Chastity* (1505; Figure 4.52) represents one notable exception; desperately wanting one of Perugino's oil paintings, Isabella d'Este wrote to Perugino in 1505 and expressed her remorse at having to instead request a painting that complemented the works already hanging in her studiolo by Andrea Mantegna (likely done using egg tempera and/or glue on canvas).³⁹² Cross-sectional staining has confirmed that Perugino applied egg tempera paints directly on the sized canvas (with no ground present) to create his *Combat between Love and Chastity* for Isabella d'Este, demonstrating that Renaissance painters would occasionally deviate from their preferred technique depending on the terms of the commission.³⁹³

possible that an *imprimatura* layer is present although Ashok Roy does discuss this feature of the painting in his article "Perugino's 'Certosa di Pavia Altarpiece': New Technical Perspectives," in *The Painting Technique of Pietro Vannucci, Called Il Perugino, Proceedings of the LabS TechWorkshop, Quaderni di Kermes*.

³⁹¹ Ibid, 46-7; Suzy Delbourgo, Jean P. Rioux, and Elisabeth Martin, "L'analyse des peintures du Studiolo d'Isabelle d'Este au Laboratoire de Recherche des Musées de France. II - Étude analytique de la matière picturale," *Laboratoire de Recherche des Musées de France, Annales* (1975): 21-8.

³⁹² Higgitt et al., "Working with Perugino: The Technique of an Annunciation attributed to Giannicola di Paolo," 105, 110; Martin and Rioux, "Comments on the Technique and the Materials used by Perugino, through the Study of a Few Paintings in French Collections," 46-9; Elisabeth Martin, "Note sur l'identification des protéines dans les liants de peinture," *Laboratoire de Recherche des Musées de France, Annales* (1975): 57-60. Staining was performed using Amido Black, a technique that is no longer considered to be a definitive method for characterizing binding media. Staining was performed using Amido Black, a technique that is no longer considered to be a definitive method for characterizing binding media.

³⁹³ Ibid; Delbourgo et al., Ibid.

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Figure 4.52: Pietro Perugino, *Combat between Love and Chastity* (1505, Musée du Louvre, Paris).

Almost thirty years after Piero's involvement in the Sistine Chapel, Michelangelo Buonarroti was commissioned by Pope Julius II to decorate its ceiling. Michelangelo, typically classified as a sixteenth-century master, created earlier works that demonstrate a mastery of both egg and oil-based mediums, a skill that was evidently passed on to his pupils including Francesco Granacci (1469-1543).³⁹⁴ Michelangelo's early apprenticeship under

³⁹⁴ Charlotte Hale, Julie Arslanoglu, and Silvia Centeno, "Granacci in the Metropolitan Museum of Art: Aspects of Evolving Workshop Practice," in *Studying Old Master Paintings:*

Ghirlandaio may have influenced the younger artist to embrace a range of techniques, an observation supported by the comprehensive analysis of his unfinished *Entombment* (c. 1504; Figure 4.53) as well as the *Manchester Madonna* (c. 1504; Figure 4.54).³⁹⁵ The condition of the former work has been compromised by previous restoration campaigns; however, tests performed using staining, FTIR, and GC-MS at the National Gallery London identified egg tempera as the primary medium while oil alone was used in the upper paint layers.³⁹⁶ Although Dunkerton alludes to Michelangelo's probable use of oil on the *Doni Tondo* in the Uffizi (painted around the same period), art historian Ezio Buzzegoli does not refer to any analytical testing performed on the painting; his conclusion that Michelangelo employed egg-oil emulsions seems largely based on visual assessment.³⁹⁷ It is entirely possible, however, that the *Doni Tondo* was executed in a manner similar to the *Entombment*, with an egg tempera base followed by transparent glazes that contain evidence of Michelangelo's topographical brushwork, a characteristic that is not commonly encountered in egg tempera

Technology and Practice, ed. Spring, Marika (London: Archetype Publications and the National Gallery, 2011), 59-64. Analysis with GC-MS confirmed the presence of egg and oil media in the Metropolitan's *The Birth of Saint John the Baptist* (c. 1506-7).

³⁹⁵ Michael Hirst and Jill Dunkerton, *Making and Meaning: The Young Michelangelo - The Artist in Rome, 1496-1501* (London: The National Gallery, 1995).

³⁹⁶ Joyce Plesters, "The 'Entombment,'" in *Michelangelo's 'Entombment of Christ': Some New Hypotheses and Some New Facts* (London: National Gallery, 1970), 21-3; Hirst and Dunkerton, *Making and Meaning: The Young Michelangelo - The Artist in Rome, 1496-1501*, 107-27. In Note 14 (p 132) it appears that Dunkerton dismisses Plesters's early conclusion that the *Entombment* was painted using pre-polymerized oil and resin based on GC-MS results obtained in 1995.

³⁹⁷ Hirst and Dunkerton, *Making and Meaning: The Young Michelangelo - The Artist in Rome, 1496-1501*, 111; Ezio Buzzegoli, "Il Restauro del Tondo Doni," *Quaderni degli Uffizi* 2 (1985), 57-8.



Figure 4.53: Michelangelo, *Entombment* (c.1504, National Gallery, London).

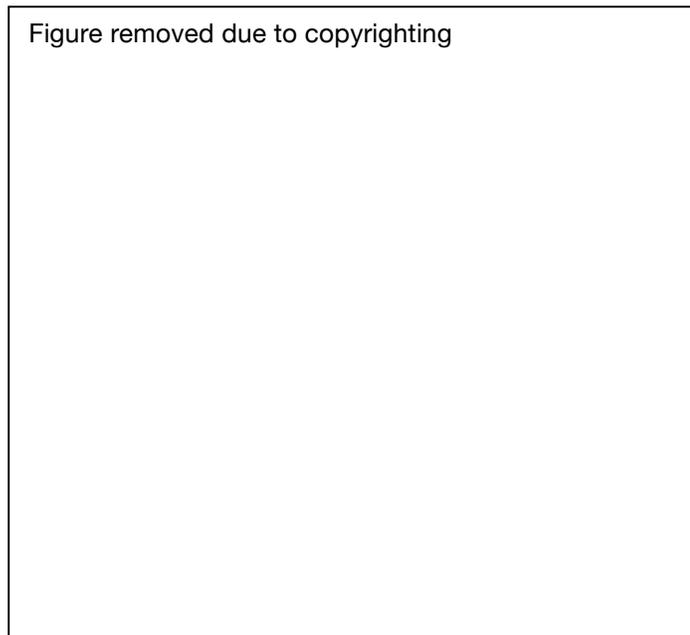


Figure 4.54: Michelangelo, *Manchester Madonna* (c.1504, National Gallery, London).

topographical brushwork, a characteristic that is not commonly encountered in egg tempera paint layers.³⁹⁸ Dunkerton also questions Buzzegoli's assessment stating that "in our analyses of many Italian paintings from this so-called transitional period from tempera to oil, the only emulsions we have found are the simple oil-enriched temperas like that used for the red lake drapery in the *Manchester Madonna*."³⁹⁹ Analysis of the latter revealed tempera as the primary binder in the black undermodeling of the Madonna's cloak, in the grey-blue sky, and in the brown-greenish grass just below Christ's instep (which also contained traces of oil that were concluded to be from superficial glazes rather than additions to the tempera); *tempera grassa* (walnut oil and egg) was found in the red lake drapery of the Madonna's dress.⁴⁰⁰ However, notations in the footnotes of the study include some confusing observations, namely the interpretation of the black undermodeling which GC-MS found to be "egg tempera, rich in egg fats, but with no indication of any oil."⁴⁰¹ As drying oils and egg yolk are known to share the same fatty acid markers, it is unclear what the authors are referring to in this statement. These particular works by Michelangelo, being unfinished and partially obscured with discolored traces of oil and/or oil-resin varnishes, are prime examples of the difficulties that analysts often face when confronted with questions relating to the characterization of egg-oil paint systems.

³⁹⁸ Hirst and Dunkerton, *Making and Meaning: The Young Michelangelo - The Artist in Rome, 1496-1501*, 114-9; Dunkerton also theorizes that the oil paint was further manipulated using a "carving or modelling tool with some form of serrated edge," an observation that requires further research to be considered a definitive possibility.

³⁹⁹ *Ibid.*, 132.

⁴⁰⁰ *Ibid.*, 94-101, 129-30.

⁴⁰¹ *Ibid.*, 129.

4.2.2 Urbino

Beyond the walls of Florence, painters working throughout central Italy in cities such as Urbino and Siena were also moving away from the traditional tempera technique. Following the appointment of Federico da Montefeltro as Duke of Urbino in 1474, artists from the north and south began to flock to the city. Federico had several diplomatic and dynastic connections with individuals who were avid collectors of Netherlandish paintings; Bartolomeo Facio describes several Eyckian paintings belonging to the Duke's nephew Ottaviano Ubaldini della Carda, who possibly resided in the ducal palace along with his collection.⁴⁰² Justus of Ghent (c. 1410 – c. 1480) had moved to Rome from Ghent some time after 1468, but by 1472 he is recorded working in Urbino completing a series of portraits depicting Illustrious Men (*Uomini Illustri*; Figures 4.55 and 4.56) for the Duke's studiolo.⁴⁰³

⁴⁰² Marina Belozerskaya, *Rethinking the Renaissance: Burgundian Arts Across Europe* (Cambridge: Cambridge University Press, 2012), 209. Facio writes the following relating to Ottaviano's collection of Eyckian paintings: There are also fine paintings of his in the possession of that distinguished man Ottaviano Ubaldini della Carda: women of uncommon beauty emerging from the bath, the more intimate part of the body being with excellent modesty veiled in fine linen, and of one of them he has shown only the face and breast but has represented the hind parts of her mirror painted on the wall opposite, so that you may see her back as well as her breast. In the same picture there is a lantern in the bath chamber, just like one lit, and an old woman seemingly sweating, a puppy lapping up water, and also horses, minute figures of men, mountains, groves, hamlets and castles carried out with such skill you would believe one was fifty miles distant from another. But almost nothing is more wonderful in this work than the mirror painted in the picture, in which you see whatever is represented as in a real mirror.

⁴⁰³ Ibid., 215-8; Michel Menu et al. "Examination of the Uomini Illustri: Looking for the Origins of the portraits in the Studiolo of the Ducal Palace of Urbino. Part 1," in *Studying Old Master Paintings: Technology and Practice*, ed. Marika Spring (London: Archetype Publications and the National Gallery, 2011), 37-43; June Osborne, *Urbino: The Story of a Renaissance City* (Chicago: University of Chicago Press, 2003), 104-8; Sir William Martin Conway, *The Van Eycks and their Followers* (London: E.P. Dutton, 1921), 174; Justus of

A recent technical study has identified oil paint in all of the portraits that were examined in addition to an oil-rich *primusel* (a northern term used to describe the layer applied atop the ground, similar to an *imprimatura*) in several paint samples.⁴⁰⁴ The study also revealed the presence of calcium carbonate or chalk, a pigment typically found in northern works, in the *primusel* layer when present; however, the authors' suggestion that Justus occasionally mixed

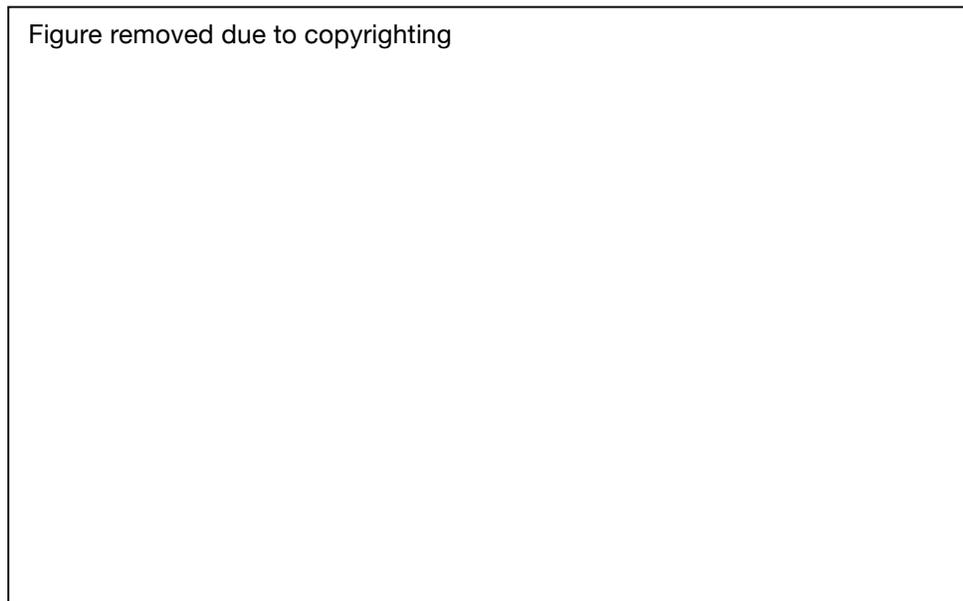


Figure 4.55 (left) and Figure 4.56 (right): Justus of Ghent, *Boethius* (left) and *Aristotle* (right) (c. 1472, Studiolo di Urbino, Galleria Nazionale delle Marche).

Ghent became a recognized master painter by the Antwerp Guild of St. Luke in 1460 and eventually relocated to the city of Ghent some four years later.

⁴⁰⁴ Rocco Mazzeo et al. "Examination of the Uomini Illustri: Looking for the Origins of the portraits in the Studiolo of the Ducal Palace of Urbino. Part 2," in *Studying Old Master Paintings: Technology and Practice*, ed. Marika Spring (London: Archetype Publications and the National Gallery, 2011), 44-51.

egg into his oil-containing primusel layer should be questioned as only ATR-FTIR was used to characterize the binders, a technique that is not able to distinguish between protein sources such as animal glue and egg tempera.⁴⁰⁵ Justus would have been instrumental in introducing the northern aesthetic to his fellow artisans working in Urbino; Nuttal has pointed out that the artist likely brought drawings connected to the workshop of Dirk Bouts to Urbino, basing the central background figure from Bouts's *Martyrdom of St. Erasmus* (c. 1458; Figure 4.57) in one of his first paintings produced for the court of Urbino, *The Communion of Apostles* (1473-5; Figure 4.58), another painting that was recently determined to have been painted in oil.⁴⁰⁶

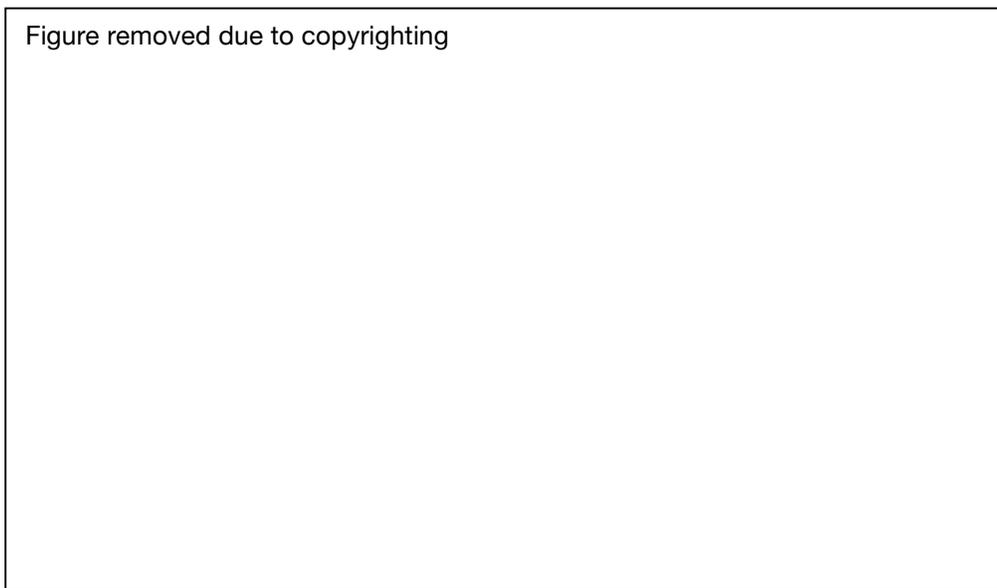


Figure 4.57 (left) and Figure 4.58 (right): Dieric Bouts, *Martyrdom of St. Erasmus* (central panel; c. 1459, Sint-Pieterskerk, Leuven; left) and Justus of Ghent, *The Communion of Apostles* (1473-5 Palazzo Ducale, Urbino; right).

⁴⁰⁵ Ibid.

⁴⁰⁶ Ibid; Nuttal, *From Flanders to Florence*, 140.

Justus was undoubtedly well-suited for Urbino's international artistic environment, meeting the criteria issued by the city's new Duke who had developed an interest in the northern aesthetic.⁴⁰⁷ It is unclear whether Duke Montefeltro asked Justus to take charge of decorating his studiolo or whether Justus was simply an assistant; however, it is certain that he participated throughout the project until its completion and was likely accompanied by another foreign painter, Pedro Berruguete from Spain.⁴⁰⁸ Berruguete is known to have been active around 1480, and it is likely that the two artists may have worked alongside one another. Both artists have been associated with several famous portraits commissioned by the Duke such as the *Portrait of Federico da Montefeltro with His Son Guidobaldo* painted c. 1475; Figure 4.59), although these works still await comparative technical analysis.⁴⁰⁹ Both Nuttal and Christiansen have alluded to Justus's knowledge of the oil technique, a skill that is briefly mentioned by the Duke's biographer and book collector Vespasiano Bisticci (1421-1498) who describes his employer as someone who "was much interested in painting, and because he could not find in Italy painters in oil to suit his taste he sent to Flanders and brought thence a master who did at Urbino many very stately picture, especially [for] Frederigo's study....He painted from life a portrait of the Duke which only wanted breath."⁴¹⁰

⁴⁰⁷ Luciano Cheles, *The Studiolo of Urbino: An Iconographic Investigation* (University Park: Pennsylvania State University Press, 1986), 13-29. In 1476 a set of eleven tapestries arrived at the court from Flanders depicting the Siege of Troy.

⁴⁰⁸ Ibid; Osborne, *Urbino: The Story of a Renaissance City*, 106-7; Pedro Berruguete is documented working in Urbino around 1477.

⁴⁰⁹ Ibid; Michel Medu et al., "Examination of the Uomini Illustri: Looking for the Origins of the portraits in the Studiolo of the Ducal Palace of Urbino. Part 1," 37-43.

⁴¹⁰ Christiansen, "The View from Italy," 41; Nuttal, *From Flanders to Florence*, 34. This record of the Duke's preference for accomplished oil painters is of note as he was also a fervent supporter of Tuscan painters suggesting that the knowledge of oil painting was not yet widely spread throughout central Italy by the 1470s.

It is possible that both Justus and Berruguete left a lasting impression on other artists working in Urbino, particularly Botticelli, Piero della Francesca, and Fra Carnevale (c. 1420/5 – 1484), all of whom appear to have incorporated oil into their workshop practice.⁴¹¹

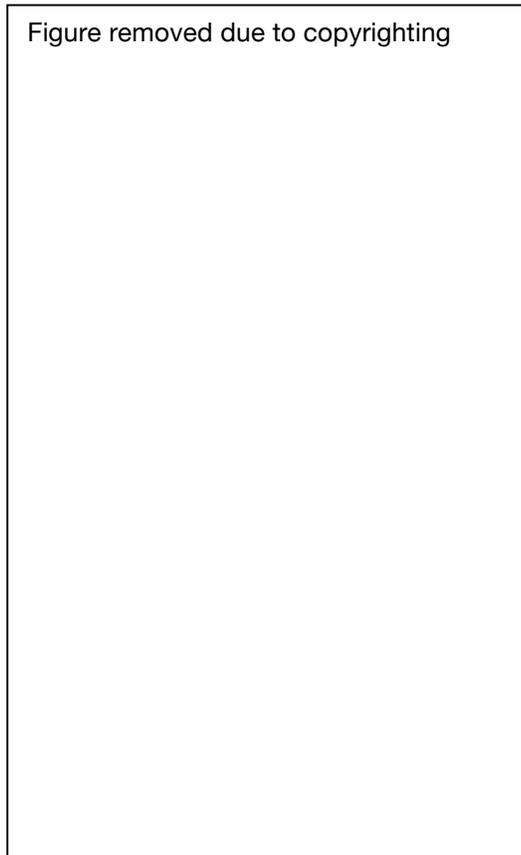


Figure 4.59: Justus of Ghent, *Portrait of Federico da Montefeltro with His Son Guidobaldo* (c. 1475, Palazzo Ducale, Urbino).

⁴¹¹ See Keith Christiansen, *From Filippo Lippi to Piero della Francesca: Fra Carnevale and the Making of a Renaissance Master* (New York: Metropolitan Museum of Art, 2005). Several works attributed to Fra Carnevale have been labeled as “tempera and oil” although no scientific analysis has been conducted to support most of these assignments. Recent analysis conducted at the National Gallery of Art in Washington points towards Carnevale’s possible use of the oil medium and is described in greater detail in Chapter 6.

4.2.3 Siena

While Urbino's artistic community was more or less dependent on the prosperity of the court, artisans working in Siena were moderated by the *Arti de Pittori*, a guild system that was similar to the *Arte e Speciali* in nearby Florence although it operated on a more modest scale.⁴¹² Siena was never able to fully recover from the Black Death that struck the city in 1348, an event soon followed by the deposition of the emperor-elect Charles IV in 1355; however, the slow recovery of the city's economic status eventually culminated in the formation of an intimate, workshop-based artistic environment, one that required all native painters to register with the guild in order to work within the city's walls.⁴¹³ Starting as early as the thirteenth century, there is evidence of more collaboration between artists rather than the cultivation of singular workshops operating under the tutelage one master.⁴¹⁴ But as the century progressed, guild statutes eventually imposed more restrictive guidelines that in turn impacted native painters as well as foreigners seeking commissions from Sieneese patrons, guidelines that regulated the distribution of work and even the materials used by artists during the Quattrocento.

⁴¹² Norman, *Painting in late medieval and renaissance Siena, 1260-1555*, 31; Benjamin David, "Past and Present in Sieneese Painting: 1350-1550," *RES: Anthropology and Aesthetics* 40 (2001): 86, accessed January 20, 2016, <http://www.jstor.org/stable/20167539>; John Adams, "Economic Change in Italy in the Fourteenth Century: The Case of Siena," *Journal of Economic Issues* 26 (1992): 132-3, accessed January 20, 2016, <http://www.jstor.org/stable/4226517>.

⁴¹³ Norman, *Painting in late medieval and renaissance Siena, 1260-1555*, 31, 72.

⁴¹⁴ David, "Past and Present in Sieneese Painting: 1350-1550," *RES: Anthropology and Aesthetics*, 86.

Guild statutes from the fourteenth century suggest that the *Arti de Pittori* were already beginning to exercise more control over daily workshop practices, demanding that painters were not to convey or reveal workshop “secrets” or else face probation as well as paying a fee.⁴¹⁵ Taking a cue from neighboring Florence, Siena also reacted in a similar manner when dealing with foreign artists, requiring foreigners to pay additional fees and as well as Sieneese workshops who wished to employ the service of a non-native artisan.⁴¹⁶ But perhaps more relevant to day-to-day workshop practice was the statute that references the use of particular materials; artists were forbidden to:

[...] employ in his work any quality of gold or silver or pigments different from that originally stipulated, such as false gold for fine gold, tin for silver, azurite for ultramarine blue, ceruse or indigo for blue, terra rossa or minium for cinnabar.⁴¹⁷

⁴¹⁵ Hayden B. Maginnis, *The World of the Early Sieneese Painter* (University City: Penn State University Press, 2000), 206. In *Chapter XV - On not revealing and discussing secrets* “Item, we hereby decree that, in order that no one dare to reveal or make known anything that was discussed in confidence or declared a secret by the Rector of the Painters’ Guild, anyone who makes manifest any of the aforementioned things will be stripped of any position of honor in the Guild for a period of two years, in addition to having to pay the Guild’s Treasurer a fine of 5 lire.”

⁴¹⁶ Maginnis, *The World of the Early Sieneese Painter*, 204-5. In *Chapter XI- That foreign painters wishing to work in Siena be bound to pay a florin* “Item, we hereby decree that any foreign painter who will wish to practice his art in Siena, before he may begin to work, will have to pay to the Painters’ Guild, in the hands of the Treasurer of the Guild, a sum of a gold florin. He must also lay down good and sufficient security up to the sum of 25 lire. No painter will be allowed to hire a foreigner unless the fee owed to the Guild has been paid and the security provided. And should the foreign painter refuse to provide security, every Rector, upon taking office, is duty bound to order all shop and wall master painters not to hire any foreign painters unless they have provided security and paid the fee owed to the Guild. Whoever will contravene the above dispositions will be punished and condemned to pay the sum of 40 soldi.”

⁴¹⁷ *Ibid.* In *Chapter XIV - On refraining to employ one type of gold for another or a pigment for another* “Item, we hereby decree that no member of the Painters’ Guild dare or presume to employ in his work any quality of gold or silver or pigments different from that originally stipulated, such as false gold for fine gold, tin for silver, azurite for ultramarine blue, ceruse or

with the consequence resulting in a fine that was paid to the guild. Yet as with most statutes and contracts that have survived from this period there remains no mention of binders or references to problematic painting techniques. By 1426, Siena's attitude towards foreign artists did not seem to change; an additional statute proclaimed that any foreign artists residing within Siena or even ten miles from the city could not establish a workshop or participate in one without the approval of three recognized masters and a fee paid directly to the Arti.⁴¹⁸

Despite the unwelcoming tone reflected by the guild's statutes, there are signs that cross-cultural exchanges occurred in Siena between artists as well as commissioners. Miniature painters from the north such as Jacquemart de Hesdin (c.1355- c.1414) and the Limbourg Brothers are known to have visited Siena as early as 1413, presumably to study the city's most celebrated pictures.⁴¹⁹ Early records also indicate that by 1428 "due Todeschi che fano Naibi," or German card painters, had registered with the Arte and by 1442 there is evidence that Jacquet d'Arras, a tapestry weaver from France, had set up a workshop in Siena.⁴²⁰ Knowledge of this workshop is known only due to a large commission of 40

indigo for blue, terra rossa or mimium for cinnabar. Whoever will contravene will be punished and fined 10 lire each time."

⁴¹⁸ Vittorio Lusini, *L'Arte del legname innanzi al suo Statuto del 1426*. (Siena: Lazzeri, 1904), 35. The statute reads as follows: I maestri senesi volevano che qualunque forestiero venisse a Siena, o presso Siena, a dieci miglia, non potesse fare bottega, ne lavorare se non approvato da tre maestri e dietro pagamento di una tassa all'Arte.

⁴¹⁹ Keith Christiansen, Laurence Kanter, and Carl Brandon Strehlke, *Painting in Renaissance Siena, 1420-1500* (New York:Metropolitan Museum of Art, 1988), 4.

⁴²⁰ Sherwood A. Fehm Jr., "Notes of the Statutes of the Sienese Painters Guild," *The Art Bulletin* 54 (1972): 200, accessed February 2, 2016, <http://www.jstor.org/stable/3048968>; Genevieve Souchal, *Masterpieces of Tapestry from the Fourteenth to the Sixteenth Century* (New York: Metropolitan Museum of Art, 1974), 13.

tapestries for Tommaso Parentucelli da Sarzana, by then Pope Nicholas V who likely encountered tapestries during his own travels to Arras. Nicholas V was not the only foreign patron who supported Sieneese artists. In 1432 Emperor Sigismund of Croatia remained in Siena for some time while he awaited recognition from Pope Eugenius IV, commissioning Domenico di Bartolo (c. 1400/1404 – 1445/1447) to paint his portrait, the earliest recorded portrait executed by a Sieneese artist.⁴²¹ Giovanni di Paolo's (c. 1403-1482) fame as a painter and manuscript artist also reached the Duke of Alfonso of Aragon in Naples, who eventually commissioned the artist to paint a copy of Dante's *Divine Comedy*.⁴²²

Just as a handful of foreign artists and patrons frequented the city, a few notable Sieneese artists managed to venture outside the city thanks to private commissions. This trend may have started as early as the thirteenth century with Duccio di Buoninsegna as Parisian tax documents from 1296/1297 list a certain "Duch de Siene" and in another instance a "Duche le lombart" is listed working elsewhere in France during the 1290s.⁴²³ Simone Martini, followed later by his brother-in-law Lippo Memmi (c. 1291-1356), also traveled to Naples and France for private commissions while a handful of other artists such as Pietro Lorenzetti (c. 1280 – 1348), Taddeo (c. 1363 – 1422) and Domenico di Bartolo, and Francesco di Giorgio (1410-1480) sought commissions closer to home.⁴²⁴ The latter was perhaps one of the most famous

⁴²¹ Christiansen et al., *Painting in Renaissance Siena, 1420-1500*, 13. Note that today the earliest surviving Sieneese portrait is attributed to Nerrocio di Landi at the National Gallery of Art in Washington.

⁴²² Ibid, 22.

⁴²³ Norman, *Painting in late medieval and renaissance Siena, 1260-1555*, 80.

⁴²⁴ Claire Guinomet, "Italian Influences" in *The Road to Van Eyck*, eds. Stephan Kemperdick and Friso Lammertse (Rotterdam: Museum Boijmans Van Beuningen, 2012), 52. Simone Martini, Lippo Memmi, and Matteo di Giovanetto da Viterbo (active 1322 to 1368) are known to have decorated the papal palace in Avignon from the 1330s onwards.

Sienese artists during the fifteenth century whose many patrons including the Duke of Urbino, praised him for his speed and skill as a painter.⁴²⁵ In describing Francesco's 1475 altarpiece in the Siena Pinacoteca, Christiansen et al. state that the artist "had acquired a rudimentary mastery of an oil (or oil-like) medium and a more carefully descriptive style-evident in the depiction of the pearls and brocades, the reflective halos, and the hands of St. Bernard."⁴²⁶ While none of Francesco's works has been subjected to technical analysis, it is possible that the Duke of Urbino was attracted to the "oil-like" appearance of the artist's paintings, something that would have appealed to the Duke's newfound taste for the northern aesthetic. However, the only surviving artwork created by Francesco for the Duke is a miniature, so it is impossible to know whether the artist intentionally altered his style of painting in order to impress his devoted patron, someone who clearly favored aesthetics associated with the oil medium.⁴²⁷

Recent technical analysis of Sienese works reveal that painters had begun to embrace the oil medium by the fifteenth century and possibly even earlier. As discussed previously, analysis of Gentile da Fabriano's *Polyptych of the Intercession* (c. 1424) was found to contain traces of oil, a technique that the artist may have encountered during his travels in Venice before his arrival in Siena.⁴²⁸ Beyond the 1420s, evidence of oil painting in Siena does not

⁴²⁵ Christiansen et al., *Painting in Renaissance Siena, 1420-1500*, 22.

⁴²⁶ Ibid.

⁴²⁷ Ibid, 30. Christiansen et al. state that in one of Francesco's latest works (an *Adoration of the Shepherds* in the church of San Domenico in Siena) he collaborated with two painters, one of whom, Berndardino Fungai, seems to have worked in oil.

⁴²⁸ Ciatti, Frosinini, and Bellucci, "Il restauro del 'Polittico dell'Intercessione' di Gentile da Fabriano, un'opera misteriosa e affascinante, considerata in passato perduta," 144, 194; Note that the authors only cite the use of cross-sectional analysis, FTIR, and solvent extraction using a 2:1 pentane/methylene chloride mixture. While it is unclear whether the latter generated an FTIR spectrum or a GC spectrum, the authors deduced the presence of drying oil

surface until the late fifteenth century. A series of paintings by The Master of the Story of Griselda (c. 1493-4) was recently subjected to extensive technical analysis; the panels were discovered to have been painted using drying oils while tempera was encountered in limited passages of color.⁴²⁹ Egg tempera was used in the green grass and in the red mantles of the *Marriage* panel (Figure 4.60), the greyish marbling of the architecture in the *Exile* panel (Figure 4.61), and in the blue-green paint of the arches in the *Reunion* panel (Figure 4.62).⁴³⁰ Other areas revealed the use of egg atop oil and even oil atop egg; the pronounced white lines in the brocade of the tablecloth in the Reunion panel were determined to be egg tempera painted atop a beige tone bound in oil. The flesh tones also revealed a more complex layering structure; figures were mostly depicted using a verdaccio tempera underlayer (found only in

from the solvent extraction process. Other samples showed the presence of proteinaceous materials (which in some instances was determined to be glue) combined with traces of fatty acids. A cross-section collected from Gentile's *Madonna and Child* (c. 1425) of the Quaratesi altarpiece also suggested the presence of oil; however, it is unclear whether analytical testing was conducted on the cross-section or whether this conclusion was based on visual examination alone. See Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 39, 64 (Note 54).

⁴²⁹ Jill Dunkerton, Carol Christensen, and Luke Syson, "The Master of the Story of Griselda and Paintings for Sienese Palaces," *National Gallery Technical Bulletin* 27 (2006): 4-71. A wide range of analytical testing was carried out by two laboratories including cross-sectional staining, FTIR, and GC-MS. At the National Gallery in London, staining and FTIR suggested that the lead white lower layer was painted in tempera but that the red lake layer contained walnut oil and tempera. At the National Gallery in Washington, GC-MS revealed both egg and oil in the red sample and the flesh, while the green was found to be mostly oil. Traces of chalk were also found in Claudia Quinta's *imprimatura* layer (bound in egg tempera), a transparent white pigment that is more commonly encountered in northern paintings.

⁴³⁰ *Ibid.*, 15-18; Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 88-96. Higgitt and White note that the red lake glaze over the gold leaf was not tested and may in fact contain oil and/or resin.

Figure removed due to copyrighting

Figure 4.60: Master of the Story of Griselda, *Marriage* (c. 1493-4, National Gallery, London).

Figure removed due to copyrighting

Figure 4.61: Master of the Story of Griselda, *Exile* (c. 1493-4, National Gallery, London).

Figure removed due to copyrighting

Figure 4.62: Master of the Story of Griselda, *Reunion* (c. 1493-4, National Gallery, London).

the *Marriage* and *Reunion* panels) with upper paint layers bound in walnut oil.⁴³¹ The authors note that while glassy additives were not found in any of the samples containing the slow drying red lake, their presence in other passages of color suggests the artist's familiarity with the oil medium while tiny "burst air bubbles" in other passages are instead attributed to the presence of an aqueous medium such as tempera.⁴³² Scholars believe that the Griselda Master likely trained with under Luca Signorelli (c.1445-1523) when the master painter continued to work in Siena after completing his frescoes in Orvieto. Signorelli's knowledge of oil painting has long been suspected but to date no scientific analysis of his paintings has been published; however, scholars feel that Signorelli left a lasting impact on the Griselda Master during his early training, prompting the Master to eventually use drying oils and apply *imprimatura* layer(s) above his gesso grounds.⁴³³ Another painting related to this series is the full-length portrait of *Claudia Quinta* (c. 1493-4; Figure 4.63) by Neroccio de' Landi (1447-1500), a painter who collaborated with the Griselda Master to create a number of portraits depicting virtuous men and women.⁴³⁴ A sample from the red robe was analyzed at the National Gallery in London and the National Gallery in Washington DC and both scientific laboratories found the presence of egg and oil, likely in the form of *tempera grassa* (walnut oil and tempera). Mixtures of egg and oil were also found in the flesh while a green sample and a sample from

⁴³¹ Higgitt and White, "Analyses of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 88-96. The authors conclude that the *Exile* panel was likely painted last as the figures are without a green verdaccio underlayer and instead possess a thin, transparent yellowish wash.

⁴³² Ibid.

⁴³³ Dunkerton, Christensen, and Syson, "The Master of the Story of Griselda and Paintings for Sieneese Palaces," 6, 41.

⁴³⁴ Ibid., 18-24.

Figure removed due to copyrighting

Figure 4.63: Neroccio de Landi, *Claudia Quinta* (c. 1490/95, The National Gallery of Art, Washington DC).

the sky tested positive for mostly egg tempera with a trace of oil.⁴³⁵ Similar results were found in the related portrait of *Sulpitia* by Pierto Orioli (1458-1496); lower layers of paint ere done in tempera with oil glazes applied during the final painting stages. Neroccio evidently continued his use of oil as suggested by a recent study of the *Madonna and Child with Saint Anthony Abbot and Saint Sigismund* (Figure 4.64) in Washington DC painted in 1494/5. As with the scientific analysis of the *Claudia Quinta*, the analytical reports do not appear to completely coincide with the subsequent publication.⁴³⁶ Initial staining tests (using Sudan Black, a stain that identifies drying oil) carried out on a number of samples indicated that the paint layer contained oil in all samples save for the Virgin's blue robe, while Amido black stains (used to identify proteins) showed the presence of protein in the paint in the same samples save for St. Sigismund's red robe.⁴³⁷ GC-MS performed on the blue mantle, the green

⁴³⁵ Ibid., 37, 66; Suzanne Q. Lomax and Michael Palmer, "Neroccio de Landi Scientific Report – 9 March, 2005," (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC). The analytical report clearly states that the flesh sample from *Claudia Quinta* was found to contain egg and oil while the National Gallery Technical Bulletin article states that the flesh tones were painted in tempera alone. Note 111 in Dunkerton, Christiensen, and Syson's "The Master of the Story of Griselda and Paintings for Sienese Palaces" further states that "staining tests and FTIR seemed to indicate that egg was used for the lead white underpaint. Both media were identified in the red lake and vermilion layer, the samples varying in the amount of of present (confirmed as walnut). On balance, therefore, the paint is probably a *tempera grassa* rather than an egg layer contaminated by later oil varnishes."

⁴³⁶ Carol Christensen et al. "Neroccio's 'Virgin and Child with Saint Anthony Abbott and Saint Sigismund' at the National Gallery of Art, Washington, DC," in *Studying Old Master Paintings: Technology and Practice*, ed. Marika Spring (London: Archetype Publications and the National Gallery, 2011), 21-7; Suzanne Q. Lomax and Michael Palmer, "Neroccio de Landi Scientific Report – 7 December 2007," (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC). Samples were collected from the Virgin's blue robe, St. Sigismund's red robe, flesh from the Virgin's neck, flesh from the hand of St. Sigismund, and the green paint from the floor tile.

⁴³⁷ Ibid.; Oddly the staining results from the sudan black are not cited in the article.

Figure removed due to copyrighting

Figure 4.64: Neroccio de Landi, *Madonna and Child with Saint Anthony Abbot and Saint Sigismund* (c. 1494/95, The National Gallery of Art, Washington DC).

tile, and the flesh sample (Virgin's neck) was found to contain mixtures of egg and oil; however, the 2011 publication states that "although a small amount of oil seemed to be present, the major component is egg, which was consistent with the results from staining."⁴³⁸ St. Sigismund's robe yielded the most confusing results; based on cross-sectional staining no

⁴³⁸ Christensen et al., "Neroccio's 'Virgin and Child with Saint Anthony Abbott and Saint Sigismund' at the National Gallery of Art, Washington, DC," 25; Lomax, Suzanne Q., and Michael Palmer, "Neroccio de Landi Scientific Report – 7 December 2007" (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC).

protein was identified in the paint; however GC-MS revealed the presence of oil and protein in the red glaze, leading the authors to characterize this passage in the painting as oil or *tempera grassa*.⁴³⁹ Christensen et al. notes that “while Neroccio may have used oil or *tempera grassa* in the red robes, he continued to paint in the discrete brushstrokes of the *tempera* technique, perhaps not fully understanding the blending qualities of the newer medium.”⁴⁴⁰ Based on technical evidence it seems that a handful of painters working in Siena in the fifteenth century were beginning to incorporate drying oils into their workshop practice. Yet in comparison to their Florentine neighbors, Siennese painters were relatively hesitant to fully abandon their *tempera*-based training even by the end of the century.

4.3 The Veneto and Alta Italia

There is ample evidence for cross-cultural exchange among fifteenth-century painters working in the Veneto and other territories, notably Padua, Mantua, Genoa, and Ferrara.⁴⁴¹

⁴³⁹ Ibid. Although the authors attribute the presence of a small phosphate peak to the presence of egg *tempera*, additions of carbon black pigment can also generate this marker. Furthermore, hydroxyproline (a marker for glue) was found to be present in the gas chromatogram, suggesting that the sample was contaminated with traces of the gesso ground therefore making it nearly impossible to confirm whether egg is in fact present.

⁴⁴⁰ Christensen et al., “Neroccio’s ‘Virgin and Child with Saint Anthony Abbott and Saint Sigismund’ at the National Gallery of Art, Washington, DC,” 25. Unless the artist is painting in thinned oils atop a very absorbant ground, it is unlikely that the individual brushstrokes would remain discernible. Strokes of oil paint, when applied side by side, would simply blend together as this is the nature of the medium.

⁴⁴¹ Bernd Roeck, “Venice and Germany: Commercial Contacts and Intellectual Inspirations,” in *Renaissance Venice and the North: Crosscurrents in the Time of Durer, Bellini, and Titian*, eds. Bernard Aikema and Beverly Louis Brown (New York: Rizzoli Intl. Publishing, 2000), 45-51; Sir Charles Lock Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, vols. I & II (1847; repr., New York: Dover Publications, 2001), 111; Oskar

Northern Italy experienced an exponential growth in art production throughout the Renaissance; its proximity to the Alps, the Balkans, and the rest of Eastern Europe fostered a unique type of cultural exchange between Italian and foreign painters. By 1400, Venice had established firmly rooted economic ties with the Byzantine and Muslim world as well as the north, solidifying the port city's reputation as an ideal center for trade and commerce. Duchies also dominated the cultural scene; wealthy families such as the Sforza in Milan, the Gonzaga in Mantua, and the Este in Ferrara were in constant competition, erecting monumental palaces that were decorated by both court painters and foreigners for hire. Italian painters who practiced in these regions were thus more likely to find themselves in close collaboration with foreign painters who were familiar with drying oils, a scenario that indirectly led to the proliferation of the oil medium in northern cities beyond the boundaries of Tuscany.

4.3.1 Venice

Little is known regarding the Venetian guild system and its impact on the adoption of painting techniques and daily workshop practice.⁴⁴² The guild system in Venice allowed for more flexibility than its counterparts in Florence and Siena during the Renaissance; although painters guilds from Venice (and nearby Padua) were excluded from exercising political power they were simultaneously allowed to act as independent organizations.⁴⁴³ While

Batschmann, *Giovanni Bellini* (London: Reaktion Books, 2008), 55; Carol M. Richardson, ed., *Locating Renaissance Art* (New Haven: Yale University Press, 2007), 93.

⁴⁴² Valentina Moncada, "The Painters' Guilds in the Cities of Venice and Padua," *RES: Anthropology and Aesthetics* 15 (1988): 105-121, accessed February 12, 2015, <http://www.jstor.org/stable/20166788>.

⁴⁴³ Moncada, "The Painters' Guilds in the Cities of Venice and Padua," 117; Peter Humfrey and Richard MacKenney, "The Venetian Trade Guilds as Patrons of Art in the Renaissance,"

Florentine painters fell under the jurisdiction of the *Arti de Medici e Speciali* (physicians and doctors), Venetian painters and other artisans belonged to their own designated groups all of which were overseen by a group of elected officials, the *Giustizia Vecchia*, responsible for monitoring the prices, conditions, and trade regulations of goods within and among the guilds. Surviving statutes (also referred to as the *capitolario* or *mariegola*) that date from the early thirteenth to fifteenth centuries suggests that the *Giustizia*'s regulations rarely pertained to workshop practices such as the mixing of colors or preparation of panels and instead tended to address administrative topics, apprenticeship guidelines, and monetary issues.⁴⁴⁴

What is perhaps more germane to the spread of oil painting in the north are the restrictions that were placed on foreign painters working in the Veneto. By 1436, painters were required to be residents of Venice before they could matriculate into the guild, a membership that was required for all practicing painters in the city (foreigners were also charged double the normal entry fee); however, given the presence of painters such as Antonello da Messina and Giovanni d'Alemagna (c. 1411-1450), it appears that these

The Burlington Magazine 128 (1986): 317-30, accessed February 12, 2015, <http://www.jstor.org/stable/882490>; Michelangelo Muraro, "The Statutes of the Venetian Arti and the Mosaics of the Mascoli Chapel," *The Art Bulletin* 43 (1961): 263-74, accessed February 12, 2015, <http://www.jstor.org/stable/3047968>; Satya Brata Datta, *Women and Men in Early Modern Venice: Reassessing History* (London: Ashgate Publishing, Ltd., 2003), 102. Padua's guild system eventually became overtaken by the Venetian guild system after the city fell to Venice around 1404. See also Richard MacKenney, *Tradesmen and Traders: The World of Guilds in Venice and Europe, c. 1250-c. 1650* (Totowa, N.J.: Barnes & Noble Books, 1987).

⁴⁴⁴ *Ibid.*; Moncada defines *Capitolario* as a collection of statutes, specifically a "book of bureaucratic dispositions and rules" while a *Mariegole* is a "book of statues with lists of members and illuminated pages"; Jill Dunkerton, "North and South: Painting Techniques in Venice," in *Renaissance Venice and the North: Crosscurrents in the Time of Durer, Bellini, and Titian*, eds. Bernard Aikema and Beverly Louis Brown (New York: Rizzoli Intl. Publishing, 2000), 93; Dunkerton cites one exception; Venetian guild statutes dating to 1278 forbade anyone from selling a painted object unless it had been varnished.

restrictions did not actively prevent foreign artists from participating in workshops or even undertaking private commissions (see Chapter 2.3).⁴⁴⁵ Venice was populated with confraternities (also referred to as *scuole*) that represented a wide range of social groups, including foreigners and artisans; *scuole* could opt to patronize a non-native painter to represent their eclectic tastes or trade.⁴⁴⁶ But above all Venice was ultimately governed by merchants. As the leading exporter of fifteenth and sixteenth-century altarpieces, it is no surprise that Venice more or less adhered to an oligarchical system control by its powerful merchant class, one that enabled its guild system to adapt to the ebb and flow of a thriving international market.⁴⁴⁷

Perhaps the most significant example of collaboration between foreign and Venetian painters involved the commission of the Eremitani frescoes. In 1448 the widow of Antonio

⁴⁴⁵ Muraro, “The Statutes of the Venetian Arti and the Mosaics of the Mascoli Chapel,” 269; Moncada, “The Painters’ Guilds in the Cities of Venice and Padua,” 109; Muraro claims this initiative began in 1436 while Moncada cites the same law as being passed as late as 1512.

⁴⁴⁶ Moncada, “The Painters’ Guilds in the Cities of Venice and Padua,” 105; Humphrey and MacKenney, “The Venetian Trade Guilds as Patrons of Art in the Renaissance,” 318-21; If a *scuole* had aristocratic connections or were connected to a luxury trade (like the silk-weavers) than they were in an excellent position to commission impressive painted altarpieces such as Vittore Carpaccio’s wall paintings depicting the *Legend of St. Ursula* for the Scuola di Sant’Orsola (1497-98) and Cima da Conegliano’s altarpiece for S. Maria dei Crociferi (c. 1495). Smaller *scuole* also occasionally managed to hire notable artists as evidenced by the *scuole sabbionai* (sand-merchants) commissioning an altarpiece by Bartolomeo Vivarini.

⁴⁴⁷ Peter Humfrey, *The Altarpiece in Renaissance Venice* (New Haven: Yale University Press, 1993), 123; —and MacKenney, “The Venetian Trade Guilds as Patrons of the Art in the Renaissance,” 317-30; Sonia Evers, “The Polyptych of Conversano by Bartolomeo Vivarini in the Accademia,” *Save Venice Journal* (1995), accessed November 15, 2015, <http://www.savevenice.org/publications/scholarly-articles/the-polyptych-of-conversano-by-bartolomeo-vivarini-in-the-accademia/>; Evers states that “more than two-fifths of the recorded altarpieces dating from the second half of the 15th-century were destined for export, a reality which contemporary legislation encouraged.”

Ovetari recruited the German painter, Giovanni d'Alemagna, together with his brother-in-law Antonio Vivarini, to work alongside two native Paduans, Nicolò Pizolo and Andrea Mantegna (also the brother-in-law of Giovanni Bellini).⁴⁴⁸ In reviewing documents that relate to the distribution of labor within the church, Holgate concludes that Giovanni and Vivarini were entrusted with the larger of the two spaces that would have been the most visible portion of the vault and therefore the most prestigious.⁴⁴⁹ Sometime after 1440, Giovanni d'Alemagna had become partners with Antonio Vivarini, quickly establishing a reputation throughout the Veneto beginning with one of their first major commissions *The St. Jerome Altarpiece* (Figure 4.65), completed in 1441 for the Venetian church of the Augustinian Hermits.⁴⁵⁰ Since Giovanni was a native German it is likely that he was recognized for his familiarity with the oil technique, a medium that the artists were specifically asked to refrain from using during the execution of the Ovetari frescoes (that sadly no longer survive) which they began in

⁴⁴⁸ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 48; Ian Holgate, "Giovanni d'Alemagna, Antonio Vivarini and the Early History of the Ovetari Chapel," *Artibus et Historiae* 24 (2003): 9-29, accessed January 20, 2016, <http://www.jstor.org/stable/1483758>; Lorne Campbell, "Cosmè Tura and Netherlandish Art," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Steven Campbell (Boston: Isabella Stewart Gardner Museum, 2002), 119; Ames-Lewis speculates that Giovanni d'Alemagna could very well be the "Giovanni da Ulma" recorded working on the Chapel of S. Massimo in the palace of the Bishop in Padua; a signed contract dating to 1437 indicates that the Bishop Pietro Donato stipulated that the walls be painted "all in oil." Holgate observes that Giovanni d'Alemagna began his practice first in Padua, possibly registering with the guild as "Giovanni Tectonico" in 1441, with Antonio Vivarini joining him later on in Venice. There is some evidence, however, evidence that the artist was active in Padua prior to registering with the guild as he was purportedly commissioned to polychrome the tomb of Raffaello Fulgosio at the Santo in Padua in 1431.

⁴⁴⁹ Holgate, "Giovanni d'Alemagna, Antonio Vivarini and the Early History of the Ovetari Chapel," 9-29.

⁴⁵⁰ Ian Holgate, "The Early History of Antonio Vivarini's 'St. Jerome' Altarpiece and the Beginnings of the Renaissance Style in Venice," *The Burlington Magazine* 143 (2001): 19-22, accessed January 20, 2016, <http://www.jstor.org/stable/889068>.

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Figure 4.65: Giovanni d'Alemagna, *The St. Jerome Altarpiece* (1441, Kunsthistorisches Museum, Vienna).

1448.⁴⁵¹ Dunkerton suggests that problems arising from the use of oil could have been due to the damp environment of Venice which could lead to drying problems.⁴⁵² This stipulation may be associated with Giovanni's (as well as his collaborators') propensity to use the oil

⁴⁵¹ Jill Dunkerton, "Cosmè Tura's Painting Technique," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Steven Campbell (Boston: Isabella Stewart Gardner Museum, 2002): 119.

⁴⁵² Ibid; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 161; Mark Clarke, *Mediaeval Painters' Materials and Techniques: The Montpelier 'Liber diversarum arcium' (c.1200-1400)* (London: Archetype, 2011), 90,143, 215.

medium or may indicate that drying oil was beginning to be more frequently used on wall paintings during this period, suggested by number of contemporary treatises including Cennini's *Il Libro d'Arte* and Alberti's *De re aedificatoria*.⁴⁵³ To date there have been practically no technical studies performed on works by Giovanni d'Alemagna; however, the evidence suggests that this artist possessed a unique style that point to the use of materials beyond traditional egg tempera. Works associated with the Vivarini workshop on the other hand have revealed a range of binders including egg- and oil-based paints.⁴⁵⁴

⁴⁵³ Cennino Cennini, *The Craftsman's Handbook, 'Il Libro dell 'Arte,'* trans. Daniel V. Thompson (1933; repr., New York: Dover Publications, 1960), 125-31; Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, 63-4. In Chapter LXXXVIII of *Il Libro d'Arte*, Cennini describes how to prepare oil to work "on walls, on panel, on iron and wherever you like." Eastlake quotes Alberti's observation about wall painting in 1472 in which he states that "there is a new invention, in which all kinds of colors applied with linseed oil are proof against all effects of the atmosphere; provided the wall on which they are spread be dry and perfectly free from moisture [within]."

⁴⁵⁴ Cosimo D. Calvano, "Fingerprinting of egg and oil binders in painted artworks by matrix-assisted laser desorption ionization time-of-flight mass spectrometry analysis of lipid oxidation by-products," *Analytical Bioanalytical Chemistry* 400 (2011): 2229-240, doi: 10.1007/s00216-011-4919-1; Marika Spring, Rachel Grout, and Raymond White, "'Black Earths': A Study of Unusual Black and Dark Grey Pigments used by Artists in the Sixteenth Century," *National Gallery Technical Bulletin* 24 (2003): 96-114; Higgitt and White, "Analysis of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," 96, Note 37; Laura Rivers, "Alvise Vivarini -Technical Study" (Technical report housed at the Winterthur/University of Delaware Program in Conservation, 2004); Calvano et al. used MADLI-TOF-SIMS and Py-GC-MS to identify the presence of egg and oil markers in samples collected from a green area as well as the red bole from Bartolomeo Vivarini's *Madonna with Child and St. Bernard, St. Nicholas, St. Vito, and St. John the Baptist* (c. 1490). Analysis of Alvise Vivarini's *Portrait of a Man* (1497), presumably using GC-MS, revealed the presence of linseed oil in the black background. A panel depicting an unknown Bishop from a larger altarpiece by Antonio Vivarini (c. 1440-44) that is now at the Walters Art Museum was analyzed using FTIR and GC-MS; while the former pointed towards the presence of egg in the paint the GC-MS was only able to confirm the presence of drying oil.

Painters from the north are recorded working in the Veneto by the early fourteenth century, soon after the arrival of Gentile da Fabriano in Venice.⁴⁵⁵ Gentile is documented as working in Venice by 1408, working on a large altarpiece for Francesco Amadi although it is still unclear whether he was a registered citizen of Venice during his stay in the city.⁴⁵⁶ Examination of his works have led scholars to believe he may have used oil as an additive and as a glaze in his paintings, giving his flesh tones in particular a “Lombardian” appearance as well his occasional incorporation of northern formats (such as the two kneeling saints in the *Madonna and Child with Saints Lawrence and Julian* painted around 1423-5; Figure 4.66).⁴⁵⁷

⁴⁵⁵ See Chapter 2.3; An artist named “Piero de Fiandra,” (possibly Petrus Christus) completed an altarpiece in 1451 for the no longer extant Santa Maria della Carita. Dieric Bouts’s tuchlein “The Entombment” (painted around 1450) could have been part of a larger, more elaborate polyptych for a Venetian church while another painted cloth by “Gianes da Brugia” has been described by Marcantonio Michiel in the collection of Leonico Tomeo in Padua. Both Marco Barbargio, who became the Doge of Venice, and the ambassador to France, Zaccaria Contarini, both had their own private portraits executed by northern artists. Another Venetian ambassador Bernardo Bembo may have also been responsible for the commission of a diptych by Hans Memling. See also Wolfgang Stechow, *Northern Renaissance Art, 1400-1600: Sources and Documents* (New Jersey: Prentice-Hall, Inc., 1966), 29-31.

⁴⁵⁶ Lorenzo Mochi Onori and Laura Laureti, eds., *Gentile da Fabriano and the Other Renaissance* (Milan: Mondadori Electra S.p.A., 2006), 25; Gentile da Fabriano appears to have traveled extensively during his career as documents place him in Venice by 1408, in Brescia from 1414-19, Fabriano in 1420, Florence from 1420-5, Siena and Orvieto in 1425, and Rome in 1426-7 (it is also possible that he traveled to Milan and Pavia around 1395).

⁴⁵⁷ Ibid, 125; Roberto Bellucci, “Tecnica e stile: Appunti su Gentile da Fabriano,” in *Gentile da Fabriano: Studi e Ricerche*, eds. Andrea G. De Marchi, Lorenzo Mochi Onori, and Laura Laureti (Milan: Mondadori Electra S.p.A., 2006), 61; Ames-Lewis, “Filippo Lippi and Flanders,” 269; A cross-section collected from Gentile’s *Madonna and Child* (c. 1425) of the Quaratesi altarpiece also suggested the presence of oil; however, it is unclear whether analytical testing was conducted on the cross-section of whether this conclusion was based on visual examination alone. See Bellucci and Frosinini, “Working Together: Technique and Innovation in Masolino and Masaccio’s Panel Paintings,” 39. Ames-Lewis points out that the kneeling saints in Fabriano’s *Madonna and Child with SS. Lawrence and Julian* reflects a northern tradition. See also Keith Christiansen, *Gentile da Fabriano* (New York: Cornell University Press, 1982).

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Figure 4.66: Gentile da Fabriano, *Madonna and Child with Saints Lawrence and Julian* (1423-5, The Frick Collection, New York).

Figure As discussed in preceding sections, technical analysis of Fabriano's triptych painted for the church of San Niccolo Oltrarno in Florence (c. 1424) revealed the possible use of

mixed media, and a paint cross-section collected from the *Madonna and Child* (c. 1425) of the Quaratesi altarpiece also suggested the use of oil.⁴⁵⁸ Further research is needed to confirm Fabriano's occasional use of drying oils; however, the artist undoubtedly impacted the next generation of painters working in Venice and may have influenced some to look beyond the traditional tempera technique.⁴⁵⁹

The young Jacopo Bellini (c. 1400- c. 1470) is documented working under the supervision of Gentile da Fabriano (along with Pisanello) in the Doge's Palace in Venice on a fresco cycle that unfortunately no longer survives.⁴⁶⁰ By 1424 Jacopo had established his own workshop in Venice and was soon receiving commissions throughout the Veneto and its outer territories, eventually attracting the attention of Niccolo d'Este in Ferrara who sent for the artist to paint a portrait of his son (now lost).⁴⁶¹ As discussed earlier, both father and son had

⁴⁵⁸ See Chapter 4.2; Ciatti, Frosinini, and Bellucci, "Il restauro del 'Polittico dell'Intercessione' di Gentile da Fabriano, un'opera misteriosa e affascinante, considerata in passato perduta," 144, 194. Note that the authors only cite the use of cross-sectional analysis, FT-IR, and solvent extraction using a 2:1 pentane/methylene chloride mixture. While it is unclear whether the latter generated an FTIR spectrum or a GC spectrum, the authors deduced the presence of drying oil from the solvent extraction process. Other samples showed the presence of proteinaceous materials (which in some instances was determined to be glue) combined with traces of fatty acids. A cross-section collected from Gentile's *Madonna and Child* (c. 1425) of the Quaratesi altarpiece also suggested the presence of oil; however, it is unclear whether analytical testing was conducted on the cross-section or whether this conclusion was based on visual examination alone. See Bellucci and Frosinini, "Working Together: Technique and Innovation in Masolino and Masaccio's Panel Paintings," 39, 64 (Note 54).

⁴⁵⁹ Lisa Monnas, *Merchants, Princes, and Painters: Silk Fabrics in Italian and Northern Paintings, 1300-1550* (New Haven & London: Yale University Press, 2008), 97-110.

⁴⁶⁰ Batschmann, *Giovanni Bellini*, 32; The frescoes depicted "the subjugation of the Emperor Frederick Barbarossa by Pope Alexander III through the intercession of the Doge, along with a battle scene."

⁴⁶¹ *Ibid*, 33-4; There is still some speculation that the artist may have accompanied his master to Brescia and Florence before returning to Venice to set up his own workshop. Upon his

already developed a taste for northern paintings and it is possible that Jacopo encountered works by Rogier van der Weyden and Jan van Eyck upon his arrival in Ferrara in 1441.⁴⁶² Throughout his career it appears that Jacopo remained faithful to traditional Italian painting techniques, although no analysis has been performed on any of his extant works.⁴⁶³ If there was any development in his use of painting media it may have occurred after his visit to Ferrara; however, Jacopo's younger half-brother Giovanni would eventually become one of the first Venetian painters to fully master the art of painting in oil.⁴⁶⁴ According to the historian Carlo Ridolfi, Giovanni Bellini first learned of the oil technique after a clandestine studio visit to Antonello da Messina, a tale that today is considered speculative at best.⁴⁶⁵

arrival in Ferrara, Jacopo Bellini supposedly entered into a portrait competition to depict with Pisanello and won. It is also speculated that the kneeling patron in Jacopo Bellini's *Madonna of Humility* (c. 1430s) in the Louvre represents the young Leonello d'Este.

⁴⁶² Frances Ames-Lewis, "Sources and Documents for the Use of the Oil Medium" in *Cultural Exchange Between the Low Countries and Italy, 1440-1600*, ed. Ingrid Alexander-Skipnes (New York: Brepols Publishers, 2007), 49, 50, 53, 55-7; Carol M. Richardson, Kim W. Woods, and Michael W. Franklin, eds., *Renaissance Art Reconsidered* (Chicester: John Wiley and Sons, Ltd., 2007), 186-9. See Chapter 2.3 for more information on northern paintings in Italian collections during the Quattrocento.

⁴⁶³ Dunkerton, "North and South: Painting Techniques in Venice," 94; Dunkerton speculates that Jacopo's *Legnaro Madonna* in the Gallerie dell'Accademia is likely painted in oil.

⁴⁶⁴ Susannah Rutherglen and Charlotte Hale, "'St. Francis in the Desert': Technique and Meaning," in *In A New Light: Giovanni Bellini's St. Francis in the Desert*, eds. Susannah Rutherglen and Charlotte Hale (New York: The Frick Collection, 2015), 81. New evidence suggests that Giovanni Bellini was Nicolo Bellini's illegitimate son and Jacopo Bellini's younger half-brother.

⁴⁶⁵ Dunkerton, "North and South: Painting Techniques in Venice," 96; Batschmann, *Giovanni Bellini*, 61; Ridolfi's story states that "all authors honor Giovanni Bellini by supposing that he openhandedly disseminated his knowledge of oil painting, of which Antonello da Messina had made a great secret. Giovanni Bellini was able to deceive Antonello da Messina as follows. He dressed up as a Venetian nobleman and went to see Antonello, who did not know him, in order to commission a portrait from him. Then Bellini observed Antonello mixing his

However, Ridolfi's dubious tale deserves some consideration; numerous paintings associated with Giovanni Bellini's workshop have been found to contain drying oil or mixed media (see Appendix C for a table summarizing analytical findings).⁴⁶⁶ Although a handful of these

pigments while painting, and in this way discovered the secret, which he then immediately made public in accordance with his sense of duty." Dunkerton points out that the oil medium was already in use in the Bellini workshop before Antonello arrived in Venice in 1475 to paint the *San Cassiano* Altarpiece.

⁴⁶⁶ Charlotte Hale, "Appendix A: The Technical Examination of 'St. Francis in the Desert,'" in *In A New Light: Giovanni Bellini's St. Francis in the Desert*, eds. Susannah Rutherglen and Charlotte Hale (New York: The Frick Collection, 2015), 168-85; Gianluca Poldi and Giovanni C. F. Villa, *Bellini a Venezia. Sette opere indagate nel loro contesto* (Milano: Silvana Editoriale S.p.A., 2008), 175-94; Cinzia Maria Mancuso and Antonietta Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," in *Giovanni Bellini and the Art of Devotion* (Indianapolis: Indianapolis Museum of Art, 2004), 136-41; R&C Scientifica, "Sezioni stratigrafiche e riconoscimento dei pigmenti a dei leganti," in *Carpaccio, Bellini, Tura, Antonello: e altri restauri quattrocenteschi della Pinacoteca del Museo Correr*, ed. Attila Dorigato (Milan: Electa, 1993), 218-9; John Mills and Raymond White, "Analyses of Paint Media," *National Gallery Technical Bulletin* 1 (1977): 57-9. GC-MS and FTIR was carried out at the Metropolitan Museum of Art to determine the presence of oil in the Frick painting. GC-MS was carried out on samples collected from a number of Bellini's works at the Galleria d'Accademia in Venice. UV microspectrofluorometric analysis was carried out on a number of paint cross-sections to confirm the presence of protein and/or oil. Three paintings from the Indianapolis Museum of Art as well as another from the Philadelphia Museum of art were found to be executed with a mixed technique. Mancuso and Gallone found "either egg and oil mixed together, or layers of pigment combined entirely with egg superposed on others entirely in oil." FT-IR and GC were used to characterize drying oil in sky and green grass in *The Transfiguration of Christ* (c. 1460) and the sky *Pieta* (c. 1460) in the Museo Correr. Mills and White indicate that the presence of oil was not able to be completely confirmed but that egg was identified using GC in the both underpriming and blue underpaint from *The Madonna of the Meadow* (late 15th c.). It should be noted that only a few of these publications provide details regarding analysis performed with gas chromatography-mass spectrometry (GC-MS) and/or Attenuated Total Reflectance-Fourier-Transform Infrared Spectroscopy (ATR-FTIR). It is the author's opinion that analysis performed using Fourier-Transform Infrared Spectroscopy (FTIR), staining of cross-sectional samples, UV microspectrofluorometric analysis, and gas chromatography not equipped with a mass spectrometer does not provide conclusive information relating to the presence of organic binders within discrete layers or even definitive characterization of individual binders. See also Jill Dunkerton, "Bellini's

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Figure 4.67 (left) and Figure 4.68 (right): Giovanni Bellini, *Crucifixion* (c.1465-70, Musée du Louvre, Paris; left) and *The Calvary* (c.1465-70, Musée du Louvre, Paris; right).

analytical results yielded questionable results (such as the unlikely application of egg tempera atop oil layers), it is evident that drying oil was in frequent use soon after Giovanni took over the Bellini workshop. Like Jacopo, Giovanni Bellini's compositions occasionally echo northern motifs, such as his *Crucifixion* (Figure 4.67) and *The Calvary* (Figure 4.68), both of which were likely executed between 1465 and 1470 in direct response to Flemish paintings present in or around Padua.⁴⁶⁷ Bellini is also one of the earliest Italian painters known to have

Technique,” in *The Cambridge Companion to Giovanni Bellini*, ed. Peter Humphrey (Cambridge: Cambridge University Press, 2004), 195-225.

⁴⁶⁷ Batschmann, *Giovanni Bellini*, 63; Batschmann states that “Jill Dunkerton has deduced that the *Crucifixion* in the Museo Correr, whose binding medium has not been analyzed, was at least partly executed in oils. Giovanni Bellini probably based this painting on a small panel originating either from Jan van Eyck's workshop or from one of his followers, which may have arrived in Padua by the mid-1450s where it was presumably copied by an Italian artist.”

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Figure 4.69: Giovanni Bellini, *Portrait of Jörg Fugger* (1474, Norton Simon Museum of Art, Pasadena).

adopted fabric supports, something that Dunkerton surmises was in direct response to northern paintings on canvas that were present in churches and private collections in and around Florence.⁴⁶⁸ Bellini's affinity for the oil medium likely attracted the attention of certain patrons who were accustomed to the northern aesthetic; in 1474 the German banker Jörg

⁴⁶⁸ Villers, "Paintings on Canvas in Fourteenth Century Italy," 348; Young, "History of Fabric Supports," 128; Dunkerton, "North and South: Painting Techniques in Venice," 94-100; Caroline Villers describes a surviving decorative banner, *Miracle at the Bridge of San Lorenzo*, at the Galleria d'Accademia in Venice while Dunkerton attributes the dessicated appearance of *The Blessed Lorenzo Giustiniani*, c. 1465, to the artist's use of a gum or glue-based medium.

Fugger chose Bellini to paint his portrait, now in the Norton Simon Museum of Art (Figure 4.69).⁴⁶⁹

The wide range of mediums and supports used by Giovanni Bellini is a unique characteristic for an Italian painter working during the fifteenth century. Dunkerton has pointed out that while some paintings by Bellini have been analyzed and found to contain oil alone, such as panels from the *Pesaro Altarpiece* (1471-83; Figure 4.70), Bellini continued to use egg tempera throughout his entire career, possibly a testament to his traditional training.⁴⁷⁰ Egg tempera has been identified as the principal medium in the *Agony in the Garden* (1459-65; Figure 4.71) and the *Blood of the Redeemer* (c.1460-65), while in other works such as the *Madonna of the Meadow* (c. 1500) and panels from *The Saint Ferrer Altarpiece* (1464-68) have been found to contain egg and oil (in the form of *tempera grassa* and/or present in discrete layers); visual examination of Bellini's paintings have also revealed fingerprints patterns, presumably in passages where the artist likely used oil (Figures 4.72 and 4.73).⁴⁷¹ Using both fingers and brushes, Bellini exploited the lengthy dry time of the oil

⁴⁶⁹ Bernd Roeck, "Venice and Germany: Commercial Contacts and Intellectual Inspirations," in *Renaissance Venice and the North: Crosscurrents in the Time of Durer, Bellini, and Titian*, Bernard Aikema and Beverly Louis Brown, eds. (New York: Rizzoli Intl. Publishing, 2000), 46.

⁴⁷⁰ Dunkerton, "Bellini's Technique," 207-10; Gianluca Poldi and Giovanni C. F. Villa, 'A new examination of Giovanni Bellini's 'Pesaro Altarpiece': Recent findings and comparisons with other works by Bellini' in *Studying Old Master Paintings: Technology and Practice*, ed. Marika Spring (London: Archetype Publications Ltd., 2011), 32; Charlotte Hale and Susannah Rutherglen, "St. Francis in the Desert: Technique and Meaning" in *In A New Light: Giovanni Bellini's St. Francis in the Desert*, eds. Susannah Rutherglen and Charlotte Hale (New York: The Frick Collection, 2015), 127-8. GC-MS analysis of two samples from the *Coronation of the Virgin* and one sample from *St. Terence* showed the presence of drying oil with no evidence of proteins, cholesterol, or lecithin.

⁴⁷¹ Gianluca Poldi, "Note quasi Sparse sul Colore e la Tecnica di Giambellino: Nuovi Studi Analitici," in *Indagando Bellini*, eds. Gianluca Poldi and Giovanni C. F. Villa (Milan: Skira,

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Figure 4.70: Giovanni Bellini, *The Coronation of the Virgin* (c. 1471-83, Pinacoteca Vaticana, Rome).

2009), 202-4; Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in *Il colore ritrovato: Bellini a Venezia*, eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 178-194; Dunkerton, "Bellini's Technique," 196-8; —, "North and South: Painting Techniques in Venice," 96; John Mills and Raymond White, "Analysis of Paint Media," *National Gallery Technical Bulletin* 2 (1978): 74-5; —, "Analysis of Paint Media," *National Gallery Technical Bulletin* 1 (1977): 58; Blue and white samples from *The Blood of the Redeemer* were tested using GC alone and found to contain egg with trace amounts of oil (determined to be contamination) while the blue paint from the mountains of *Agony in the Garden* was found to contain egg; See also Stefano Volpin and Lorenzo Lazzarini, "Il colore e la tecnica pittorica della Pala di San Gonne di Giovanni Bellini," *Quaderni della Soprintendenza ai beni artistici e storici di Venezia* 19 (1994), 29-37; Fingerprints have been encountered in twentieth-century tempera paintings by Andrew Wyeth but are far less frequently found in traditional Italian tempera paintings. Egg tempera, unless emulsified with a considerable amount of oil paint, cannot be easily manipulated once the paint has been applied to the support. This may explain the presence of fingerprints observed on the surface of the *Madonna and Child* (c. 1480/85) in the National Gallery of Art in Washington.



Figure 4.71: Giovanni Bellini, *Agony in the Garden* (1459-65, National Gallery, London).

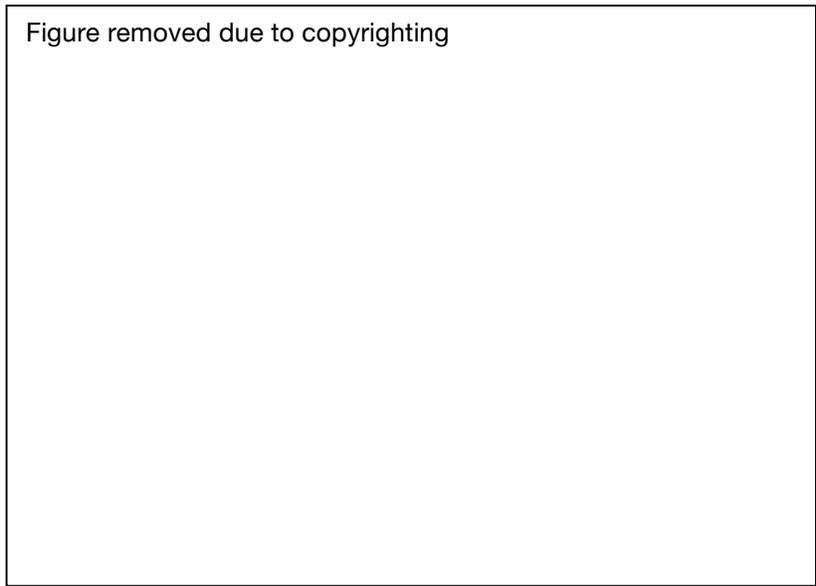


Figure 4.72: Giovanni Bellini, *St. Francis in Ecstasy* (1475-80, The Frick Collection, New York).



Figure 4.73: Detail of fingerprints in Giovanni Bellini's *St. Francis in Ecstasy* (1475-80, The Frick Collection, New York).⁴⁷²

medium to further manipulate his compositions long after applying the paint. Works by Bellini's pupil, Cima de Conegliano (c. 1459-c. 1517), suggest that worthy apprentices in the Bellini workshop were likely introduced to the oil technique. While Bellini was involved in painting large-scale canvas paintings (likely in oil) for the Sala del Gran Consiglio, Cima da Conegliano began to produce a number of altarpieces for churches throughout the Veneto region.⁴⁷³ Oil alone was found in *The Incredulity of St Thomas* (1502-4), two panels from the S. Maria dei Crociferi altarpiece (c. 1500), as well as the central panel of an altarpiece commissioned by the Scuola di San Rocco (*St. Catherine of Alexandria*, c. 1502); however, a number of other works, including the small *The Virgin and Child with a Goldfinch* (c. 1505),

⁴⁷² James Elkins, "The Most Beautiful Paintings in the World," *The Huffington Post*, accessed April 10, 2016, <http://www.huffingtonpost.com/james-elkins/the-most-beautiful-paintings-in-the-world.html>.

⁴⁷³ Dunkerton, "North and South: Painting Techniques in Venice," 100; — et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 200.

revealed the presence of tempera in the lighter colors, underpaint, and admixed with oil.⁴⁷⁴ Based on these analyses it appears that Cima, like his master, exploited both mediums throughout his career, although his larger commissions appear to have been mostly executed in oil.

The Bellini and Vivarini workshops were rivaled by one other enterprise in the *Veneto* region, a workshop that has also been tied to the adoption of the oil medium. Scientific analysis has confirmed Carlo Crivelli's use of the oil technique during the latter half of his career. While Crivelli's hatched brushwork is characteristic of the traditional Italian approach, at least three paintings at the National Gallery in London from the second half of the artist's career indicate the use of mixed media. Both the *Madonna and Child Enthroned with Donor* (1470; Figure 4.74) and *The Dead Christ Supported by Two Angels* (1470-5; Figure 4.75) were found to contain both drying oil and egg tempera in painted passages that emulate marbled surfaces.⁴⁷⁵ Crivelli's later works also reveal the use of drying oils and mixed media;

⁴⁷⁴ Dunkerton, "North and South: Painting Techniques in Venice," 100; — et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 200; —, "The Restoration of Two Panels by Cima de Conegliano," *National Gallery Technical Bulletin* 21 (2000): 64, 69; — and Ashok Roy, "The Technique and Restoration of Cima's 'The Incredulity of St. Thomas,'" *National Gallery Technical Bulletin* 10 (1986): 10, 26; Mills and White, "Analysis of Paint Media," *National Gallery Technical Bulletin* 3 (1979): 66-7. Using GC-MS, oil was identified in white, red lake, and verdigris-containing samples in *St. Catherine of Alexandria* and in orange-brown and green glazes in St. Thomas's robe in *The Incredulity of St Thomas*. Using GC, blue paint from the mountains and the red-brown parapet were found to contain tempera (possibly with trace drying oil considered to be contamination) in *The Virgin and Child with a Goldfinch* while the green paint from the leaves was found to contain mostly oil with small additions of egg. GC was also used to confirm the presence of linseed oil in two panels from the S. Maria dei Crociferi altarpiece in London. Solubility tests (the specificity of which is highly speculative) also pointed towards the presence of egg tempera in *The Crucifixion* in the Barber Institute and *Christ among the Doctors in Warsaw* (analytical technique is not specified).

⁴⁷⁵ Suzanne Q. Lomax, "Carlo Crivelli Scientific Report – 3 December, 2007" (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art,

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Figure 4.74 (left) and Figure 4.75 (right): Carlo Crivelli, *Madonna and Child Enthroned with Donor* (1470, The National Gallery of Art, Washington DC; left) and *The Dead Christ Supported by Two Angels* (1470-5, National Gallery, London; right).

Washington, DC). Jill Dunkerton and Raymond White, “The Discovery and Identification of an Original Varnish on a Panel by Carlo Crivelli,” *National Gallery Technical Bulletin* 21(2000):71-6. For the Washington panel GC-MS revealed the presence of drying oil and egg tempera in samples collected from the marbled plinth and the red background (hydroxyproline was also detected indicating that some of the amino acids may represent traces of ground that were present in both samples). FTIR also revealed amide stretching bands in the sample collected from the marbling. For the London panel GC-MS identified egg tempera and walnut oil in the dark green paint of the marbling and the crown of thorns.

tempera grassa was found in an areas of white paint and possibly the green of the Virgin's mantle in *The Annunciation with St. Emidius* (1486) as well as the green cloak of the Virgin in *Virgin and Child with Saints Francis and Sebastian* (1491) while *The Vision of the Blessed Gabriele* (1489-90) and the *Madonna della Rondine* (c. 1490-2; Figure 4.76) contain egg and oil in separate passages, tempera grassa, and complex layering of both media.⁴⁷⁶ This suggests that Crivelli had a personal relationship with his materials, confirming that the artist was fully aware of the aesthetic appearance that would result from his decisions relating to the use of a range of binding media.

⁴⁷⁶ Mills and White, "The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," 72-7; —, "Organic Analysis in the Arts: Some Further Paint Medium Analyses," *National Gallery Technical Bulletin* 2 (1978):74-5; —, "Analyses of Paint Media," *National Gallery Technical Bulletin* 11 (1987): 92-3; Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 14 (1993): 87-92; Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 32. It is unclear what specific analytical techniques were used to identify the binders in the *Annunciation of Saint Emidius*, however it is assumed the authors employed GC-MS and FTIR. For *The Vision of the Blessed Gabriele* staining, heating tests, and GC were used to identify egg and oil was found in the azurite containing sky, the flesh of the saint's foot, and the beige paint depicting the winding path while the green foliage was executed using a black layer containing egg with a top layer consisting of verdigris and lead white bound in egg and oil. The *Madonna della Rondine* contains mixed media for the green of the book, the blue of the Virgin's mantle, and the red cloak of St. Jerome, while egg alone is found in the flower pot as well as the marbling, all identified using GC-MS.

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Figure 4.76: Carlo Crivelli, *Madonna della Rondine* (1490-2, National Gallery, London).

4.3.2 Padua

Carlo Crivelli, Andrea Mantegna, and Alvise and Bartolomeo Vivarni were all documented serving as apprentices in Francesco Squarcione's workshop located in Padua.⁴⁷⁷ By 1440, Squarcione's workshop was thriving, and although little is known regarding his preferred painting techniques, works created by several of his students have been analyzed and found to contain drying oil and mixed media.⁴⁷⁸ Examination of Andrea Mantegna's

⁴⁷⁷ Holmes, *Fra Filippo Lippi: The Carmelite Painter*, 113; Leopardi, "Aesthetic Hybrids: Interpreting Carlo Crivelli's Ornamental Style," 50-69; Campbell, "Cosme Tura and Court Culture," 11; Gilbert, *Italian Art 1400-1500*, 34.

⁴⁷⁸ See sections in this chapter on works by Crivelli, Mantegna, and the Vivarini workshop. While Vincenzo Foppa has not been traced directly to Squarcione's workshop, he is generally thought to have trained in Padua; a handful of his works have been analyzed and found to contain both egg and oil paint media. Two paintings attributed to Foppa at the Philadelphia Museum of Art were examined using FTIR and GC-MS; while the *Virgin and Child* (1490) was found to be mainly egg, the *Portrait of an Elderly Gentleman* (c. 1495-1500) was painted using *tempera grassa* and completed in oil. A lead white and carbon black-containing *imprimatura* was also found in the *Portrait of an Elderly Gentleman* (c. 1495-1500) while the *imprimatura* layer found in *The Virgin and Child* (1490) is pigmented with carbon black and red earth pigment. The latter finding is a curious one as this painting is purportedly painted using egg tempera for much of the picture. Regarding Foppa's *Adoration of the Kings* (1480s/90s), GC-MS found the presence of heat-bodied walnut oil as the principal medium used in the light colored paint from the stone ruin while other areas of the painting (the *sgraffito*) were found to contain egg tempera. For information on the Philadelphia paintings see Beth Price, Teresa Lignelli, and Jan Carlson, "Investigating Foppa: Painting Materials and Structure," *Art et Chimie, la Couleur. Actes du Congrès* (2000): 209-12. For information on Foppa's *Adoration* see Jill Dunkerton and Carol Plazzotta, "Vincenzo Foppa's 'Adoration of the Kings,'" *National Gallery Technical Bulletin* 21 (2001):18-28. For information on Foppa's use of a secco paints see Lorenzo Appolonia, Giovanni Bortolaso, and Lucia Toniolo, "Vincenzo Foppa Frescoes at S. Eustorgio Church in Milan: Investigations on Pigments and Media by means of Classic and New Scientific Techniques," in *Abstracts of Art et Chimie, la Couleur, Congrès International sur l'apport de la Chimie aux oeuvres d'art, 16-18 September, Paris, 1998*, eds. Marie-Pierre Pomies, Jean-Claude Dran, M. Gunn, Elisabeth Martin, Michel Menu, Daniele Giraudy, and Sylvie Colinart (Paris: CNRS Editions, 1998), 153-4.

oeuvre suggests that he was perhaps more willing to explore new techniques in comparison to his contemporaries though he did not abandon the traditional egg tempera medium altogether.⁴⁷⁹ A technical study carried out on his *San Luca Altarpiece* (1453; Figure 4.77) identified the presence of egg tempera and oil, with the latter present in the form of green and blue glazes.⁴⁸⁰ Mantegna was only about 22 years of age when he completed the series, which suggests that the oil medium was already being used in Squarcione's studio. Mantegna's early use of canvas as a support is exceptionally unique; technical studies have identified at least 41 paintings on fabric confirming that the artist experimented with a variety of aqueous-based media (glue, egg, and/or casein), likely influenced by imported distemper (glue mixed with pigments) paintings arriving from the north.⁴⁸¹ Mantegna's ability and willingness to adopt

⁴⁷⁹ Jane Martineau, ed., *Andrea Mantegna* (London & New York: Royal Academy of Arts and the Metropolitan Museum of Art, 1992), 243; Jennifer Fletcher, "Mantegna and Venice" in *Mantegna and 15th-century Court Culture*, eds. Francis Ames-Lewis and Anka Bednarek (London: University of London, Birbeck College, 1993), 19; Giovanni Agosti and Dominique Thiebaut, eds., *Mantegna*, (Paris: Musee du Louvre, 2008) 232-5. Mantegna's *Crucifixion* (c. 1456-9) at the Louvre and the *Man of Sorrows* (c. 1485-1500) in Copenhagen have both been identified as having been painted in egg tempera.

⁴⁸⁰ Antonietta Gallone, "Studio analitico dello strato pittorico nel Polittico di San Luca di Andrea Mantegna," in *Il Polittico di San Luca di Andrea Mantegna (1453-1454) in Occasione del Suo Restauro*, ed. Sandrina Bandera Bistoletti (Firenze: Cantini Editore, 1989), 67-9; The medium was found to be the following throughout: Animal glue for the gesso preparation layer (anhydrite); egg tempera for the colors with the exception of the blue and copper-green glazes where the presence of oil was also revealed (the type of analysis used to confirm the presence of organic binders is unknown; the authors performed cross-sectional analysis and refer to the use of "micro-chemical tests").

⁴⁸¹ Andrea Rothe, "Andrea Mantegna's 'Adoration of the Magi,'" in *Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995*, eds. Arie Wallert, Arie, Erma Hermens, and Marja F.J. Peek (Los Angeles: Getty Publications, 1995), 111-16; —, "Mantegna's Paintings in Distemper," in *Andrea Mantegna*, ed. Jane Martineau (London & New York: The Royal Academy of Arts and The Metropolitan Museum of Art, 1992), 80-8; Jill Dunkerton, "Mantegna's Painting Techniques," in *Mantegna and 15th Century Court Culture*, eds.

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Figure 4.77: Andrea Mantegna, *San Luca Altarpiece* (1453-4, Pinacoteca di Brera, Milan).

Frances Ames-Lewis and Anka Bednarek (London: Birkbeck College, 1993), 26-38; Villers, "Paintings on Canvas in Fourteenth Century Italy," 347; Suzanne Boorsch and Keith Christiansen, *Andrea Mantegna* (New York: Metropolitan Museum of Art, 1993), 80-8; Delbourgo, Rioux, and Martin, "L'analyse des peintures du Studiolo d'Isabelle d'Este au Laboratoire de Recherche des Musées de France. II - Étude analytique de la matière picturale," 21-8. Suzanna M. Halpine, "Andrea Mantegna Scientific Report –1990" (Scientific report housed in the Paintings Conservation Department at the National Gallery of Art, Washington DC. Halpine identified the use of egg tempera on Mantegna's *The Christ Child Blessing* (on canvas) using HPLC while scientists at the Getty Conservation Institute found glue to the predominant binder used in his paintings on fabric. Dunkerton has also expressed doubt as to whether the artist actually used casein as a binder based on the analytical methods used to confirm the presence of the material (see Chapter 5, section 5.2.3).

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Figure 4.78: Andrea Mantegna, *The Holy Family* (c.1485, Gemäldegalerie, Dresden).

new materials continued throughout his career as analysis on a much later work, *The Holy Family* (c. 1485; Figure 4.78) in Dresden, again confirmed the presence of egg and oil in mixed form, indicating the use of a true tempera grassa medium.⁴⁸² Mantegna eventually

⁴⁸² Christoph Scholzel, "The restoration and painting technique of the Holy Family by Mantegna in the Dresden Gallery," in *TECHNE Hors-serie: La technique picturale d'Andrea Mantegna*, eds. Michel Menu and Elisabeth Ravaud (Paris: Centre de Recherche et de Restauration des Musees de France-CNRS/UMR 171, 2009), 106-113. From the analytical report: Four samples were taken from the edge of the painting and the medium was analyzed (at the GCI). GC-MS revealed a tempera emulsion consisting of egg and linseed oil in approximately equal proportions. Two further samples taken from the center of the painting further confirmed this. All of the samples also contained glue, however, which may have come not from the binding agent itself but from the ground or from earlier restoration work, particularly from the glue lining.

traveled to Mantua in 1460 to work for Francesco Gonzago and his wife Isabella d'Este, both of whom came from families who were avid collectors of Flemish oil paintings.⁴⁸³ The d'Este family in particular has been associated with a number of Renaissance Italian painters who were beginning to shift away from the traditional tempera medium.

4.3.3 Ferrara

By the early 1430's, Niccolo d'Este III had risen to power in Ferrara, attracting both Italian and foreign artisans to seek work opportunities in the city; two Sienese artisans, a painter by the name of Angelo da Maacaginno and a tapestry weaver named Boteram, are documented working in Ferrara as early as 1444.⁴⁸⁴ Boteram, who had recently returned from Brussels, would have certainly been aware of Rogier van der Weyden and may have even influenced Maccaginno to explore the "new" Flemish medium; the contemporary historian Ciriaco d'Ancona noted Angelo's propensity for imitating the "renowned art of Rogier and of the extraordinary genius of the [northern artists]."⁴⁸⁵ With an acquired taste for works by

⁴⁸³ Richard A. Goldthwaite, *Wealth and the Demand for Art in Italy 1300-1600* (Baltimore and London: Johns Hopkins University Press, 1993), 244; Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197; See Chapter 2 for more information regarding the d'Este family's patronage as well as *Cosmè Tura: Painting and Design in Renaissance Ferrara*, ed. Steven Campbell (Boston: Isabella Stewart Gardner Museum, 2002).

⁴⁸⁴ Campbell, "Cosmè Tura and Netherlandish Art," 81; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50, 57.

⁴⁸⁵ Campbell, "Cosmè Tura and Netherlandish Art," 71, 83-5; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 49, 50, 53; Richardson, Woods, and Franklin, eds., *Renaissance Art Reconsidered*, 186-7, 205-206. Until 1476, weavers residing in Brussels had to be competent at creating sketches and even painting in order to generate cartoons or preparatory studies for their tapestry designs. There was a documented dispute in 1476

Rogier van der Weyen, it is no surprise that Leonello d'Este was eventually drawn to work of Maccagnino, hiring the artist in 1449 to decorate the studiolo within his summer Palace of Belfiore.⁴⁸⁶ In 1448, Ciriaco writes that Angelo Maccagnino was painting figures of the Muses Clio and Melpomene (Figures 4.79) in oil; additional documents reveal that the court apothecary was ordered to provide the artist with linseed oil for painting the figures.⁴⁸⁷

To ensure that the studiolo would be created in an international style, Leonello also requested the involvement of Michele Pannonio, a Hungarian artist who had been active in Ferrara as early as 1415.⁴⁸⁸ Michele Pannonio was placed in charge of the Belfiore studiolo upon Maccagnino's death in 1456, soon after which he recruited the young Cosme Tura as his

between the painters' guild and the tapestry-makers' guild in Brussels regarding who was responsible for designing and creating preparatory cartoons for tapestries.

⁴⁸⁶ Ibid. Leonello d'Este purportedly purchased at least four paintings from Rogier, often sending his representative Paolo di Poggio to retrieve the works of art in Bruges.

⁴⁸⁷ Campbell, "Cosmè Tura and Netherlandish Art," 85; Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50; Jill Dunkerton, "Cosme Tura's Painting Technique," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, Steven Campbell, ed. (Boston: Isabella Stewart Gardner Museum, 2002), 111; Dunkerton writes that the accounts for the January record in 1449 state the court apothecary supplied "a measure of linseed oil" for "Master Angelo the painter to paint figures in oil for the studio." Humanist writer Ludovico Carnone's account dating between 1475 and 1476 states that the two Muses were by Angelo, "who mixed his colors with oil in a consummate manner."

⁴⁸⁸ Dunkerton, 107; Patrick Matthiesen, *From Borso to Cesare d'Este: The School of Ferrara, 1450-1628* (London: Matthiesen Fine Art Ltd., 1984), 58; Miklos Boskovits, "Ferrarese Painting about 1450: Some New Arguments" *The Burlington Magazine* 120, no. 903 (1978): 370-81; Pannonio may have assisted Gentile da Fabriano to work on the Strozzi Chapel in 1423.

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Figure 4.79 (left) and Figure 4.80 (right): Angelo Maccagnino, *Melpomene* (c.1448-9, Museo di Belle Arti, Budapest; left) and Cosme Tura's *Calliope* (1460, National Gallery, London; right).

assistant.⁴⁸⁹ Tura may have first encountered the oil medium during his early training in Squacione's studio as the artist was commissioned to create painted leather crests (likely

⁴⁸⁹ Ames-Lewis, "Sources and Documents for the Use of the Oil Medium," 50. Ames-Lewis states that Tura is first recorded working in Ferrara in June of 1451 when he was called upon to estimate "the value of pennants for trumpets painted 'on both sides with gold and blue, outlined with oil colors'." This is another early reference to the use of oil as a medium and it is possible that it was the preferred material to use on flexible canvas supports.

executed in oil) as early as 1452.⁴⁹⁰ In 1460, Leonello's successor Borso d'Este, appointed Cosme Tura as lead court painter, entrusting Tura with the completion of the Muse and Allegorical paintings (Figure 4.80) that were to decorate the walls of the studiolo. From a technical and historical standpoint it seems that Tura may have become more adept with the oil medium during these subsequent years; examination of several paintings from this period has confirmed that the artist employed both egg tempera and oil painting techniques.⁴⁹¹ Furthermore, documents dating to 1469 reveal that Borso d'Este commissioned Tura to decorate the interior of the Belriguardo chapel, specifically ordered the artist to use drying oils.⁴⁹² Although it is impossible to know which of these paintings we can directly attribute to

⁴⁹⁰ Ibid; Dunkerton, "Cosme Tura's Painting Technique," 113. Dunkerton writes that "in April 1452, Tura himself was paid for decorating a crest for a palio race. These were apparently made of boiled leather, a surface unsuitable for aqueous media such as tempera; therefore they were probably painted using an oil-based binder."

⁴⁹¹ Jill Dunkerton, Ashok Roy, and Alistair Smith, "The Unmasking of Tura's 'Allegorical Figure': A Painting and its Concealed Image," *National Gallery Technical Bulletin* 11 (1987): 5-35; Dunkerton, "Cosme Tura's Painting Technique," 107-51; Tura is thought to have completed the London panel, and examination has revealed that the underpainting (presumably executed by Maccagnino) was done in egg tempera. Much of the final image, however, was completed using drying oils, with linseed being utilized for darker colors and walnut oil being used for whites and lighter shades. The other three paintings by Tura at the National Gallery in London include his *Galleria Colonna*, the *St. Jerome*, and the *Virgin Annunciate*. All three possess egg tempera in the underpainting and/or the lighter passages of paint, while oil is used as a glaze for areas requiring rich, saturating colors. For example Tura's use of walnut oil combined with red lake gives St. Paul's velvet red robe is given a lifelike texture in the *Galleria Colonna* while a similar type of medium was found in the upper paint layers of the throne in the *Virgin Annunciate*. Tura was also clearly accomplished as both an egg tempera painter and an oil painter, and analysis of other paintings have even shown that he would occasionally paint using a glue-based medium. See also Susana M. Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's The Annunciation with Saint Francis and Saint Louis of Toulouse," *Studies in Conservation* 37 (1992): 22-38.

⁴⁹² Dunkerton, "Cosme Tura's Painting Technique," 119.

Tura, the technical evidence corroborates the fact that Tura and other painters of the Ferrarese court were very capable of employing northern painting techniques by the 1450s, a tradition likely continued by Tura's pupils.⁴⁹³

Both Ercole de'Roberti (c. 1451-1469) and Francesco del Cossa (c. 1430 – c. 1477) trained or worked alongside Tura in Ferrara and may have continued to use the oil medium throughout the remainder of their careers.⁴⁹⁴ Analysis of the pendant portrait *Ginevra Bentivoglio* (c. 1474/77; Figure 4.81) by Ercole identified the presence of egg and oil in passages containing red and white colors, a curious find as both portraits appear as if they are painted in tempera from a stylistic standpoint.⁴⁹⁵ Ercole eventually moved to Bologna to study under (or with) Francesco del Cossa who by the early 1470s had set up his own successful workshop.⁴⁹⁶ Vasari's account of Ercole's work on a fresco cycle in a Bolognese chapel refers to the artist's use of "*a secco*," another indication that Ercole may have applied egg and/or oil additions to his frescoes, a technique that may have been introduced by Tura, or later on by Cossa.⁴⁹⁷ Scarcely any works by Cossa have been analyzed save for his *St. Vincent Ferrer* (c.

⁴⁹³ See *Cosme Tura e Francesco del Cossa: L'arte a Ferrara nell'eta di Borso d'Este*, ed. Mauro Natale (Ferrara: Ferrara Arte, 2007).

⁴⁹⁴ Ibid, Luke Syson, "Tura and the "Minor Arts": The School of Ferrara," in *Cosmè Tura: Painting and Design in Renaissance Ferrara*, Steven Campbell, ed. (Boston: Isabella Stewart Gardner Museum, 2002), 54, 60.

⁴⁹⁵ Suzanne Q. Lomax, "Ercole de'Roberti Scientific Report – 1995" (Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC). Samples from the white highlight of the scarf and a red sample from the bottom edge revealed the presence of both egg and using GC-MS.

⁴⁹⁶ Syson, "Tura and the "Minor Arts": The School of Ferrara," 60.

⁴⁹⁷ Eastlake, *Methods and Materials of Painting of the Great Schools and Masters*, 148.

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Figure 4.81 (left) and 4.82 (right): Ercole di Roberti, *Ginevra Bentivoglio* (c. 1474/77, The National Gallery of Art, Washington DC; left) and *Saint Vincent Ferrer* (c. 1473-5, National Gallery, London; right).

1473-5; Figure 4.82), a central panel belonging to a polptych in San Petronio, Bologna.⁴⁹⁸

Though the principal medium was determined to be egg tempera, the authors reveal that both

⁴⁹⁸ Alistair Smith, Anthony Reeve, and Ashok Roy, "Francesco del Cossa's 'St. Vincent Ferrer,'" *National Gallery Technical Bulletin* 5 (1981): 54-7. All samples were analyzed using GC, staining, and heating tests.

samples from the black of the habit and the red pedestal were “very rich in egg medium” with other sections of the composition appearing rather “thickly painted.” As the analysis was performed nearly thirty years ago using only GC, staining, and heating tests, it may be that certain areas of the picture were executed using drying oils, either as additions or glazes.

Over the past fifty years, technical studies of Quattrocento paintings have become less reliant on simple visual analysis and increasingly influenced by advancements in instrumental methodology. That being said, scholars who focus on this transitional period in art are less likely to be conscious of shifts in attitude regarding the efficacy and accuracy of analytical approaches used to characterize binders in Renaissance paintings. Tracing the evolution of oil painting in Italy requires each city and/or region to be considered separately, including cross-cultural events, interactions, and collaborations; recent scholarship has highlighted the gradual influx of northern art across the Alps and its impact on Quattrocento painting, inspiring Italian artists to emulate their northern counterparts and ultimately abandon traditional tempera practice. Just as Renaissance scholars have come to acknowledge the impact of oil in Italian art, scientists have begun to recognize another narrative, the unwritten history outlining the development of organic analysis as it pertains to the analysis of paintings. In many ways, the improvements in technical analysis parallel the improvements in Renaissance art historical studies: past results and conclusions are now being re-evaluated and re-considered, in particular the characterization of egg-oil paints in Quattrocento artworks. The transition from egg tempera to oil in Italy during the fifteenth and early sixteenth centuries marks one of the great leaps within the history of painting and will remain a topic of interest as the field of technical art history continues to flourish. While scholars continue to offer new art historical perspectives, scientists and conservators have yet to review and reflect on how technological advancements have impacted our understanding of traditional painting practices, a topic that is extensively covered in the following chapter.

Chapter 5

DEVELOPMENTS IN THE ANALYSIS OF EGG- AND OIL-BASED PAINT SYSTEMS: PAST, PRESENT, AND FUTURE DIRECTIONS

The primary aim of this chapter is to provide a summary of analytical techniques that have been commonly used to identify binding media in easel paintings since the 1930s, outlining the benefits and limitations associated with each method's ability to characterize egg- and oil-based paints and exploring techniques that may offer new possibilities for future research. The history of media analysis in the field of conservation can help to elucidate some of the discrepancies encountered in the literature relating to the characterization and chemical analysis of fifteenth-century Italian paintings.⁴⁹⁹ A survey of relevant scientific publications, both past and present, reveals that this area of research has witnessed significant progress since the turn of the century while relatively minor advancements have been made over the past thirty years, a surprising phenomenon given the vast improvements in analytical instrumentation and data processing. I will demonstrate that past technical studies focusing on Quattrocento paintings now require re-evaluation; more recently scholars have identified a number of factors that can hamper organic analysis including pigment interference, detection limits, the migration of mobile chemical markers (e.g. fatty acids), the formation of degradation products, and the potential contamination of restoration materials (e.g. oil-resin coatings, glue-based adhesives, etc.).⁵⁰⁰ Finally, general notions relating to paint handling and

⁴⁹⁹ Refer to Chapter 4 for more specific information relating to technical information associated with various Quattrocento painters and workshops.

⁵⁰⁰ Ilaria Bonaduce et al., "New Insights into the Ageing of Linseed Oil Paint Binder: A Qualitative and Quantitative Analytical Study," *PLoS ONE* 7 (2012): e49333,

techniques are often overlooked in scientific publications focusing on Italian Medieval and Renaissance paintings, leading to misinterpretation and false conclusions regarding the use of binding media.

To analyze Quattrocento paintings, conservators and scientists are generally interested in the presence and/or relative amounts of amino acids, fatty acids, and dicarboxylic acids when characterizing egg-oil paint systems, a term that will be used in the subsequent sections to describe paintings that potentially contain discrete layer(s) of egg and/or oil. All of the

doi:10.1016/j.chroma.2009.06.033; Rocco Mazzeo et al., "Attenuated total reflection micro FTIR characterization of pigment-binder interaction in reconstructed paint films," *Analytical Bioanalytical Chemistry* 392 (2008): 65-76, doi: 10.1007/s00216-008-2126-5; Marika Spring et al., "ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London," *Analytical Bioanalytical Chemistry* 392 (2008): 37-45, doi: 10.1007/s00216-008-2092-y; Ester B. Ferreira, Jerre van der Horst, and Jaap J. Boon, "Chemical aspects of the binding media of the Oranjezaal ensemble: an insight into 17th century Netherlandish materials and methods," in *ICOM Committee for Conservation Preprints, 14th Triennial Meeting, The Hague, 12-16 September 2005*, ed. Isabelle Verger. vol. II (London: James & James, 2005), 774-82; Marika Spring and Catherine Higgitt, "Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media," in *Medieval Painting in Northern Europe: Techniques, Analysis, Art History*, ed. Jilleen Nadolny (London: Archetype, 2006), 223-29; Jaap J. Boon, Katrien Keune, and Joyce Zucker, "Imaging Analytical Studies of Lead Soaps Aggregating in Preprimed Canvas Used by the Hudson River School Painter F.E. Church," *Microscopy and Microanalysis* 11 (2005): 444-5, doi: 10.1017/S1431927605505579; Jaap J. Boon, Frank Hoogland, and Katrien Keune, "Chemical Process in Aged Oil Paints Affecting Metal Soap Migration and Aggregation," in *AIC Specialty Group Postprints, 34th Annual Meeting in Providence, Rhode Island, 16-19 June 2006*, ed. Helen Mar Parkin (Washington DC: American Institute for Conservation, 2007), 18-25; Katrien Keune et al., "Comparative Study of the Effect of Traditional Pigments on Artificially Aged Oil Paint Systems using Complementary Analytical Techniques" in *ICOM Committee for Conservation Preprints, 15th Triennial Meeting, New Delhi, 22-26 September 2008*, ed. Janet E. Bridgland. vol. II (London: James & James, 2008), 833-42; Michael R. Schilling and Herant P. Khanjian, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media," *Journal of the American Institute for Conservation* 35 (1996): 123-44, doi: 10.2307/3179992.

aformentioned chemical markers can be found in aged egg yolk while traditional drying oils tend to only possess certain fatty and dicarboxylic acids.⁵⁰¹ Considerable attention has been devoted to the chemical composition of these binders, as they have been used by artists throughout the history of easel painting.⁵⁰²

⁵⁰¹ Traces of amino acids may be present from the crushed flaxseeds, walnuts, and/or poppyseeds. The relative amount of amino acids in traditional drying oils depends entirely on how the drying oil is prepared and processed.

⁵⁰² David A. Peggie, "The Chemistry and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century," in *Science and Art: The Painted Surface*, eds. Antonio Sgamellotti, Brunnetto G. Brunetti, and Costanza Miliani (Cambridge: The Royal Society of Chemistry, 2014), 209-29; Maria Perla Colombini and Francesca Modugno, "Organic Materials in Art and Archaeology," in *Organic Mass Spectrometry in Art and Archaeology*, eds. Maria Perla Colombini and Francesca Modugno (Sussex: John Wiley & Sons, 2009), 3-9; Michael R. Schilling, "Paint media analysis" in *Scientific Examination of Art: Modern Techniques in Conservation and Analysis* (Washington DC: The National Academies Press, 2005), 186–205, accessed January 23, 2016, <http://www.nap.edu/read/11413/chapter/14#188>; Alan Phenix, "The Composition and Chemistry of Eggs and Egg Tempera," in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, eds. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997), 11-20; Jaap J. Boon et al., "Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films," in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, ed. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997): 35-56; John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, (1987; repr., Oxford: Butterworth-Heinemann, 1996), 31-48, 84-94; Michael R. Schilling, Herant P. Khanjian, and Luiz A. C. Souza, "Gas chromatographic analysis of amino acids in ethylchloroformate derivatives, Part I: Composition of proteins associated with art objects and monuments," *Journal of the American Institute for Conservation* 35 (1996): 45–59, doi: 10.2307/3179937; Schilling and Khanjian, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media," 123-44; —, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part III: Identification of Proteinaceous Binding Media by Interpretation of Amino Acid Composition Data," in *ICOM Committee for Conservation Preprints, 11th Triennial Meeting, Edinburgh, Scotland, 1-6 September 1996*, ed. Janet E. Bridgland (London: James & James, 1996), 211-19; Susana M. Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's The Annunciation with Saint

Egg proteins are comprised of polypeptide chains, unique sequences of seventeen (out of twenty-one) amino acids (Figures 5.1, 5.2, and 5.3). In addition to proteins (approx. 35-45%), dried egg yolk films also consist of a fairly high percentage of lipids (approx. 41-65%) with a trace amount of cholesterol (approx. 2-3%).⁵⁰³ Even after the yolk is emulsified with pigments and allowed to cure, these chemical markers will continue to experience a series of changes; amino acids will undergo oxidation and alkylation, the polyunsaturated fatty acids will undergo cross-linking through auto-oxidative polymerization, and the cholesterol fraction often becomes so degraded through oxidative processes that it is difficult impossible to detect (particularly in the presence of inorganic pigments).⁵⁰⁴ Metal ions from the pigments or additional drying agents can accelerate some of these oxidation reactions and, combined with

Francis and Saint Louis of Toulouse," *Studies in Conservation* 37 (1992): 22–38, doi: 10.2307/1506434; John S. Mills, "The Identification of Binding Media – An Introduction" in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 69-71; John S. Mills and Raymond White, "The Identification of Paint Media from their Sterol Composition – A Critical View," *Studies in Conservation* 20 (1975): 176-82, doi: 10.2307/1505737; Sheldon Keck and Theodore Peters, "Identification of Protein-containing Paint Media by Quantitative Amino Acid Analysis," *Studies in Conservation* 14 (1969): 75-82, doi: 10.2307/1505349; John S. Mills, "The Chromatography Examination of Paint Media. Part 1. Fatty Acid Composition and Identification of Dried Oil Films," *Studies in Conservation* 2 (1966): 92-107, doi: 10.2307/1505447.

⁵⁰³ Phenix, "The Composition and Chemistry of Eggs and Egg Tempera," 11-20; Maria Perla Colombini and Francesca Modugno, "Organic Materials in Art and Archaeology," 8; Mills and White, *The Organic Chemistry of Museum Objects*, 42, 87-88; Boon et al., "Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films," 39-49. Note that water is the largest component found in egg yolks, followed by proteins and lipids (respectively) so these numerical values reflect the composition of egg yolk as a dry solid. In addition to triacylglycerols, phospholipids are also a component of the lipid fraction; however, the latter is almost completely converted into other species after short-term aging.

⁵⁰⁴ Ibid.; Adam Karpowicz, "Ageing and Deterioration of Proteinaceous Media," *Studies in Conservation* 26 (1981): 153-60, doi: 10.2307/1505885; Katrien Keune, "Binding medium,

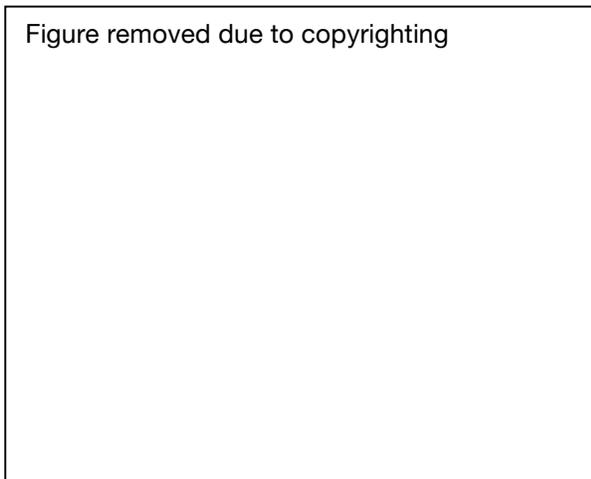


Figure 5.1: Schematic diagram illustrating the general structure of an amino acid. The R side chain group represents the location of various functional groups that are specific to each of the twenty-one amino acids found in nature.⁵⁰⁵

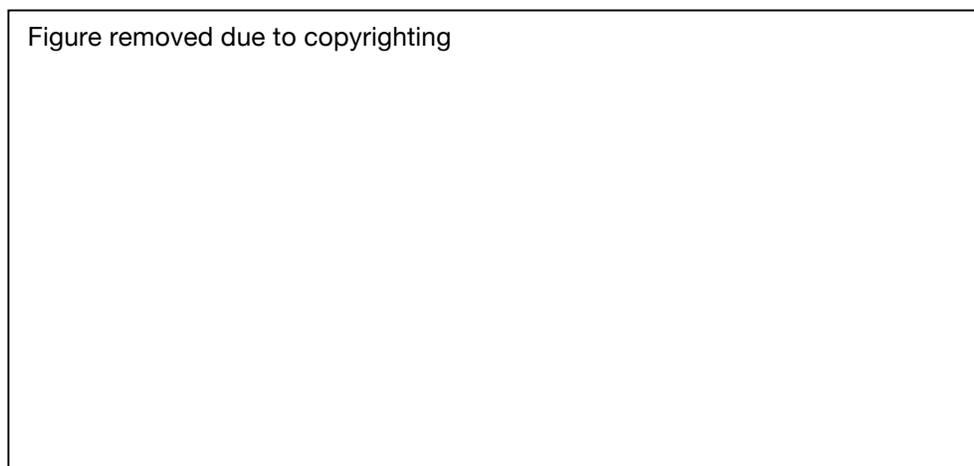


Figure 5.2: An example of a poly-peptide chain containing a series of amino acids connected via peptide bonds.⁵⁰⁶

pigments and metal soaps characterised and localised in paint cross-sections” (PhD diss., University of Amsterdam, 2005), 33-34.

⁵⁰⁵ “Amino Acids,” NutrientsReview, accessed February 2, 2016, <http://www.nutrientsreview.com/proteins/amino-acids>.

Figure removed due to copyrighting

Figure 5.3: Table taken from Alan Phenix's 1996 publication summarizing the relative amounts (weight %) of various amino acids (left column includes abbreviations for specific amino acids) detected in egg yolk/white. Note the variation from one publication to the next, an indication that the initial amounts of amino acids in fresh samples is either variable and/or is a product of different experimental procedures. In either case, this reported variation may effect the relative ratios of amino acids in aged paint samples.⁵⁰⁷

⁵⁰⁶ "Protein," National Center for Biotechnology Information Genetics Review, last modified September 29, 1999, <http://www.ncbi.nlm.nih.gov/Class/MLACourse/Original8Hour/Genetics/protein.html>.

⁵⁰⁷ Phenix, "The Composition and Chemistry of Eggs and Egg Tempera," 14.

other naturally occurring mechanisms, can exacerbate the formation of degradation products; Schilling and Khanjian were able to identify the amino acids that remained detectable in the presence of reactive pigments even after significant aging (Figure 5.4), while Boon et al. and Phenix have summarized some of the degradation products created by amino acids (Figure 5.5).⁵⁰⁸ It is worth noting that the relative amount of stable amino acids (amino acids substituted with alkyl groups: valine, alanine, isoleucine, leucine, glycine, proline, and hydroxproline) is considerably lower in egg tempera (approx. 40%) than animal glues (approx. 70%) which may account for some of the difficulties involved with the identification of egg-based paints versus glue-containing paints and ground layers.⁵⁰⁹ With the advancements in chromatography and mass spectrometry, the relative ratios of these stable amino acids have been used to characterize protein binders; however, pigment interference and degradation processes can hamper full and consistent recovery of all amino acids present in a sample not to mention the potential presence of amino acids from restoration materials and other substances (Figure 5.4 and 5.5). More recently, efforts have been made to identify the more stable and intact peptide chains instead of relying on the recovery of individual amino acids (a potentially unreliable procedure for the various reasons discussed above). Peptide chains are not only specific to certain classes of proteins but can also be linked to individual animal species (see section 5.3.1). Such techniques that may be less affected by

⁵⁰⁸ Boon et al. "Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films," 35-56; Schilling and Khanjian, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media," 123-44.

⁵⁰⁹ Schilling and Khanjian, *Ibid.*

Figure removed due to copyrighting

Figure 5.4: Table taken from Schilling and Khanjian's 1996 publication featuring the seven amino acids (alanine, valine, isoleucine, leucine, glycine, proline, and hydroxyproline) that were determined to be stable markers for the identification of egg yolk and animal glue after subjecting reference samples to artificial aging. The ability to differentiate between egg yolk and animal glue rests on the presence of one single amino acid. If all amino acids save for hydroxyproline (OHP) are successfully recovered then the paint binder is generally characterized as egg tempera. If all seven amino acids are recovered the relative ratios of various markers can be calculated to determine if animal glue alone is present or whether both egg- and glue-based materials are present in the sample.⁵¹⁰

⁵¹⁰ Ibid., 140.

Figure removed due to copyrighting

Figure 5.5: Table taken from Boon et al.'s 1996 publication summarizing the de-amidation, oxidation, and elimination products associated with specific amino acids. It has been suggested that the formation of these degradation products affect the full recovery of amino acids during analysis of aged paint samples. This can ultimately lead to misinterpretation of the paint binder particularly when various ratios of amino acids are used to differentiate between egg yolk, egg white, glue, and/or mixtures of proteinaceous materials.⁵¹¹

⁵¹¹ Boon et al. "Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films," 48.

external factors that can affect the detection of proteins in 500-year-old Italian paintings.⁵¹² As stated previously, aged egg tempera paints share the same fatty acid/dicarboxylic acid chemical markers that can be found in aged oil paint films. In both types of paint binders, these fatty substances undergo similar processes that are responsible for the drying and curing of the paint film (although the evaporation of water is mostly responsible for the drying of egg tempera paints). Fresh drying oils (e.g. linseed, walnut, and poppyseed) are comprised of polyunsaturated triglycerides (Figure 5.6 and 5.7); for linseed oil, at least 50% of the fatty acid composition consists of linolenic acid (C18:3; a hydrocarbon chain consisting of 18

⁵¹² Win Fremout et al., “Classification of protein binders in artist’s paints by matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry: An evaluation of principal component analysis (PCA) and soft independent modelling of class analogy (SIMCA),” *Rapid Communications in Mass Spectrometry* 25 (2011): 1631-40, doi: 10.1002/rcm.5027; Inez D. van der Werf et al., “A simple protocol for Matrix Assisted Laser Desorption Ionization – time of flight – mass spectrometry (MALDI-TOF-SIMS) analysis of lipids and proteins in single microsamples of paintings,” *Analytica Chimica Acta* 718 (2012): 1-10, doi:10.1016/j.aca.2011.12.056; Daniel P. Kirby, Katherine R. Phillips, and Narayan Khandekar, “Implementation of MALDI mass fingerprinting in a museum laboratory for the identification of proteins in works of art,” accessed February 17, 2016, <http://www.ndt.net/article/art2011/papers/KIRBY%20-%20M%201.pdf>; Ethan Alexander Perets et al., “Carboxy-terminated immuno-SERS tags overcome non-specific aggregation for the robust detection and localization of organic media in artworks,” *Analyst* 140 (2015): 5971–5980, doi: 10.1039/c5an00817d; Giorgia Sciutto et al., “Development of a multiplexed chemiluminescent immunochemical imaging technique for the simultaneous localization of different proteins in painting micro cross-sections,” *Analytical and Bioanalytical Chemistry* 399 (2011): 2889–2897, doi: 10.1007/s00216-010-4258-7; Hae Young Lee et al., “Development and application of an ELISA method for the analysis of protein-based binding media of artworks,” *Analytical Methods* 7 (2015): 187–196, doi:10.1039/c4ay01919a; Melissa Palmieri et al., “Development of an analytical protocol for a fast, sensitive and specific protein recognition in paintings by enzyme-linked immunosorbent assay (ELISA),” *Analytical and Bioanalytical Chemistry* 399 (2011): 3011–3023, doi: 10.1007/s00216-010-4308-1; Laura Cartechini et al., “Immunodetection of proteins in ancient paint media,” *Accounts of Chemical Research* 43 (2010): 867–876, doi: 10.1021/ar900279d; Joy Mazurek et al., “Antibody assay to characterize binding media in paint,” in *ICOM Committee for Conservation Preprints, 15th Triennial Meeting, New Delhi, 22-26 September 2008*, ed. Janet E. Bridgland, vol. II (London: James & James, 2008), 678–685.

carbon atoms with 3 double bonds) while linoleic (C18:2) and oleic acids (C18:1) are present in lower amounts.⁵¹³ These double bonds serve as reactive sites, and through various mechanisms that are influenced by temperature, light, oxygen, and metal ions (e.g. pigments and/or driers) a glycerol-ester-based polymeric network is eventually formed creating a paint film that is dry to the touch. The quantity of linoleic acid is highest in fresh linseed oil, giving linseed a higher proportion of reactive sites thus accounting for its faster drying rate as compared to walnut and poppyseed oil (Figure 5.7). Metal ions present in pigments can also accelerate drying; current research has determined the following order of metal cations in terms of drying rate, with copper creating some of the faster drying films: Cu > Co > Pb > Mn > Fe.⁵¹⁴ Conversely, some materials (such as bituminous browns and organic lake pigments) possess antioxidant properties and can dramatically slow the drying rate of an oil film. In addition to the formation of bonds (cross-linking), bonds are also broken during the curing process; such mechanisms are responsible for the formation of di-carboxylic acids (Figure 5.8) such as suberic (C8), azelaic (C9), and sebacic (C10). Further oxidation and hydrolytic reactions also lead to the formation of free fatty acids (Figure 5.8) including myristic (C14), palmitic (C16), and stearic (C18), all of which will remain mobile throughout the paint film until they migrate towards the surface (a phenomenon referred to as “efflorescence”) or until they become stabilized within the polymeric network (e.g. bonding with positively charged ions from the metal containing pigments). Mobile fractions of oil films can increase over time

⁵¹³ Mills and White, *The Organic Chemistry of Museum Objects*, 31-41. See also Maria Perla Colombini and Francesca Modugno, “Organic Materials in Art and Archaeology,” 6-9. Note that the relative percentage of linolenic acid is much lower for walnut and poppyseed oils, accounting for their slower drying rate as compared with linseed.

⁵¹⁴ Jan Pokorny, “Major factors affecting the autoxidation of lipids,” in *Autoxidation of Unsaturated Lipids*, ed. H.W.S. Chan (London: Academic Press, 1987), 141-207.

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Figure 5.6: An example of a triglyceride (top structure) commonly found in materials containing fatty substances. The fatty acids (R1, R2, R3) can be similar in composition or different, containing between 9 and 24 carbon atoms with anywhere between 0 (saturated fatty acids) and 3 (unsaturated) double bonds. The structure below is an example of a triglyceride that can be found in both egg yolk and drying oils with R1, R2, and R3 corresponding to palmitic acid, oleic acid, and linolenic acid, respectively.⁵¹⁵

⁵¹⁵ “Triglyceride,” Biodiesel Chemistry, last accessed April 2, 2016, <http://biodieseleducation.org/Literature/Documents/Biodiesel%20Chemistry.htm> ; “Method of Converting Triglycerides to BioFuels,” accessed February 28, 2016, <http://www.google.com/patents/US20080071125>.

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Figure 5.7: Table taken from Mills and White's *The Organic Chemistry of Museum Objects* listing the relative percentages of triglycerides found in drying and non-drying oils. Note that of the three commonly used oils in traditional Western easel painting, linseed contains the highest amount of linoleic acid (C18:3) and therefore cures at a faster rate than walnut or poppyseed oil, respectively. Ratios of palmitic and stearic fatty acids (C16:0 and C18:0, respectively) have been used to distinguish between various drying oils, egg yolk, and mixtures of egg and oil.⁵¹⁶

⁵¹⁶ Mills and White, *The Organic Chemistry of Museum Objects*, 33.

Figure removed due to copyrighting

Figure 5.8: Structures of dicarboxylic acids (suberic, azelaic, and sebacic) and free fatty acids (myristic, palmitic, and stearic) that are commonly present in egg and/or oil paint binders and therefore used for characterization.

depending on a number of factors including the presence of certain pigments and environmental conditions. It is for this reason that fatty acids and dicarboxylic acids can be easier to extract from degraded oil and/or egg tempera films as opposed to amino acids that can remain covalently bonded within peptide chains.

One of the greatest challenges involved with the analysis of egg-oil paint systems is that both binders share similar fatty acid/dicarboxylic acid chemical markers (Figure 5.8, 5.9, and 5.10). On the other hand, the analysis of fatty substances is perhaps less challenging than the analysis of amino acids/peptides, as the recovery of free fatty acids derived from degraded lipids found in both drying oils and proteinaceous sources generally requires a much simpler extraction process (see section 5.2.3). While considerable emphasis has been placed on the relative ratios of fatty acids and dicarboxylic acids in the characterization of egg-oil paint systems, recent research has identified several factors (e.g. environmental storage/display conditions, pigment interference, the presence of restoration materials, migration of free fatty acids, etc.) that can influence these ratios. A similar problem is encountered when amino acid ratios (or even the absence/presence of particular amino acids) are used to determine the origin of a proteinaceous binder as additional materials commonly used in artistic practice can contribute to the overall amount of amino acids detected during analysis (Figure 5.11).⁵¹⁷ Furthermore, there is currently no single method that can be used to identify the wide range of binding media potential present within paint/ground layers as many of these materials are complex compounds comprised of many of the same elements (e.g. carbon, oxygen,

⁵¹⁷ Schilling and Khanjian, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media," 142; Susanna M. Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," *Conservation Research* 51 (1995): 33, accessed February 7, 2016. <http://www.jstor.org/stable/42621984>; R.H. de Silva, "The Problem of the Binding Medium Particularly in Wall Painting," *Archaeometry* 6 (1963): 56-64, doi: 10.1111/j.1475-4754.1963.tb00580.x.

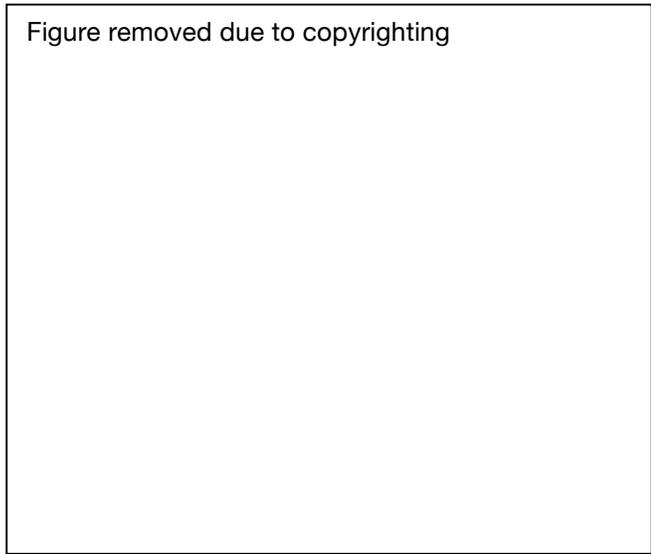


Figure 5.9: A table taken from Alan Phenix's 1996 publication summarizing relative amounts (%) of fatty acids that are detectable in egg yolk.⁵¹⁸



Figure 5.10: Schematic illustrating the relative amounts of fatty acid and dicarboxylic acids that are generally compared in order to characterize egg and/or oil paint systems. Intermediate ratios of palmitic to stearic (P/S) and azelaic/palmitic (A/P) can be more challenging to interpret as tempera grassa (egg and oil mixtures) can generate similar ratios associated with walnut oil, mixtures of different oils, and/or contamination from restoration materials. Often additional analysis is required to confirm the presence of protein in the paint sample.

⁵¹⁸ Phenix, "The Composition and Chemistry of Eggs and Egg Tempera," 14.

hydrogen).⁵¹⁹ Chromatographic methods that have been found to be the most successful at recovering these chemical markers are not well-suited for the analysis of complex multi-layered paint/ground systems. It is often difficult (or impossible) to confirm where recovered fatty acids or amino acids are present within a cross-sectional paint sample. Complementary techniques are therefore often used to co-localize these markers; ATR-FTIR imaging (see section 5.2.2) has proven somewhat useful and cross-sectional staining techniques may also help in identifying components within a paint cross-section. However, recent studies have pointed towards other techniques that will allow for the characterization of proteins and/or oil markers within intact cross-sectional samples (see section 5.3.2). Such an approach is an improvement as it allows for chemical mapping of chemical markers; for example, amino acids that are found to co-localize with an un-pigmented film on the surface of a cross-section may indicate the presence of glue applied during previous consolidation of the paint layer(s). An awareness of our instrumental limitations, past and present, will better inform scientists, conservators, and art historians who continue to work in tandem in an effort to develop a better understanding of painting techniques practiced throughout the Quattrocento.

⁵¹⁹ Maria Teresa Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” *Analytical Chimica Acta* 621 (2008): 109-39, doi:10.1016/j.aca.2008.05.056. See also *Organic Mass Spectrometry in Art and Archaeology*, eds. Maria Perla Colombini and Francesca Modugno (Sussex: John Wiley & Sons, 2009) and John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, (1987; repr., Oxford: Butterworth-Heinemann, 1996).

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Figure 5.11: Table taken from Schilling and Khanjian's 1996 publication listing the seven stable amino acids (alanine, valine, isoleucine, leucine, glycine, proline, and hydroxyproline) that have been identified in a range of organic materials. The presence of amino acids markers from unoriginal materials (e.g. gum arabic-based paints used for retouching, glues used as consolidants, gums used as adhesives to apply facing tissue, etc.) can contaminate the paint samples and lead to misinterpretation of the original binder used by the artist.⁵²⁰

⁵²⁰ Schilling and Khanjian, "Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media," 142.

5.1 Early Analytical Techniques used in Paintings Conservation

5.1.1 Early Developments in Chemical and Heating Tests

Analytical techniques used to characterize organic binding media in easel paintings experienced a complex evolution throughout the twentieth century, an evolution that is often overlooked in present-day initiatives involving the technical study of Quattrocento paintings.⁵²¹ Early attempts to identify the presence of glues, gums, oils, resins, and waxes were limited to chemical tests (the complete or partial exposure of a paint sample to various solvents and/or aqueous solutions) and heating tests (recording the temperature at which a paint sample began to liquefy and/or burn); these were minor improvements over “wiping” tests that had been used during the eighteenth and nineteenth centuries, a procedure that involved wiping the surface of a painting with water or other solvents in an effort to determine the nature of the binder.⁵²² Chemical and heating tests were employed up until the 1960s/’70s

⁵²¹ Mills and White, *The Organic Chemistry of Museum Objects*, 14-30, 169-95; Jilleen Nadolny, “A history of early scientific examination and analysis of painting materials ca. 1780 to the mid-twentieth century,” in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Butterworth-Heinemann, 2012), 336-340; Joyce Townsend and Jaap J. Boon, “Research and Instrumental Analysis in the Materials of Easel Paintings,” in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Butterworth-Heinemann, 2012), 341-366; Noelle L.W. Streeton, *Perspectives on the Painting Technique of Jan van Eyck: Beyond the Ghent Altarpiece* (London: Archetype Publications, 2013), 9-20; Karin Groen, “Perspectives on the evolution of science for art history and conservation, and its current state,” in *Paintings in the Laboratory: Scientific Examination for Art History and Conservation*, ed. Esther van Duijn (London: Archetype Publications, 2014), 3-13.

⁵²² Jilleen Nadolny, “The First Century of Published Scientific Analyses of the Materials used in Historical Painting and Polychromy, circa 1780-1880,” *Reviews in Conservation* 4 (2003): 40.

(possibly even later) and while such methods offered perspective into the physical properties of a paint sample, they often led to oversimplified or even incorrect judgments relating to binding media.⁵²³ The presence of restoration materials, degradation products, and/or inorganic pigments, for example, could easily affect the results of chemical/heating tests, analytical methods that were described as “rough and ready” by National Gallery scientist Joyce Plesters.⁵²⁴ Scholar Jilleen Nadolny has identified a number of early publications that demonstrate the wide range of results generated by such tests; chemical/heating tests performed on a *Madonna and Child* panel (related to the school of Pietro Perugino) in 1828

⁵²³ Nadolny, “The First Century of Published Scientific Analyses of the Materials used in Historical Painting and Polychromy, circa 1780-1880,” 40; —, “A history of early scientific examination and analysis of painting materials ca. 1780 to the mid-twentieth century,” 337-8; Streeton, *Perspectives on the Painting Technique of Jan van Eyck: Beyond the Ghent Altarpiece*, 21-6; Lorenzo Lazzarini, “La pala Barbarigo di Giovanni Bellini: L’analisi di laboratorio,” *Quaderni della Soprintendenza dei Beni Artistici e Storici di Venezia*, 3 (1983): 23-7; Marianne Odlyha, “A Novel Approach to the Problem of Characterizing Binding Media,” in *ICOM Committee for Conservation Preprints, 9th Triennial Meeting, Dresden, 26-31 August, 1990*, ed. By Kirsten Grimstad, vol. I (Los Angeles: ICOM Committee for Conservation, 1990), 57-61; Elisabeth Martin, “Some Improvements in Techniques of Analysis of Paint Media,” *Studies in Conservation* 22 (1977): 63, doi: 10.2307/1505703; Marie-Christine Gay, “Essais d’identification et de localisation des liants picturaux par des colorations spécifiques sur coupes minces,” *Laboratoire de recherche des musées de France - Annales* (1970): 8-24; Joyce Plesters, “Cross-sections and Chemical Analysis of Paint Samples,” *Studies in Conservation* 2 (1956): 127, 129-130, doi: 10.2307/1505000; Paul Coremans, Rutherford J. Gettens, and Jean Thissen, “La Technique des ‘Primitifs Flamands,’” *Studies in Conservation* 1 (1952): 20, doi: 10.1179/sic.1952.002; George L. Stout, “One Aspect of the So-Called Mixed Technique,” *Technical Studies in the Field of the Fine Arts* 7 (1938): 59-72; Rutherford J. Gettens, “Microscopic Examination of Specimens from an Italian Painting,” *Technical Studies in the Field of the Fine Arts* 3 (1935): 170-1.

⁵²⁴ Plesters, “Cross-sections and Chemical Analysis of Paint Samples,” 128-9; Nadolny, “A history of early scientific examination and analysis of painting materials ca. 1780 to the mid-twentieth century,” 339; —, “The First Century of Published Scientific Analyses of the Materials used in Historical Painting and Polychromy, circa 1780-1880,” 40-3; Rutherford J. Gettens, “A Microsectioner for Paint Films,” *Technical Studies in the Field of the Fine Arts* 1 (1932): 20-8.

by two German scientists may represent the first instance of paint binder characterization carried out on a Quattrocento painting.⁵²⁵ By the early twentieth century, paintings were approached as complex, multi-layered objects, and with new developments in cross-sectional microscopy and other analytical techniques, chemical/heating tests were eventually abandoned and no longer considered to be reliable methods for the identification of paint binders.

5.1.2 Cross-sectional Microscopy and Related Techniques

Paint cross-sections are microscopic paint samples (generally collected along the edges of paintings or near existing losses or cracks) that can provide important information relating to paint stratigraphy, pigments, and/or the presence of unoriginal restoration materials. At present, paint samples are typically embedded in a clear resin (e.g. polyester, epoxy) that is allowed to harden over several hours; the resin is polished smooth, exposing a portion of the paint sample that can then be observed under high magnification (Figure 5.12).

Line-drawing renditions of paint cross-sections can be found in publications as early as the mid-1850s, as scientists began to recognize the importance of preserving and

⁵²⁵ Nadolny, “The First Century of Published Scientific Analyses of the Materials used in Historical Painting and Polychromy, *circa* 1780-1880,” 45. Jilleen Nadolny has identified perhaps one of the earliest references to the organic analysis of an Italian painting; German scientists Geiger and Reimann determined that a school of Pietro Perugino painting depicting a *Madonna and Child* contained a “ground of gypsum (and lime) bound with egg, carbon black, lead oxide, organic green, medium fig milk and egg” based on chemical tests performed in 1828. It is unknown whether this particular artwork has been revisited using more modern analytical methods, but systematic examination and analysis of paintings from this period suggest that it is nearly impossible to determine the presence of fig milk in a paint layer using heat/solubility tests nor is it likely that an egg-containing ground is present. Nadolny has also listed a technical study carried out in 1809 by the Italian Chemist Branchi but only the gilded areas of Italian panel and wall paintings were analyzed (presumably in an attempt to identify the mordant/adhesive).



Figure 5.12: Example of a prepared cross-section collected from a seventeenth-century oil on canvas. The central image shows the original size of the paint sample while the upper right image is the same paint sample viewed at 200x magnification (showing a thin layer of overpaint covering the underlying original paint layers and red ground).⁵²⁶

documenting the original stratigraphy of an artwork.⁵²⁷ In 1932 Rutherford J. Gettens, a scientist at the Fogg Art Museum, published a schematic for an elaborate “paint micro-

⁵²⁶ “Cross-sectional Microscopy,” accessed February 20, 2016, <http://www.artcons.udel.edu/about/kress/examination-techniques-and-scientific-terms/cross-sectional-microscopy>.

⁵²⁷ Nadolny, 42-3; —, “A history of early scientific examination and analysis of painting materials ca. 1780 to the mid-twentieth century,” 339.

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Figure 5.13: Girolamo di Benvenuto, *Madonna and Child with Saints Nicholas of Tolentino, Monica, Augustine, and John the Evangelist* (c. 1505, Fogg Art Museum, Harvard University).

sectioner,” a device which was presumably used to collect and prepare cross-sectional samples from Girolamo di Benvenuto’s *Madonna and Child with Saints Nicholas of Tolentino, Monica, Augustine, and John the Evangelist* (c. 1505, Figure 5.13).⁵²⁸ Gettens

⁵²⁸ Gettens, “A Microsectioner for Paint Films,” 20-8; —, “Microscopic Examination of Specimens from an Italian Painting,” 165-73. See also Rutherford J. Gettens, “The Cross-sectioning of Paint Films,” *Technical Studies in the Field of Fine Arts* 4 (1936):18-22.

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Figure 5.14: George L. Stout's interpretation of cross-sections collected from a *Crucifixion* attributed to the Pollaiuolo workshop, featured in his 1938 article on Quattrocento painting technique entitled "One Aspect of the So-Called Mixed Technique."⁵²⁹

⁵²⁹ George L. Stout, "One Aspect of the So-Called Mixed Technique," *Technical Studies in the Field of the Fine Arts* 7 (1938): 70.

summarized his findings two years later in what and may be one of the earliest recorded publications to include black-and-white reproductions of paint samples collected from a Quattrocento painting. George L. Stout soon followed with a more intimate look at a number of Italian paintings in the Fogg Art Museum's collection in his 1938 article entitled "One Aspect of the So-Called Mixed Technique"; while images of cross-sections as well as results from chemical tests were included in the article, many of Stout's conclusions (such as the use of tempera paint applied over un-pigmented oil sizing) were largely based on visual examination (Figure 5.14).⁵³⁰ It was not until after Paul Coremans's 1953 publication (which focused on the restoration and analysis of Jan van Eyck's *Adoration of the Mystic Lamb*) that color images of paint cross-sections began to appear in technical publications.⁵³¹ Two years after Coremans's publication, in 1955, scientist Joyce Plesters published a series of cross-sections representing Quattrocento paintings in the collection of the National Gallery in

⁵³⁰ Stout, "One Aspect of the So-Called Mixed Technique," 59-72. Stout presents a summary of written sources that allude to the evolution of oil painting in Italy but warns his reader to "keep away from hypotheses and from apochyphal anecdotes about how the great change occurred." On the other hand, some of the conclusions regarding the use of tempera atop oil layers would require additional analysis to confirm Stout's observations; the following observation appears to have been solely based on the examination of cross-sectional samples and microscopic/visual assessment of the surface of paintings: One use of the oil pellicle in connection with tempera paint has been noticed in a few works of the fifteenth century in Italy. Often it has appeared only with microscopic examination or during restoration, for the oil is placed underneath films of relatively lean tempera paint.

⁵³¹ Nadolny, "A history of early scientific examination and analysis of painting materials ca. 1780 to the mid-twentieth century," 339; Streeton, *Perspectives on the Painting Technique of Jan van Eyck*, 15-16; See also Paul Coremans, ed., *L'Agneau Mystique au Laboratoire: Examen et Traitement* (Anvers: De Sikkel, 1953). Note that Jilleen Nadolny has identified a number of early references and publications relating to the use and reproduction of paint cross-sections.

London (in addition to results relating to binding media based on chemical/heating tests).⁵³² To this day cross-sectional microscopy has continued to play an important role in the technical analysis of artworks, particularly in the examination and study of traditional easel paintings.⁵³³

Paint cross-sections can provide information relating to paint stratigraphy and the application of materials (wet-into-wet, un-pigmented interlayers, etc.); however, they must be used in tandem with other techniques in order accurately characterize egg-oil paint systems encountered in Quattrocento paintings. As early as 1905, the German scientist Wilhelm Ostwald found that various chemical tests performed on the surface of exposed paint cross-sections could assist with the characterization of binding media and/or pigments (Wilhelm's work was later translated into English in 1936), although Gettens's publication in 1935 identified potential problems with certain chemical tests generating "false positive" results.⁵³⁴

⁵³² Plesters, "Cross-sections and Chemical Analysis of Paint Samples," 110-57. For Plesters's first publication concerning the preparation of cross-sectional paint samples see Joyce Plesters, "The preparation and study of paint cross sections," *The Museums Journal* 54 (1954): 97-101.

⁵³³ Karen Ashworth, "The examination of a tabernacle altarpiece," in *The Hamilton Kerr Institute: The First Ten Years - Hamilton Kerr Institute Bulletin*, ed. Ian McClure. No. 1 (Cambridge: Hamilton Kerr Institute of the Fitzwilliam Museum, 1988), 82-96; Ann Massing and Nicola Christie, "'The Hunt in the Forest' by Paolo Uccello." In *The Hamilton Kerr Institute: The First Ten Years - Hamilton Kerr Institute Bulletin*, ed. Ian McClure. No. 1 (Cambridge: Hamilton Kerr Institute of the Fitzwilliam Museum, 1988), 30-47.

⁵³⁴ Narayan Khandekar, "Preparation of Cross-sections from Easel Paintings," *Reviews in Conservation* 4 (2003): 52-3; Mills and White, *The Organic Chemistry of Museum Objects*, 177-78; Wilhelm Ostwald, "Iconoscopic Studies, I. Microscopic Identification of Homogeneous Binding Mediums," *Technical Studies in the Field of Fine Arts* 4 (1936): 135-44; —, "Iconoscopische Studien, I. Mikroskopische Nachweis der einfachen Bindemittel," *Sitzungsber der Koniglich Preussischen Akademie der Wissenschaften* 5 (1905): 167-74. Although chemical tests appeared to confirm the presence of egg yolk as the primary paint binder in a cross-sectional sample from Girolamo di Benvenuto's painting (Figure 5.13), Gettens obtained a false positive reaction for the presence of an arsenic-containing pigment.

Nearly twenty years later, in 1955, Joyce Plesters published a list of chemical tests and staining solutions that could be applied directly to the surface of paint samples and included results obtained from cross-sections collected from paintings by Masaccio, Botticelli, Cosme Tura, and Pollaiuolo.⁵³⁵ Plesters also outlined some of the remaining challenges that faced scientists when distinguishing between certain classes of materials using these techniques, particularly the characterization of oil-resin mixtures and the ability to differentiate between animal glue and egg tempera.⁵³⁶

In contrast to chemical tests (which were dependent on the success of a reaction and whether it was visible to the naked eye), staining solutions offered the advantage of creating a distinct visual effect based on changes in color depending on the presence of certain materials present within the paint and ground layers (such as proteins in egg yolk and/or glue and lipids in drying oils). In the 1970s, after Plesters, Meryl Johnson, Elizabeth Packard, and others began to turn more often to cross-sectional microscopy and staining techniques to better understand the transition from egg tempera to oil paint in fifteenth-century Italy; however, there was no unanimity about what stains generated the most accurate and consistent results.⁵³⁷ In the preceding decades, Plesters had encouraged the use of Nile Blue as a stain

⁵³⁵ Khandekar, "Preparation of Cross-sections from Easel Paintings," 52-3; Plesters, "The preparation and study of paint cross sections," 110-57.

⁵³⁶ Plesters, 130.

⁵³⁷ Khandekar, 58; Mills and White, 177-8; Marie-Christine Gay, "Application of the Staining Method to Cross-sections in the study of the Media of Various Italian Paintings of the Fourteenth and Fifteenth Centuries," in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 78-83; —, "Essais d'identification et de localisation des liants picturaux par des colorations spécifiques sur coupes minces," 8-24; Meryl Johnson and Elizabeth Packard, "Methods for the identification of binding media in Italian paintings of the fifteenth and sixteenth century," *Studies in Conservation* 16 (1971): 145-64, doi: 10.2307/1505494; Elisabeth Martin, "Note sur l'identification des protéines dans les liants de peinture," *Laboratoire de Recherche des*

for drying oils and Acid Fuschin for proteins; however, Meryl Johnson and Elizabeth Packard offered alternative options (Sudan Black B for oils and Ponceau S for proteins) in their 1971 article “Methods for the identification of binding media in Italian paintings of the fifteenth and sixteenth century.”⁵³⁸ Elizabeth Packard was a leading voice in painting conservation in the mid-twentieth century (serving as chief paintings conservator at the Walters Art Gallery). Packard worked together with Meryl Johnson, a scientist from the University of Michigan, generating an exhaustive study that involved the examination of cross-sections collected from nearly 450 paintings, artworks that represented the “period of transition during the Renaissance, at the end of the fifteenth and the beginning of the sixteenth century, when considerable use of mixed media could be expected.”⁵³⁹ Johnson and Packard provided a detailed outline describing the various methods of sample preparation as well as the general benefits and drawbacks of cross-sectional staining; potential issues relating to staining techniques included the quality of water used to dissolve the solutions (the presence of metal ions and other substances could affect staining results), the “age” of the staining solutions (old solutions may not produce similar results and may even be ineffective), interactions with the mounting resin, the presence of certain inorganic materials (certain pigments would react

Musées de France, Annales (1975): 57-60; —, “Some Improvements in Techniques of Analysis of Paint Media,” 63-4; Suzy Delbourgo, Jean P. Rioux, and Elisabeth Martin, “L’analyse des peintures du Studiolo d’Isabelle d’Este au Laboratoire de Recherche des Musées de France. II - Étude analytique de la matière picturale,” *Laboratoire de Recherche des Musées de France, Annales* (1975): 21-8.

⁵³⁸ Khandekar, 58; Plesters, 130; Johnson and Packard, “Methods for the identification of binding media in Italian paintings of the fifteenth and sixteenth century,” 145-64.

⁵³⁹ Johnson and Packard, 146.

adversely to the stains and dark pigments made it difficult to assess the staining reaction), and the time required before a staining reaction was considered “complete.”⁵⁴⁰

Johnson and Packard’s early conclusions that were based on cross-sectional staining should be revisited as the body of knowledge relating to traditional painting practice has grown considerably since 1971. The first case study cited in their article seems to have produced a false positive result for drying oils; a cross-section from *The Blessing Christ* by Pietro da Rimini (c. 1340-49, Figure 5.15) was determined to contain a white underlayer (possibly the gesso ground?) bound in oil, followed by a layer containing copper “resinate” and oil, with a final layer of green bound in tempera.⁵⁴¹ There is no evidence to suggest that early Trecento artists would routinely apply tempera paints atop oil-containing layers, a technique that would inevitably have led to problems with reticulation and proper adhesion (due to the presence of thin aqueous-based paints atop thick, oily layers).⁵⁴² While the authors point out that this particular painting was a unique exception (tempera paint was the predominant binder found on paintings from this same period), other case studies presented in the article raises additional questions; cross-sectional staining of a sample collected from a

⁵⁴⁰ Ibid, 146-53. The polyester resin used by Johnson and Packard would occasionally react with a stain known as Ponceau S (a sodium salt of a diazo dye that produces a red color when in contact with proteins).

⁵⁴¹ Ibid., 155-6. Note that the term “copper resinate” has been used ubiquitously in the technical literature; however, recent studies have shown this term to be both mis-leading and problematic in its origin. See also Margareit van Eikema Hommes, “Interpreting historical sources on painting materials and techniques: The ‘myth’ of copper resinate and the reconstruction of indigo oil paints,” in *Art of the Past: Sources and Reconstructions*, eds. Mark Clarke, Joyce Townsend, and Ad Stijnman (London: Archetype Publications, 2005), 16-23.

⁵⁴² Ibid, 150, 156. While Johnson and Packard go into great detail regarding the type of grounds that they encountered throughout the study, they do not elaborate on the inorganic pigment(s) present in this “white” layer particularly whether or not lead white and/or calcium-containing pigments were identified.

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Figure 5.15: Excerpt from Meryl Johnson and Elizabeth Packard's 1971 publication featuring a cross-sectional diagram associated with Pietro da Rimini's *The Blessing Christ* (c. 1340-49, Walters Art Museum, Baltimore).⁵⁴³

painting depicting *St. Helena* (now attributed to Francesco Morandini, c. 1575) suggested the use of tempera as a yellow glaze applied atop oil layers, again an unlikely use of the medium.⁵⁴⁴

⁵⁴³ Ibid., 156.

⁵⁴⁴ Ibid., 157-8. The authors also found the flesh tones to contain tempera, leading them to conclude that this "continued use of egg tempera implies a mistrust of the drying properties of oil," a statement that contradicts much of what is now known based on technical research and

Two additional case studies presented by Johnson and Packard generated results that are more conceivable. A sample from a green marbled area of Nicola di Maestro Antonio da Ancona's *St. John the Baptist* (c. 1490-99; Figure 5.16) demonstrated the presence of six layers of tempera paint followed by a top layer of green paint bound in oil (Figure 5.16) while the authors describe a sample from the green mantle of the Madonna in Botticelli's *Madonna and Child with Infant Saint John* (1495-99; Figure 5.17) a weak "oil-tempera-oil" paint system atop a glue ground (Figure 5.17).⁵⁴⁵ The dotted line in the drawing of the Botticelli cross-section is intriguing and may even allude to a separation of the aqueous (egg tempera) and oil (drying oil) phases in a emulsified paint layer (*tempera grassa*), a possibility that has recently been postulated in the interpretation of other paint systems as well as the analysis of other works by Botticelli.⁵⁴⁶ From a practical standpoint, the technique involving the

written evidence (see Chapters 3 and 4 for more information relating to the early use of oil painting in Medieval and Renaissance Italy). It should be noted that Karin Groen has found evidence of proteinaceous additions to white/light highlights in a number of seventeenth-century Dutch and Flemish paintings so it is not entirely impossible that protein (egg yolk and/or glue) is occasionally present as an addition oil-based paint layers; however, the suggestion that a thin "glaze" of egg tempera paint was applied over a slick oil film is unlikely. See also Karin Groen, "Investigation of the Use of Binding Medium by Rembrandt: Chemical Analysis and Rheology" in *Paintings in the Laboratory: Scientific Examination for Art History and Conservation*, ed. Esther van Duijn (London: Archetype, 2014), 76-81, 90.

⁵⁴⁵ Ibid.

⁵⁴⁶ Groen, "Investigation of the Use of Binding Medium by Rembrandt: Chemical Analysis and Rheology," 76-81, 90; Patrick Dietemann et al., "A Colloidal Description of Tempera and Oil Paints, Based on a Case Study of Arnold Bocklin's Painting 'Villa am Meer II' (1865)," *e-Preservation Science* 11 (2014), 29-46, accessed January 29, 2015, http://www.morana-rtd.com/e-preservation-science/2014/ePS_2014_a5_Dietemann.pdf; Johann Koller and Ursula Baumer, "'Er [...] erprobte die seltsamsten methoden, um öle zum malen [...] zu finden.' Leonardos rolle in der frühen italienschen ölemaleri," in *Leonardo da Vinci, Die Madonna mit der Nelke*, eds. Cornelia Syre, Jan Schmidt, and Heike Stege (Munich: Alte Pinakothek and Schirmer/Mosel, 2006), 155-71; Johann Koller, Irene Fiedler, and Ursula Baumer, "Vermeers Maltechnik – eine Mischtechnik. Untersuchung der Bindemittel auf dem Gemälde 'Bei der Kupplerin,'" in *Johannes Vermeer – Bei der Kupplerin*, eds. Uta Neidhardt and Marlies Giebe

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Figure 5.16: Excerpt from Meryl Johnson and Elizabeth Packard’s 1971 publication featuring a cross-sectional diagram associated with Nicola di Maestro Antonio da Ancona’s *St. John the Baptist* (c. 1490-99, Walters Art Museum, Baltimore).⁵⁴⁷

(Dresden: Michel Sandstein Verlag 2004), 65–75; —, “Die Bindemittel auf Dürers Tafelgemälden,” in *Albrecht Dürer. Die Gemälde der Alten Pinakothek*, eds. Gisela Goldberg, Bruno Heimberg and and Martin Schawe (Munich: Edition Braus 1998), 102–19. Recent studies have found small amounts of egg present in oil-based paints in works by Vermeer, Rembrandt, Stefan Lochner, Albrecht Durer, and Leonardo da Vinci as well as a number of late medieval Cologne paintings. Further analysis is needed to in order to confirm these analytical findings. For a summary of technical findings associated with works by Botticelli see Chapter 4, section 4.2.1.

⁵⁴⁷ Johnson and Packard, 157.

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Figure 5.17: Excerpt from Meryl Johnson and Elizabeth Packard's 1971 publication featuring a cross-sectional diagram associated with Botticelli's *Madonna and Child with Infant Saint John* (1495-99, Walters Art Museum, Baltimore).⁵⁴⁸

application of oil paint over tempera is perfectly plausible and one that is likely present in other Quattrocento works from this period. On the other hand, it is unlikely that the stain Sudan Black B is able to successfully distinguish between chemical markers associated with

⁵⁴⁸ Ibid., 158.

oil-containing paints/varnishes applied by the artist from those that may originate from restoration coatings/overpaint.⁵⁴⁹

Marie-Christine Gay, a scientist at the Louvre, questioned Packard and Johnson's findings in her 1976 publication focusing on cross-sectional staining.⁵⁵⁰ Gay dismissed Packard and Johnson's interpretation of Sudan Black staining results as well as their decision to carry out staining on embedded "thick" cross-sections as opposed to thin sections that could be cut and prepared from the parent sample.⁵⁵¹ Gay stated that Sudan Black B "only gives good results on liquid fatty materials" and that stains were likely to be preferentially absorbed by porous regions of thick cross-sections and "infiltrate cracks and discontinuities between layers."⁵⁵² On the other hand, Gay's own results are somewhat problematic; staining performed on a number of samples from Italian paintings (dating from the fourteenth to the sixteenth century) suggested the presence of an oil size atop the gesso ground followed by layers of tempera paint while a Trecento painting was determined to only contain oil-based paint (Figure 5.18). Like Johnson and Packard, however, Gay called attention to fact that stains were currently unable to differentiate between whole egg, egg yolk, and egg white, and that such materials could only be identified by applying fluorescent antibodies to thin sections

⁵⁴⁹ Further analysis is necessary to confirm whether this top layer of oil paint is indeed original to the picture

⁵⁵⁰ Gay, "Application of the Staining Method to Cross-sections in the study of the Media of Various Italian Paintings of the Fourteenth and Fifteenth Centuries," 79.

⁵⁵¹ *Ibid.* This is a similar layering system that was suggested by Stout in 1938; however, it is unlikely (or at least uncommon) to encounter oil sizing atop gesso grounds from paintings of this period. Future analysis and examination of Italian paintings dating from the twelfth to the fifteenth century may help to further elucidate this matter.

⁵⁵² *Ibid.*

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Figure 5.18: Excerpt from Marie-Christine Gay's 1976 article featuring the interpretation of cross-sectional samples based on observed staining reactions.⁵⁵³

of paint samples.⁵⁵⁴

Subsequent publications continued to demonstrate a general lack of consensus regarding the accuracy and reliability of staining techniques, frequently using cross-sections collected from Quattrocento paintings as case studies. Soon after Gay's publication, Elisabeth Martin (a chemist employed at the Research Laboratory of the Musées du Louvre) declared in her 1977 article that Sudan Black was no longer considered reliable, stating that "the use of

⁵⁵³ Ibid, 79-81.

⁵⁵⁴ Ibid, 79; Johnson and Packard, 153-4.

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Figure 5.19: A Excerpt from Elisabeth Martin's 1977 article featuring the interpretation of cross-sectional samples based on observed staining reactions using the Amido Black series (NA₁, NA₂, and NA₃).⁵⁵⁵

lysochromic stains has been abandoned [...] since dried oils do not satisfactorily play the role of solvent for them."⁵⁵⁶ Martin instead presented three new classes of stains, two of which offered the promise of distinguishing between the various categories of proteins (e.g. glue, egg, and casein).⁵⁵⁷ Martin demonstrated the efficacy of the Amido Black stain series by

⁵⁵⁵ Martin, "Some Improvements in Techniques of Analysis of Paint Media," 66.

⁵⁵⁶ Martin, 63.

⁵⁵⁷ Ibid, 63-4.

reporting the results observed on cross-sections collected from Italian paintings (Figure 5.19), once again repeating the trend of introducing new staining techniques while abandoning those cited in earlier publications.⁵⁵⁸ Interestingly, a handful of these stains continued to be used throughout the subsequent decades and some institutions still turn to staining in an attempt to characterize binding media.⁵⁵⁹

R.H. de Silva's 1963 study demonstrated foresight regarding the future problems that plagued the conservation science community in the decades that followed.⁵⁶⁰ Although the article focuses primarily on organic binders encountered in wall paintings, R.H. de Silva's 1963 study demonstrates incredible foresight regarding future problems that will be discussed in sections 5.2 and 5.3. The author, an archaeologist by profession, conducted a series of tests on known references as well as samples collected from wall paintings and found that nearly all tests could generate false positive reactions and even false negatives. The general premise of the study was an attempt to expose the dangers of drawing conclusions relating to historical

⁵⁵⁸ Ibid, 66. Martin does confirm that acid fuschin (i.e. Ponceau S) can still be used to identify proteins and thus does not completely dismiss Johnson and Packard's work; however, the Amido Black series presented by Martin offered an additional benefit of being able to distinguish between aged and unaged egg yolk and/or glue.

⁵⁵⁹ Liliane Masschelein-Kleiner, "Analysis of paint media, varnishes, and adhesives," in *Scientific Examination of Easel Paintings – PACT, Journal of the European Study Group on Physical, Chemical, and Mathematical Techniques Applied to Archaeology*, eds. Roger van Schoute and Hélène Verougstraete-Marcq, no. 13 (Strasbourg: Council of Europe-Parliamentary Assembly, 1986), 186-9. I had the opportunity to perform a number of staining tests with the scientists at the National Gallery of Art in Washington DC between 2008-2010. See Chapter 6, section 6.2 for more information on staining.

⁵⁶⁰ de Silva, "The Problem of the Binding Medium Particularly in Wall Painting," 56-64.

painting practice based on these singular reactions. De Silva accounted for these discrepancies by going further and citing scientific studies that had identified problematic components found in gums (starches and sugars), proteins (glues, casein, egg yolk/white), and drying oils (linseed), listing all of the trace components and/or impurities that could give rise to misinterpretation:

The possibility of the presence of the following constituents and impurities in the media listed below is to be recognized (sic):

Vegetable gums - proteins.
Proteinaceous medium- fats, carbohydrates.
Drying oils- carbohydrates, proteins.

In the examination of a paint medium by microchemical tests, carbohydrate, amino acid and glycerol (to take the most general case) might be detected. The conclusions that may be drawn from such an example are:

- (a) Binding medium - mixture of vegetable gum, egg tempera (or glue), drying oil.
- (b) Binding medium - emulsion of drying oil with plant gum.
Impurity - protein from oil or gum or both.
- (c) Binding medium - emulsion of drying oil and egg.
Impurity, minor constituent - carbohydrate from oil, carbohydrate from egg, or both.
- (d) Binding medium - tempera of egg and plant gum.
Constituent - fatty matter from egg.
- (e) Binding medium - drying oil.
Impurity - protein debris, carbohydrate from mucilage.
- (f) Binding medium - egg tempera.
Constituents - fatty matter major constituent, carbohydrate minor constituent.⁵⁶¹

In the 1960s, de Silva recommended follow-up testing with paper chromatography (PC), a technique that initially demonstrated promise in the early development of organic analysis (now no longer considered practical for the characterization of binding media)

⁵⁶¹ Ibid., 62.

showed considerable promise as a reliable method.⁵⁶² De Silva's work can be extrapolated to the analysis of easel paintings; his observations relating to egg tempera can be considered a predication of the challenges relating to the analysis of Quattrocento paintings, particularly relating to the fact that both egg yolk and drying oils share the same "fatty matter." De Silva's additional prescient concerns included the possible interference of pigments, insufficient sample size, and the impact of degradation products, all of which have shown to have an impact on the organic analysis of paintings in recent times.

5.1.3 Early Developments in Chromatography

By the 1960s, thin layer chromatography (TLC) began being used to characterize the organic materials present in artworks.⁵⁶³ A relatively simple and inexpensive technique, TLC

⁵⁶² Mills and White, *The Organic Chemistry of Museum Objects*, 15-7; --, "The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," 72-7; Karel Macek and Mojmir Hamsik, "Paper Chromatography – A New Method for the Characterization of Binding Media," *Umeni* 2 (1954): 58; Margaret Hey, "The Analysis of Paint Media by Paper Chromatography," *Studies in Conservation* 3 (1958): 183-93, 183-93. doi: 10.2307/1505009. Note that by this period, thin-layer chromatography (TLC) was gradually replacing paper chromatography (PC) as the former was considered to be a more refined technique.

⁵⁶³ Mary Striegel and Jo Hill, *Thin-Layer Chromatography for Binding Media Analysis* (Los Angeles: The J. Paul Getty Trust 1996), 1-18; Domenech-Carbo, "Novel analytical methods for characterising binding media and protective coatings in artworks," 122-23; John S. Mills and Raymond White, "Organic Analysis in the Arts: Some Further Paint Medium Analyses," *National Gallery Technical Bulletin* 2 (1978): 72. In their 1978 publication Mills and White attribute the early evolution of paint analysis to the "discovery and development of the chromatographic methods for separating mixtures into their components: paper-chromatography in the mid-1940s, gas-chromatography in the early fifties and thin-layer chromatography some ten-years later." However it has been difficult to locate early sources describing the application of gas-chromatography to the analysis of binding media that date to the 1950s.

can be used to separate and identify different components present in a mixture. The procedure generally involves dissolving a sample in a solution (the “liquid” phase) which then travels via capillary action over and/or through specially prepared plates or silica beds (the “solid” phase); patterns left behind on the TLC plate/bed are then compared to known references in order to classify the type of wax, protein, carbohydrate, etc. that may be present within the same paint sample.⁵⁶⁴ Johnson and Packard were likely the first to apply this technique to the analysis of Quattrocento paintings; they claimed that TLC could be used to detect the non-saponifiable components (e.g. cholesterol) in egg yolk and drying oils, allowing for the differentiation between different drying oils as well as the detection of egg and oil mixtures (Figure 5.20).⁵⁶⁵ Four years later two scientists at the National Gallery in London, John S. Mills and Raymond White, found that this particular method of TLC “was incapable of such specificity,” particularly in regards to the characterization of drying oils.⁵⁶⁶ White later recalled his reservations with the technique, stating that “TLC really wasn’t of any great use

⁵⁶⁴ TLC is generally described as a separation technique that utilizes a bed of silica, pre-coated kieselgel or microcrystalline cellulose that is attached to glass or aluminum. See Mary Striegel and Jo Hill, *Thin-Layer Chromatography for Binding Media Analysis* (Los Angeles: The J. Paul Getty Trust 1996).

⁵⁶⁵ Johnson and Packard, 154-5; Meryl Johnson, Henry E. Rosenberg, and Raymond P. Skowronski, “Thin-Layer Chromatography of Sterols on Magnesium Trisilicate,” *Studies in Conservation* 16 (1971): 165-7, doi: 10.2307/1505494. In their 1971 article, Johnson and Packard state the following: The sterols extracted from Italian paintings chromatographed as well as the sterols from fresh materials. We found that this was a particularly good method for confirming the presence of egg tempera in paintings in which we had not expected to find it, because cholesterol, which is found in large quantities in egg yolk, has a distinctive chromatographic pattern. It was also possible to distinguish between the sterols found in the different oils present in the painting samples and detect mixtures of egg tempera and oil, or of two oils, in the same sample.

⁵⁶⁶ Mills, “The Identification of Binding Media – An Introduction,” 69-71; — and White, *The Organic Chemistry of Museum Objects*, 178; —, “The Identification of Paint Media from their Sterol Composition – A Critical View,” 176-82. In response to Johnson et. al.’s chromatogram

Figure removed due to copyrighting

Figure 5.20: Excerpt from Meryl Johnson et al.'s 1971 article featuring the observed patterns generated by references and paint samples on a prepared thin-layer chromatography plate.⁵⁶⁷

and sometimes gave sort of falsely possible things.”⁵⁶⁸

(shown in Figure 5.8) Mills and White stated the following in their 1975 publication: Egg-yolk non-saponifiables were also isolated though in fact these revealed only a single TLC spot or GC peak corresponding to cholesterol. Rather puzzlingly the chromatogram illustrated by Johnson et al. shows four spots both for the egg-yolk non-saponifiables and for the cholesterol standard. Which of these actually corresponds to cholesterol was not indicated. [...] It can be seen that the oils would not be easy to distinguish one from another even in the fresh state by quantitative measurement, and probably walnut and poppyseed could not be so distinguished. Cholesterol is well separated from the oil sterols and consequently the presence of egg in oils is potentially detectable.

⁵⁶⁷ Johnson, Rosenberg, and Skowronski, “Thin-Layer Chromatography of Sterols on Magnesium Trisilicate,” 166.

⁵⁶⁸ “Raymond White oral history interview conducted by Rachael Morrison, 1 December, 2009,” FAIC Oral History File housed at the Winterthur Museum, Library, and Archives.

Although TLC was determined to be ill-suited for the identification of oils in comparison to GC, scientists continued to use the technique well into the 1990s for the analysis of proteins, waxes, resins, and carbohydrates.⁵⁶⁹ Mary Striegel and Jo Hill's 1996 publication presented the method as a reliable technique for the characterization of binding media (with the exception of drying oils) and provided a series of case studies demonstrating the efficacy of TLC.⁵⁷⁰ The Striegl-Hill text does not include examples relating to Italian paintings; however, the results obtained from paint samples collected from a Roman-Egyptian sarcophagus warrant some consideration. The paint binder was ultimately identified as animal glue based on comparisons with other reference samples and further analysis performed using gas chromatography; but simple visual analysis of the TLC plate reproduced in the publication does not seem to generate clear and convincing results (Figure 5.21).⁵⁷¹ Based on these results, as well as other technical studies, the presence of pigments can affect the TLC pattern that is generated, possibly leading to misinterpretation of the results. Furthermore, it is often challenging to effectively separate friable, thin paint/ground layers from samples that are typically measurable only on a micron scale so contamination between paint/ground layers (not to mention restoration materials and coatings) is also a factor that could influence the

⁵⁶⁹ Liliane Masschelein-Kleiner, "An Improved Method for the Thin-Layer Chromatography of Media in Tempera Paintings," *Studies in Conservation* 19 (1974): 207-11, doi: 10.2307/1505726; —, "Analysis of paint media, varnishes, and adhesives," 192-4; Domenech-Carbo, "Novel analytical methods for characterising binding media and protective coatings in artworks," 122-23. See also Mary Striegel and Jo Hill, *Thin-Layer Chromatography for Binding Media Analysis* (Los Angeles: The J. Paul Getty Trust, 1996).

⁵⁷⁰ Striegel and Hill, *Thin-Layer Chromatography for Binding Media Analysis*, 81-2. Note that Striegel and Hill do summarize potential systems (using reversed phase plates) that "may be useful in separating sterols and may lead to a method of identification of oils."

⁵⁷¹ *Ibid.*, 43-4.

Figure removed due to copyrighting

Figure 5.21: Excerpt from Striegel and Hill's 1996 publication featuring the patterns generated by references and paint samples on a prepared TLC plate. While the best visual match with the paint sample (far right) appears to be egg yolk mixed with lead white (second from right), further analytical tests using gas chromatography found a positive match with animal glue instead.⁵⁷²

⁵⁷² Ibid.

appearance of the TLC patterns. As of 2016, TLC is no longer commonly used by museum laboratories; the technique has largely been replaced thanks to improvements in other chromatography methods.

The inability of TLC to successfully identify different drying oils was likely one of the reasons why Mills and White began to consider another form of chromatography altogether – gas liquid chromatography (GLC or GC). Both Mills and White specialized in organic analysis and brought this expertise to the National Gallery in London. Mills had been using capillary column chromatography to characterize natural resins since his arrival at the National Gallery London in 1951; however, it was not until around 1962/3 that he began to apply gas chromatography to the analysis of paint samples.⁵⁷³ Developed in the late 1960s, GC is a separation technique based on the boiling point and polarity of individual compounds, a technique that was further adapted by Mills following Nathan Stolow's (a conservation scientist who was then based at the National Gallery in Canada) pioneering work in an attempt to differentiate between pigmented and un-pigmented reference paint films bound with linseed, walnut, and poppyseed oil.⁵⁷⁴ In recalling his early years at the National Gallery soon

⁵⁷³ Garry Thompson, John Mills, and Joyce Plesters, "The Scientific Department of the National Gallery," *The National Gallery Technical Bulletin* 1 (1977): 25; Mills, "The Chromatography Examination of Paint Media. Part 1. Fatty Acid Composition and Identification of Dried Oil Films," 92-107; "Joyce Plesters-Brommelle oral history interview conducted by Tina Leback-Sitwell, 2 July, 1978," FAIC Oral History File housed at the Winterthur Museum, Library, and Archives; Mills and White, "The Identification of Paint Media from their Sterol Composition – A Critical View," 176. Like TLC, column chromatography is a separation technique that involves a liquid phase (in this case a liquid sample) that is passed through a column filled with a solid phase (e.g. alumina, etc.).

⁵⁷⁴ Nathan Stolow, "The application of gas chromatography in the investigation of works of art," in *Application of Science in the Examination of Works of Art*, vol. 2 (Boston: Museum of Fine Arts, 1965), 172-83; Mills, "The Chromatography Examination of Paint Media. Part 1. Fatty Acid Composition and Identification of Dried Oil Films," 92-107; Thompson, Mills, and Plesters, "The Scientific Department of the National Gallery," 25-26; Mills and White, "The Identification of Paint Media from their Sterol Composition – A Critical View," 176-82; —,

after his arrival in 1969, Raymond White summarized some of the challenges that both he and Mills faced during the initial stages of their research:

And, when I got to the chemistry laboratory I was just simply appalled because there was a gas chromatograph, quite a primitive gas chromatograph, a PAN gas chromatograph, well dating from the early '60s and so forth. But, it had just been plumbed in, the hydrogen lines would have just been glued, “[laughs]”, glued into the... and the whole, every surface, every inch of the bench was just littered with old experiments and so forth. It was unbelievable; I went into a state of shock. I thought, ‘My God! It would take me five years to get some order into this’.

That [GC] was novel at the time and also very problematic. Of course, in those days we had to, we required much larger samples than we do now. And so, the scope for something was much more, much more limited. We had really quite primitive equipment, very difficult equipment, if you could keep the old PAN gas chromatograph working and so forth, you know, in terms of leaks and some custom couplings and that weren't too sophisticated as they are now. That was one thing. Then, we didn't really have proper integrators, so if you didn't, as a matter of experience and judgment get it about right then some of your peaks would sail off the paper and then you wouldn't be able to do the palmitate/stearate and the azelate to palmitate ratios and so forth. So, it calls for very fine, there was a need for very fine judgment. And, the most annoying and challenging things was we had an old Honeywell chart recorder and that was the only means of recording the data in those days, which had a sort of ink reservoir which regularly blocked up or just stopped running in the middle of the trace and so forth. So, it was an absolute nightmare, an absolute nightmare to ensure that you actually got the results for a run. And, John was absolutely superb at handling that machine, that beast.⁵⁷⁵

Some of these obstacles were alleviated with National Gallery's purchase of a Pye 104 Gas Chromatograph in 1970 (first introduced in 1964), an instrument that enabled them to improve

The Organic Chemistry of Museum Objects, 15-7; Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 125-6; Townsend and Boon, “Research and Instrumental Analysis in the Materials of Easel Paintings,” 349-51.

⁵⁷⁵ “Raymond White oral history interview conducted by Rachael Morrison, 1 December, 2009,” FAIC Oral History File housed at the Winterthur Museum, Library, and Archives.

their systematic approach to the analysis of binding media.⁵⁷⁶ In 1976, Mills and White formally presented their results obtained from a number of Italian paintings at the National Gallery (along with other Old Master works), one of the earliest recorded publications outlining the analysis of traditional easel paintings using GC (Figure 5.22).⁵⁷⁷ The following year marked the establishment of the annual journal series the *National Gallery Technical Bulletin*; with each publication Mills and White contributed their analysis of binding media complete with lists outlining the materials found in paintings dating from the thirteenth to the nineteenth centuries, a trend they continued over the next twenty years.⁵⁷⁸

⁵⁷⁶ Ibid; Thompson, Mills, and Plesters, “The Scientific Department of the National Gallery,” 25-26. Raymond White states the following in his 2009 interview: And, eventually trying to persuade the powers at be that we really needed something a little less perverse “[laughs]” and variable in its...and, eventually, we managed to get funding for a Pye 104 gas chromatograph which was a much more reproducible system, much more sort of foolproof. It had proper couplings and a decent flame ionization detector that didn’t block up at the drop of a hat. And, a better chart recorder that “[laughs]” didn’t, sort of, block up and run out of, you know, stop recording as it were. And then, various improvements in the sort of couplings and the supply and so forth.

⁵⁷⁷ Mills and White, “The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis,” 72-7. Note that Liliane Masschelein-Kleiner presented her research relating to the analysis of proteins in easel paintings using GC equipped with mass spectrometry in the same publication. See also Liliane Masschelein-Kleiner, “Contribution to the Study of Aged Proteinaceous Media” in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 84-7.

⁵⁷⁸ John S. Mills and Raymond White, “Analyses of Paint Media,” *National Gallery Technical Bulletin* 1 (1977): 57-9; —, “Organic analysis in the arts: Some further paint medium analyses,” *National Gallery Technical Bulletin* 2 (1978): 71-6; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 3 (1979): 66-7; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 4 (1980) 65-7; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 5 (1981): 66-7; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 7 (1983): 65-7; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 9 (1985): 70-1; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 11 (1987): 92-5; —, “Analyses of paint media,” *National Gallery Technical Bulletin* 12 (1988): 78-9; —, “Paint Media Analyses,” *National Gallery Technical Bulletin* 13 (1989): 69-

Mills and White continued to refine and develop GC methods dedicated to the characterization of oil-containing paint samples; simultaneous efforts by others were being devoted to the analysis of proteinaceous media (e.g. egg yolk, egg white, glue, and casein). Echoing Mills and White's concern over the accuracy of TLC in 1969, paintings conservator Sheldon Keck and chemist Theodore Peters outlined the technique's inability to successfully identify certain classes of proteins and instead suggested ion-exchange chromatography as a possible solution.⁵⁷⁹ Their research was followed by Liliane Masschelein-Kleiner's research published in 1975, a study ahead of its time for the application of GC equipped with mass spectrometry (see Section 5.2.3) for the study of proteinaceous materials in artworks.⁵⁸⁰ Like Mills and White, Masschelein-Kleiner, a conservation scientist at the Royal Institute for Cultural Heritage in Brussels, was involved early on in the analysis of paint binders and organic art materials. Masschelein-Kleiner analyzed a sample from the blue sky of *Christ between St. Thomas and St. John the Baptist* (possibly attributed to Cristoforo Scacco, c. 1495-1503, see Figures 5.23 and 5.24) using GC and detected the presence of animal glue based on the amino acid profile, an unlikely (but not impossible) choice of binder given the

71; —, "Paint Media Analyses," *National Gallery Technical Bulletin* 14 (1993): 86-94; —, "Paint Media Analyses," *National Gallery Technical Bulletin* 16 (1995): 85-95; —, "Paint Media Analyses," *National Gallery Technical Bulletin* 19 (1998): 74-95.

⁵⁷⁹ Keck and Peters, "Identification of Protein-containing Paint Media by Quantitative Amino Acid Analysis," 75-82. Keck and Peters state the following in regards to early PC and TLC methods that were used in the characterization of proteins: In the case of proteins which contain unique amino acids, such as hydroxyproline in gelatin, the use of paper or thin layer chromatography may lead to identification of the type of protein. However, for casein, glair (egg white) and egg yolk, the amino acid composition is not sufficiently distinctive to permit differentiation by a qualitative or semi-qualitative technique.

⁵⁸⁰ Liliane Masschelein-Kleiner, "Contribution to the Study of Aged Proteinaceous Media" in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 84-7.

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Figure 5.22: Excerpt from Mills and White's 1976 publication summarizing the interpretation of analysis performed using gas chromatography conducted on Italian paintings at the National Gallery, London.⁵⁸¹

⁵⁸¹ Mills and White, "The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," 74.

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Figure 5.23 (left) and 5.24 (right): Cristoforo Scacco's *Christ between St. Thomas and St. John the Baptist* (attr., c. 1495-1503, Musée Royaux des Beaux-Arts de Belgique, Brussels) as it appeared during the 1940s (left) and as it appears today post-restoration (right).⁵⁸²

period and style of the painting. Nothing is stated in the article relating to the painting's problematic conservation history; these findings may demonstrate that in the 1970s scientists were still becoming aware of the complications posed by the presence of restoration materials.⁵⁸³ There were other challenges associated with amino acid analysis, a problem that was summarized by Mills and White in their 1978 article explaining why the process was often "discouraging":

⁵⁸² Federico Zeri, "Two Early Cinquecento Problems in South Italy," *The Burlington Magazine* 96 (1954): 146-52. The image depicted in Figure 5.23 can be found on page 152 of Zeri's article.

⁵⁸³ *Ibid.* Based on the photograph taken of the painting in the 1940s based on its current appearance today, the panel painting has clearly experienced substantial losses throughout the

Because the various groups of natural materials encountered as paint media are so different chemically, quite different approaches have to be taken for their preparation for gas-chromatography and in actually carrying this out. Thus separate samples may be needed for the different procedures. A separate sample would indeed be required if one were going to follow up a fatty acid examination, which had seemed to suggest the presence of egg in addition to oil, by a study of the amino acid composition of the proteinaceous component of the suspected egg. This would be a desirable check in doubtful cases and we ourselves do this occasionally. The lengthy procedure is, however, discouraging involving as it does acid hydrolysis, ion-exchange to remove dissolved metal ions, two stages of derivatization and then gas-chromatography.⁵⁸⁴

In the same article, Mills and White referred their readers to other analytical procedures that appeared to be making some progress in regards to the analysis of proteins; however, it is crucial to note the implication of Mills and White's statement regarding the analysis of binding media in Quattrocento paintings. Based on their pioneering work of the 1960s and '70s, Mills and White found that more evidence was needed in order to confirm the presence of egg yolk in a paint layer, not to mention the characterization of egg-oil mixtures.⁵⁸⁵ While their analytical procedure was able to successfully reveal the relative amount of fatty acids (markers shared by both drying oils and egg yolk) in a sample, it was not altogether a

paint and ground layers. It is not impossible that Masschelein-Kleiner's analysis was contaminated by the presence of animal glue from previous consolidation efforts.

⁵⁸⁴ Mills and White, "Organic Analysis in the Arts: Some further Paint Medium Analyses," *National Gallery Technical Bulletin*, 72-3.

⁵⁸⁵ Ibid; Mills and White, "The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," 72. In their 1976 article Mills and White commented on the challenges presented by the possible presence of mixed media compounded by the fact that conclusions often relied on only a few samples: This latter possibility and that of mixed media were added complications which we were perhaps unwilling to dwell upon overmuch since they seemed just too demanding of the method. The further complication [...] of the possibility of the use of different media in the different layers of the painting's structure, could also hardly be coped with in the absence of supplementary techniques.

conclusive method to determine the presence of protein from egg or even a mixed egg-oil paint system. Subsequent studies performed by Mills and White and other scientists thus sought to utilize complementary techniques that could address these challenges, efforts that were fostered by the growing number of questions relating to the egg-oil transition in fifteenth-century Italy.

5.2 Analysis of Binding Media: Current Methods and Recent Trends

5.2.1 Recent Developments in Cross-Sectional Staining

Despite significant advancements in the field of chromatography, such techniques remain ill-suited for the analysis of individual layers present in cross-sectional samples. Chromatography typically requires that samples are broken down both physically and chemically in order to successfully extract components of various organic binders. This procedure makes it difficult (and often impossible) to confirm what type of material resides in each layer of ground, paint, and varnish. In an effort to overcome this disadvantage, conservators and scientists have continued to research the development of cross-sectional staining techniques and improve upon methods used by their predecessors. In 2012, Richard Wolbers (a paintings conservator and professor at the University of Delaware) et al. summarized some of the problems associated with past staining solutions, describing them as “cumbersome” to apply, requiring frequent “rinsing” during and in between application of successive stains, and delivered in alcoholic or acidic solutions that may have caused irreversible damage to original materials within the sample.⁵⁸⁶ By 1987, a series of

⁵⁸⁶ Mills and White, “The Identification of Paint Media from their Sterol Composition – A Critical View,” 178; Khandekar, “Preparation of Cross-sections from Easel Paintings,” 58;

fluorochrome stains used in the biomedical fields were shown to be potentially useful for the identification of proteins, carbohydrates, and fatty substances within discrete paint/ground layers, work that was expanded upon over subsequent decades (Figure 5.25).⁵⁸⁷ Three years later, in 1990, a comprehensive study identified one particular stain (a 10% aqueous solution of dimethylformamide at a pH of 5.6) to be the most successful at identifying proteins.⁵⁸⁸ In response to this sudden surge in staining research, Dr. John S. Mills and Dr. Raymond White expressed some of their concerns in *The Organic Chemistry of Museum Objects* (1996), stating that the literature is lacking “in adequate control experiments on known test samples, checking for the effects of mixtures and different pigments.”⁵⁸⁹ However, an article published the same year by Stephan Schäfer (a paintings conservator who trained at both the University of Delaware and the University of Cologne) failed to disprove Mills and White’s criticism; however, Schäfer’s work did present the field with additional fluorochrome stains that could

Richard Wolbers, Susan Buck, and Peggy Olley, “Cross-section Microscopy Analysis and Fluorescent Staining,” in *Conservation of Easel Paintings: Principles and Practice*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 326-35.

⁵⁸⁷ Ibid; Richard Wolbers, *Cleaning Painted Surfaces: Aqueous Methods* (London: Archetype Publications Ltd., 2000), 167-83; — and Gregory Landrey, “The use of direct reactive fluorescent dyes for the characterization of binding media in cross-sectional examinations,” in *American Institute for Conservation Preprints, 15th Annual Meeting, Vancouver, BC, 20-24, May, 1987* (Washington DC: American Institute for Conservation 1987), 168-202.

⁵⁸⁸ Ibid; Wolbers and Landrey, Ibid; V.P. Golikov and V.N.Kireyeva, “Study of Spatial Distribution of Protein Bindings in situ by means of Reactive Dyes,” in *ICOM Committee for Conservation Meeting, Preprints, 9th Triennial Dresden, Dresden, 26-31 August, 1990*, ed. Kirsten Grimstad, vol. I (Los Angeles: ICOM Committee for Conservation 1990), 24-8.

⁵⁸⁹ Mills and White, “The Identification of Paint Media from their Sterol Composition – A Critical View,” 178.

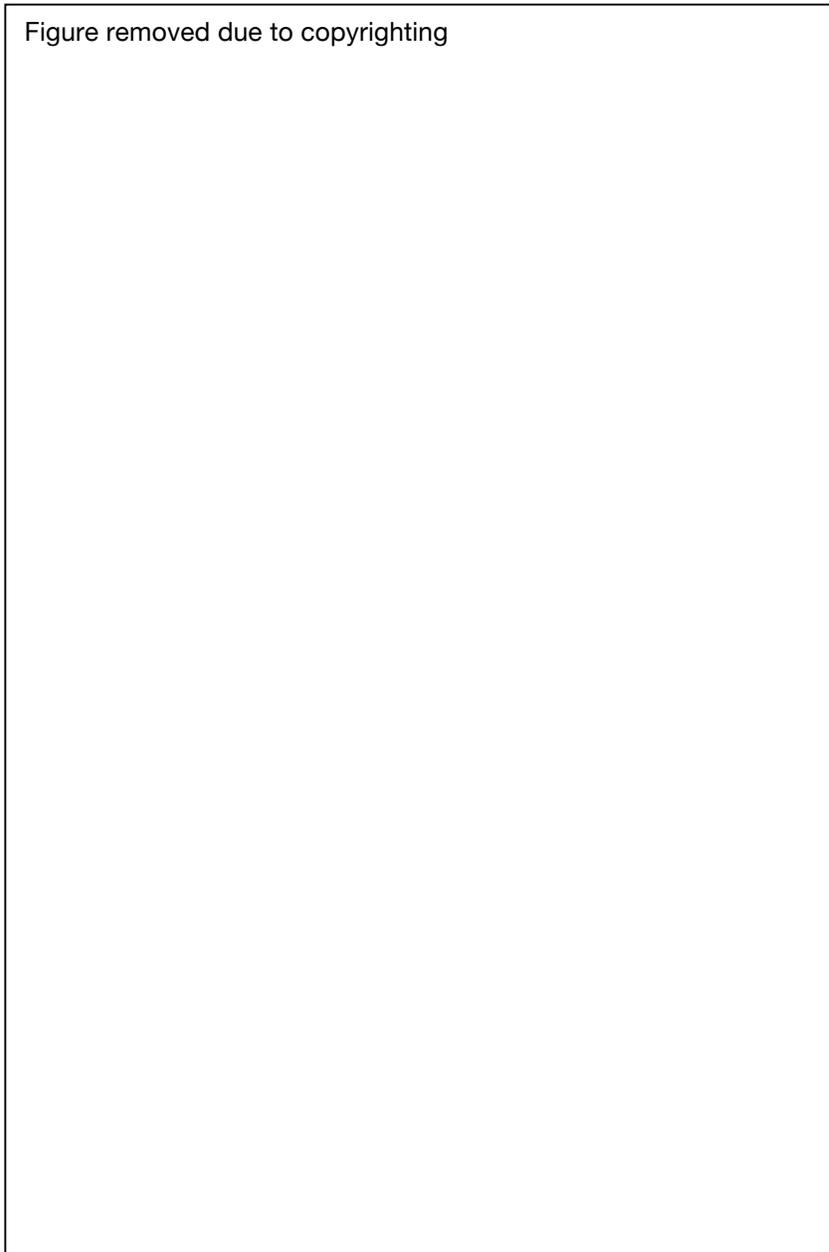


Figure 5.25: Excerpt from Wolbers's 2000 publication listing a number of fluorescent stains that are recommended for identifying organic binding media in cross-sectional samples.⁵⁹⁰

⁵⁹⁰ Wolbers, *Cleaning Painted Surfaces: Aqueous Methods*, 183.

be used for the identification of binding media.⁵⁹¹ Theoretically, fluorochrome stains offer an improvement in both selectivity and sensitivity; early publications featuring the use of fluorescent staining methods presented case studies with promising results, and authors were equally forthcoming regarding potential issues that may lead to misinterpretation. For example, if a stain is rinsed from the surface of a cross-section using incorrect procedures or allowed to remain on the surface for an inappropriate length of time, the results can be compromised. In addition, if a cross-section is handled improperly, oils or proteinaceous materials that come in contact with the surface can produce a false positive result or prevent a stain from reacting with the substrate. Fluorescent stains are also prone to quenching or photo-bleaching: the former occurs when an electron-deficient material forms a complex with the fluorescent dye, while photo-bleaching, or fading, can be attributed to overexposure to oxygen and light. Furthermore, as with traditional stain solutions used in the past, some fluorescent stains are delivered in solvents that may cause certain materials in a cross-section to dissolve. As many of these stains were originally intended for fresh biological samples, they may not always produce consistent results with aged materials and reactions may be further inhibited by the presence of pigments. While twenty-first-century publications continue to present case studies that demonstrate the efficacy of fluorescent stains, there remains a consistent lack of comprehensive and systematic testing on both fresh and aged reference samples (see Chapter 6, section 6.2). Without comparing staining results on known samples it is exceedingly

⁵⁹¹ Steven Schäfer, “Fluorescent staining techniques for the characterization of binding media within paint cross-sections and digital image processing for the quantification of staining results,” in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, eds. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997): 57-64.

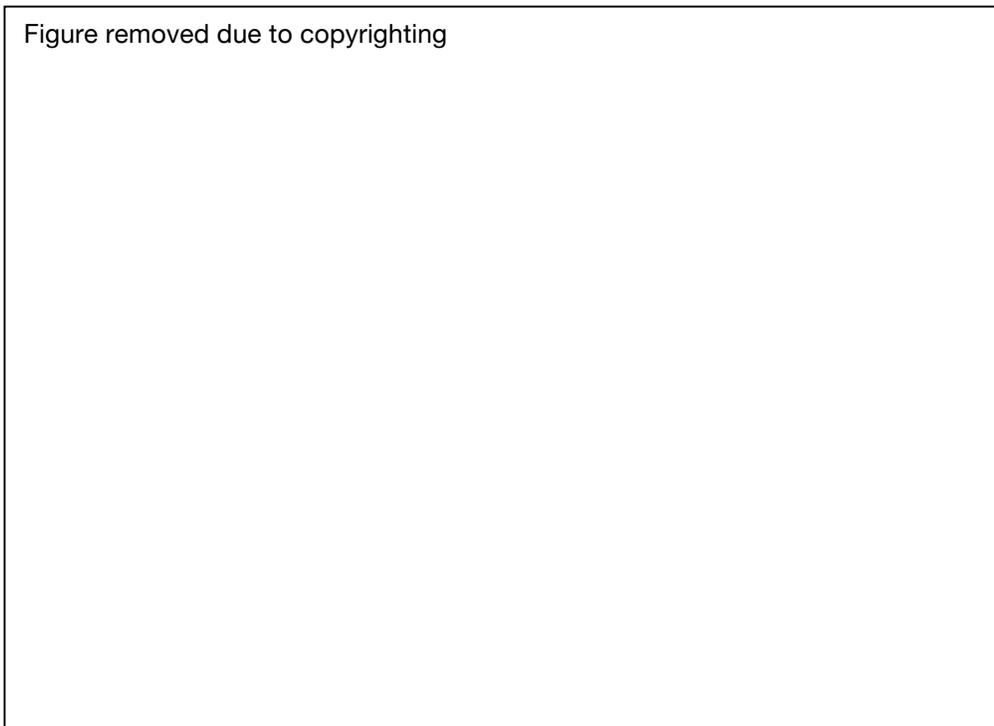


Figure 5.26: A cross-section from a nineteenth-century painting featured in Dietemann et al.'s 2016 publication as seen in visible light (upper left), fluorescent light using a filter set (upper right; BP 450-490 nm, LP 515 nm), fluorescent light after staining with SYPRO Ruby for the detection of proteins (lower left and detail in lower right). Complementary analysis performed using ATR-FTIR imaging generated spectral results that did not always correspond to the staining pattern observed using the SYPRO Ruby fluorescent stain.⁵⁹²

difficult to be aware of potential false positive and false negatives that might be associated with a particular fluorescent or non-fluorescent stains (Figure 5.26).⁵⁹³ Despite this curious

⁵⁹² Patrick Dietemann et al., "Analysis of complex tempera binding media combining chromatographic techniques, fluorescent staining for proteins and FTIR-FPA imaging," Unpublished manuscript, 2016. I am grateful to Dr. Patrick Dietemann for sharing his unpublished research.

⁵⁹³ Abbie Vandivere, e-mail message to author, 26 August, 2015; Melanie Gifford et al., "New Findings on the Painting Medium of the Washington Annunciation," Presentation at the Van Eyck Studies Colloquium, 19-21 September 2012. I am grateful to Dr. Abbie Vandivere for sharing her conference notes with me from the *Van Eyck Studies Colloquium*. Note that

trend in staining research, scientists have continued to use fluorochrome staining techniques in an attempt to differentiate between egg- and oil-based materials present in Old Master paintings.⁵⁹⁴

Improvements in the immunobiology field prompted Packard and Johnson in the early 1970s to consider the possibility of tagging fluorochrome stains to antibodies, compounds that are designed to bond with specific sites found on organic markers (sites referred to as epitopes).⁵⁹⁵ As with their research on cross-sectional stains, Packard and Johnson's initial results on egg-tempera reference paints using these immunological fluorescence microscopy (IFM) showed some promise.⁵⁹⁶ In some instances antibodies can be tailored to bind to

Melanie et al. retracted their initial conclusion cited in a 1993 publication that were based largely on staining results. An ultramarine glaze on the Wahington's Annunciation by Jan van Eyck was thought to be primarily bound in protein (results from the GC-MS were ambiguous and no protein was detected in HPLC) but revisitation of the same blue paint years later confirmed that only oil was present and that the Amido Black stain has simply been absorbed into the porous ultramarine layer.

⁵⁹⁴ Dietemann et al., "Analysis of complex tempera binding media combining chromatographic techniques, fluorescent staining for proteins and FTIR-FPA imaging," *Ibid.*; Steven Schäfer, "Luminescent Metal Chelate Stain and its Application Protocol for the Identification of Proteinaceous Binding Media within Paint Cross Section," in *Coloured Glazes on Metal Leaf from the Baroque and Rococo*, eds. Erwin Emmerling, Michael Kühenthal, and Mark Richter (Munich: Verlag der Anton Siegl Fachbuchhandlung, 2013), 709–13; —, "New developments in fluorescent staining of oil and proteinaceous binding media within paint cross-sections," in *AIC Paintings Specialty Group Postprints, Richmond, Virginia, 16-20 April, 2007* (Washington DC: American Institute for Conservation Paintings Specialty Group, 2007), 7; Mark Richter, Steven Schäfer, and Annelies van Loon, "El Tratado 'Arte de la Pintura' de Francisco Pacheco y su Influencia en la Técnica de Ejecución de las Encarnaciones en la Escultura Alemana del Siglo XVIII: Primeros Resultados Obtenidos de An.lisis Avanzados Realizados en Micromuestras," in *GE-IIC Congress Preprints, Investigación en Conservación-Restauración, Barcelona, 9-11 November 2005* (Barcelona: University of Barcelona, 2005), 225-234.

⁵⁹⁵ Johnson and Packard, "Methods for the identification of binding media in Italian paintings of the fifteenth and sixteenth century," 153-4.

⁵⁹⁶ *Ibid.*

Figure removed due to copyrighting

Figure 5.27: Schematic from Cartechini et al.'s 2010 publication demonstrating the preparatory steps involved with immunofluorescence microscopy (IFM).⁵⁹⁷

epitope sites that are associated with certain materials that fall within the same class, differentiating casein from glue, glue from egg, and so on; fluorochromes are then attached to a secondary antibody and observed using the appropriate excitation wavelength (Figure 5.27).⁵⁹⁸

⁵⁹⁷ Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 867-76; Arlen Heginbotham, Victoria Millay and Michael Quick, "The Use of Immunofluorescence Microscopy and Enzyme-Linked Immunosorbent Assay as Complementary Techniques for Protein Identification in Artists' Materials," *Journal of the American Institute for Conservation* 45 (2006): 89-105, accessed December 29, 201. <http://www.jstor.org/stable/40026490>.

⁵⁹⁸ Ibid.

By the late 1980s, scientists and conservators were using IFM techniques to identify proteinaceous materials in easel paintings and polychrome sculptures.⁵⁹⁹ Leopold Kockaert (another scientist at the Royal Institute for Cultural Heritage in Brussels) and two scientists who specialized in IFM declared the technique to be suitable artworks dating from the twelfth to the seventeenth centuries based on results obtained from fresh and aged reference samples.⁶⁰⁰ On the other hand, a few samples generated false negative results and problems were encountered with porous samples (generating potential false positives), auto-fluorescent pigments/binder (fluorescence that is generated simply by exciting the sample with a certain excitation wavelength), and with fluorochromes that were similar in color to certain pigments.⁶⁰¹

Beginning around 2008, recent efforts spearheaded by the Getty Conservation Institute (GCI) and the University of Perugia have attempted use IFM to address questions relating to possible pigment interference and ageing processes, focusing on the analysis of wall painting samples from Giotto's frescoes in Assisi.⁶⁰² Their results seemed promising; in general IFM did not appear to be hampered by most pigments or artificial ageing and casein was identified

⁵⁹⁹ Richard Wolbers, "Aspects of the cleaning of a pair of portraits attributed to William and Richard Jennys," in ." In *American Institute for Conservation Preprints, 16th Annual Meeting, New Orleans, 1-5 June, 1998* (Washington, DC: American Institute for Conservation, 1988), 245-60; Leopold Kockaert, Phillipe Gausset, and Muriel Dubi-Rucquoy, "Detection of Ovalbumin in Paint Media by Immunofluorescence," *Studies in Conservation* 34 (1989): 183-188, doi: 10.2307/1506285.

⁶⁰⁰ Kockaert et al., "Detection of Ovalbumin in Paint Media by Immunofluorescence," 183-8.

⁶⁰¹ Ibid.

⁶⁰² Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 867-76; Manuela Vagnini et al., "Identification of proteins in painting cross-sections by immunofluorescence microscopy," *Analytical and Bioanalytical Chemistry* 392 (2008): 57-64, doi: 10.1007/s00216-008-2041-9.

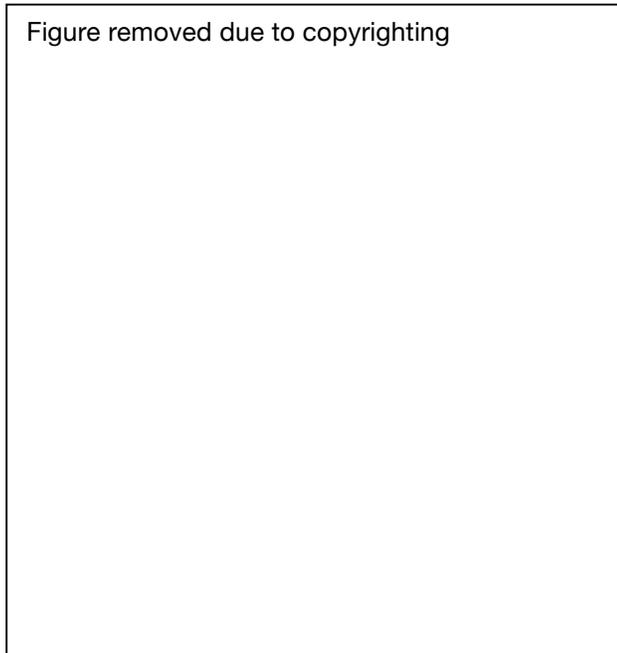


Figure 5.28: A cross-section from frescoes attributed to Giotto featured in Cartechini et al.'s 2010 publication as seen in (a) visible light at 100x (b) in fluorescent light at 488 nm using a band-pass filter 505-550 nm (c) after application of the immunological assay for casein by labeling with FITC fluorophore and (d) the suppression of the background auto-fluorescence using a laser excitation technique (488 nm).⁶⁰³

in *a secco* paint layers present in a cross-sectional sample from the Assisi frescoes (Figure 5.28).⁶⁰⁴ Like Kockaert, however, the group struggled with the auto-fluorescence generated by some of the samples. While Cartechini et al. were able to employ various microscopy techniques to suppress the auto-fluorescence, the final image resulted in a weak overall signal, prompting the group to modify their approach using IFM combined with laser scanning and quantum dots to detect proteins in egg tempera references.⁶⁰⁵ To date, Giotto's fresco cycle

⁶⁰³ Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 872.

⁶⁰⁴ Ibid.

⁶⁰⁵ Ibid., 873-4.

appears to the last Italian artwork to be examined using this technique and further research is still needed to confirm its ability to characterize egg-oil paint systems.

The potential problems with IFM and the autofluorescence of pigments/binders have inspired scientists to explore the applicability of enzyme-linked immunosorbent assay (ELISA) techniques to the identification of proteinaceous binders in paint samples in 2010.⁶⁰⁶ Similar to IFM, ELISA relies on the use of an enzyme-conjugated secondary antibody to generate a spectrophotometric reading; the greater the absorbance of light at a given wavelength, the greater the amount of material in the sample (Figure 5.29). While IFM offers spatial results, direct ELISA techniques have also been compared on samples collected from Italian easel and wall paintings.⁶⁰⁷ The University of Perugia was also able to perform both IFM and ELISA on three samples containing *a secco* paint from Giotto's Assisi frescoes

⁶⁰⁶ Ibid., 867-76; Heginbotham, Millay and Quick, "The Use of Immunofluorescence Microscopy and Enzyme-Linked Immunosorbent Assay as Complementary Techniques for Protein Identification in Artists' Materials," 89-105; Palmieri et al., "Development of an analytical protocol for a fast, sensitive and specific protein recognition in paintings by enzyme-linked immunosorbent assay (ELISA)," 3011-23; Lee et al., "Development and application of an ELISA method for the analysis of protein-based binding media of artworks," 187-96; Fang Ren et al., "Influence of pigments and protein aging on protein identification in historically representative casein-based paints using enzyme-linked immunosorbent assay," *Analytical and Bioanalytical Chemistry* 408 (2016): 203-15, doi: 10.1007/s00216-015-9089-0; Philip Klausmeyer, "An immunological approach to the analysis of art materials: The effect of aging and pigment interaction on antigenic detection of proteinaceous paint binding media using an improved protocol for enzyme-linked immunosorbent assays" (PhD diss., Clark University, 2009).

⁶⁰⁷ Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 867-76; Lee et al., "Development and application of an ELISA method for the analysis of protein-based binding media of artworks," 187-96; Palmieri et al., "Development of an analytical protocol for a fast, sensitive and specific protein recognition in paintings by enzyme-linked immunosorbent assay (ELISA)," 203-15.

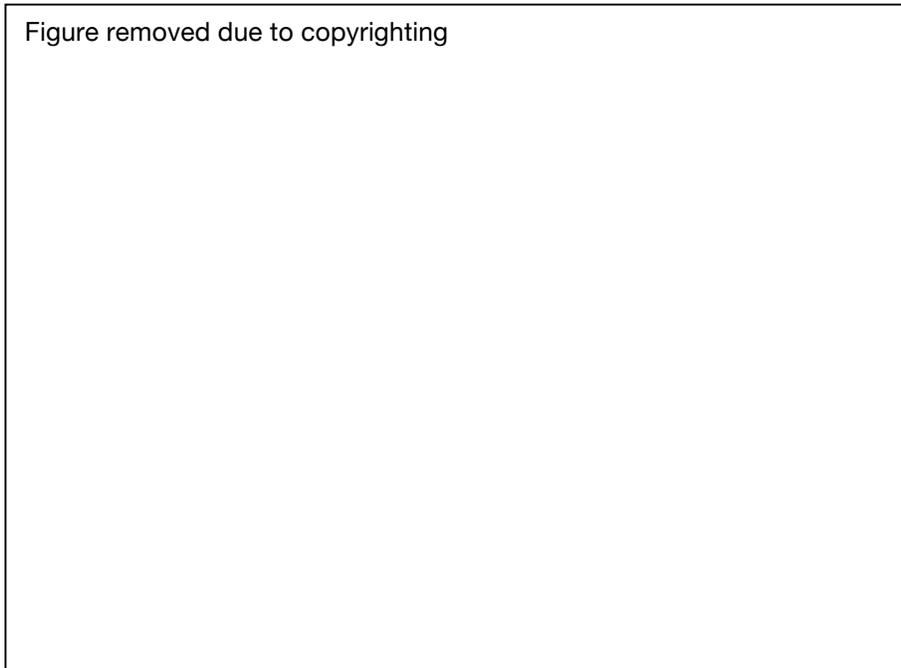


Figure 5.29: Schematic from Cartechini et al.'s 2010 publication demonstrating the preparatory steps involved with enzyme-linked immunosorbent assay (ELISA).⁶⁰⁸

described above, identifying casein in two and egg tempera in a third.⁶⁰⁹ Their findings corresponded to analytical results obtained with IFM techniques as well as GC-MS (despite the curious assignment of fatty acids including oleic to the casein), although GC-MS analysis of Giotto's frescoes in the Chapel of the Magdalena in the National Museum of the Bargello (*Paradise*, c. 1335) identified egg tempera alone as the primary binder in the *a secco* paints.⁶¹⁰ In 2015, a collaborative project between scientists from the Metropolitan Museum

⁶⁰⁸ Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 869.

⁶⁰⁹ Palmieri et al., "Development of an analytical protocol for a fast, sensitive and specific protein recognition in paintings by enzyme-linked immunosorbent assay (ELISA)," 203-15.

⁶¹⁰ Palmieri et al., "Development of an analytical protocol for a fast, sensitive and specific protein recognition in paintings by enzyme-linked immunosorbent assay (ELISA)," 3021; Gwenaëlle Gautier, "A reliable analytical procedure for the characterization and identification

of Art and a number of other institutions involved the application of ELISA techniques to samples collected from a double-sided banner attributed to Spinello Aretino (*Saint Mary Magdalene Holding a Crucifix, The Flagellation*, c. 1395-1400; Figure 5.30).⁶¹¹ While oil and protein were identified in the lowest paint layer(s) using ATR-FTIR (see section 5.2.2 for more information on ATR-FTIR), the upper paint layers the upper paint layers were more difficult to characterize.⁶¹² GC-MS (see section 5.2.3 for information on chromatography-mass spectrometry techniques) also yielded somewhat confusing results, pointing towards the presence of egg and possibly collagen.⁶¹³ Using ELISA, the authors identified the presence of egg, glue, and gum, attributing the presence of glue to the gesso ground, the egg as the primary binder, and gum as a possible contamination from restoration materials (e.g. aqueous-based retouching paints). While this case study shows excellent promise for the applicability of ELISA to the analysis of materials present in Quattrocento paintings, this technique is still not able to provide spatial results to help locate where these organic binders are present in multi-layered cross-sections. Furthermore, additional studies have demonstrated the potential issues caused by ageing processes as well as the presence of certain pigments, with egg

of proteinaceous binding media in wall paintings” (PhD diss., University of Pisa, 2009), 165-9. In one sample, GC-MS showed a low amount of di-carboxylic acids compared to the amount of mono-carboxylic acids present; these were assigned to fatty acids present in the casein binder however the presence of oleic acid in the chromatogram is a strong indication that the sample contained a certain amount of drying oil that had not completely undergone the polymerization/oxidation process and was therefore likely applied in more recent times. See section 5.2.3 for more information relating to analysis of paint samples using GC-MS.

⁶¹¹ Lee et al., “Development and application of an ELISA method for the analysis of protein-based binding media of artworks,” 192-3.

⁶¹² Ibid.

⁶¹³ Ibid.

tempera paints in particular often generating fairly low to poor protein signals using ELISA.⁶¹⁴



Figure 5.30: Spinello Aretino's *Saint Mary Magdalene Holding a Crucifix, The Flagellation* (c. 1395-1400, The Metropolitan Museum, New York).⁶¹⁵

⁶¹⁴ Ibid., 193-5; Ren et al., "Influence of pigments and protein aging on protein identification in historically representative casein-based paints using enzyme-linked immunosorbent assay," 203-15; Cartechini et al., "Immunodetection of Proteins in Ancient Paint Media," 868-71; Klausmeyer, "An immunological approach to the analysis of art materials: The effect of aging and pigment interaction on antigenic detection of proteinaceous paint binding media using an improved protocol for enzyme-linked immunosorbent assays" (PhD diss., Clark University, 2009).

5.2.2 Spectroscopic Techniques

By the late 1980s, various spectroscopic techniques were being used to characterize the presence of organic binders in works of art. Scientists Antonietta Gallone (Politecnico di Milan) and Giovanni Bottiroli (CNR, University of Pavia) were among the first to use UV-vis spectrophotometry to identify certain pigments as well as binders on a number of frescoes and easel paintings by fourteenth and fifteenth-century Italian artists.⁶¹⁶ Spectroscopic techniques

⁶¹⁵ Lee et al., “Development and application of an ELISA method for the analysis of protein-based binding media of artworks,” 192.

⁶¹⁶ Giovanni Bottiroli, Antonietta Gallone, and Elena Bernacchi, “Microfluorometric techniques as applied to the analysis of binding media and varnishes in color samples taken from paintings,” in *Scientific methodologies applied to works of art. Proceedings of the symposium, Florence, Italy 2-5 May 1984*, ed. Paolo L. Parrini (Milan: Montedison Progetto Cultura, 1986), 168-71; Ingrid C. Alexander and Antonietta Gallone Galassi, “A study of Piero della Francesca's ‘Sacra Conversazione’ and its relationship to Flemish painting techniques,” in *ICOM Committee for Conservation 8th Triennial Meeting: Sydney, Australia, 6-11 September 1987, Preprints*, ed. Kirsten Grimstad, vol. 1 (Los Angeles: Getty Conservation Institute, 1987), 9-12; Giovanni Bottiroli and Antonietta Gallone, “Studio stratigrafico della pellicola pittorica: pigmenti e leganti,” in *Ricerche sull’affresco absidale della Chiesa di Sant’Agat al Monte di Pavia* (Milan: Accademia di Scienze e Lettere, 1996), 207-21; —, “Application of Microspectrofluorometric Techniques to the Study of Binding Media in Samples from Paintings: the Case of Leonardo’s ‘Last Supper,’” in *Proceedings of 5th International Conference of Non-destructive testing, microanalytical methods and environmental evolution for study and conservation of works of art, Budapest, 24-28 September, 1996*, 159-71; --, “La tecnica di microspettrofluorimetria applicata all’analisi dei leganti: La Pala di San Berndardino di Piero della Francesca,” in *La Pala di San Berndardino di Piero della Francesca*, eds. Emanuela Daffra and Filippo Trevisani (Firenze: Quaderni di Brera, 1997), 91-5; Antonietta Gallone, “Masaccio and Masolino Scientific Report –2001/2,” Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art; Cinzia Maria Mancuso and Antonietta Gallone, “Giovanni Bellini and His Workshop: A Technical Study of Materials,” in *Giovanni Bellini and the Art of Devotion*, ed. Rhonda Kasl (Indianapolis: Indianapolis Museum of Art, 2004), 129-52; Giovanni Bottiroli, Antonietta Gallone, and Barbara Masala, “Microspectrofluorometric analysis of organic binders,” in *Bolletino d’Art - The Scrovegni Chapel: Materials used in the painting technique – Study and Research by the ICR*, ed. Giuseppe Basile (Rome: Istituto poligrafico e zecca dello stato, 2005), 83-104.

used in the UV-vis region rely on the unique fluorescent (or photo-luminescent) properties associated with certain materials when temporarily excited with a ultraviolet light source.⁶¹⁷ Although the technique can be applied in situ (i.e. non-destructively to the surface of artworks using a hand-held instrument), Bottiroli and Gallone have used UV-vis spectroscopy to characterize discrete layers present in multi-layered cross-sections (a technique also referred to as microspectrofluorimetry).⁶¹⁸ Using this approach the authors have identified egg as the primary binder in *a secco* paints (with oil used for certain highlights) in samples collected from Giotto's frescoes housed within the Scrovegni chapel in Padua.⁶¹⁹ Egg was also discovered in cross-sectional samples from Leonardo da Vinci's *Last Supper* including in the ground, priming, and paint layers (Figure 5.31).⁶²⁰ The authors present a clear outline

⁶¹⁷ Ibid.; Domenech-Carbo, "Novel analytical methods for characterising binding media and protective coatings in artworks," 114-5; Londa J. Larson, Kyeong-Sook Kim Shin, and Jeffery I. Zink, "Photoluminescence Spectroscopy of Natural Resins and Organic Binding Media of Paintings," *Journal of the American Institute for Conservation* 30 (1991): 89-104, accessed February 20, 2016. <http://www.jstor.org/stable/3179519>.

⁶¹⁸ Bottiroli and Gallone, "Studio stratigrafico della pellicola pittorica: pigmenti e leganti" 207-21; —, "Application of Microspectrofluorometric Techniques to the Study of Binding Media in Samples from Paintings: the Case of Leonardo's 'Last Supper,'" 159-71; —, "La tecnica di microspettrofluorimetria applicata all'analisi dei leganti: La Pala di San Berndardino di Piero della Francesca," 91-5 Gallone, "Masaccio and Masolino Scientific Report –2001/2," Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art; Mancuso and Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," 129-52; Bottiroli, Gallone, and Masala, "Microspectrofluorometric analysis of organic binders," 83-104.

⁶¹⁹ Bottiroli, Gallone, and Masala, "Microspectrofluorometric analysis of organic binders," 83-104. In some samples the authors found egg and oil but concluded that the traces of oil were likely from overlying oil-based paints applied as highlights.

⁶²⁰ Bottiroli and Gallone, "Application of Microspectrofluorometric Techniques to the Study of Binding Media in Samples from Paintings: the Case of Leonardo's 'Last Supper,'" 159-71. The ground was found to contain quartz, calcium carbonate, and magnesium carbonate bound in egg (although parts of the ground were impregnated with oil and glue). The priming (approx. 10-15 microns) was found to contain lead white (probably bound in egg/glue and oil)

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Figure 5.31: Schematic from Bittiroli and Gallone's 1996 publication illustrating the authors' interpretation of the organic binder distribution (using UV-vis spectroscopy) in a paint cross-section collected from Leonardo da Vinci's *The Last Supper*. The problematic restoration history and condition of the work complicated the results as the authors found oil (olio), glue (colla), and egg (uovo) in several samples.⁶²¹

but in many instances the priming was contaminated with a brown-colored restoration material. The characterization of the paint binder was more difficult; however the authors state that the binder is protein-based and is likely egg tempera. It should be noted that in 2006 Mauro Matteini reported the presence of *tempera grassa* in underlying paint layers in a cross-sectional sample collected from *The Last Supper*, although his findings were based on cross-sectional staining with Amido Black and solvent tests. See Mauro Matteini, "Metodologie analitiche applicate alla caratterizzazione, stato di conservazione e restauro di pitture murali" in *Far East Asian mural paintings: Diagnosis, conservation and restoration*, ed. Rocco Mazzeo (Ravenna: Longo Editore, 2006), 41.

⁶²¹ Bittiroli and Gallone, "Application of Microspectrofluorometric Techniques to the Study of Binding Media in Samples from Paintings: The Case of Leonardo's 'Last Supper,'" 170.

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Figure 5.32: Figure from Mancuso and Gallone's 2004 publication showing the luminescence reference spectra (from left to right) for glue, egg yolk, drying oil, and resin. Note that complex mixtures and/or the presence of restoration materials can cause shifts in the position of these spectral curves, leading to possible misinterpretation of the actual binder(s) present.⁶²²

describing their criteria for characterizing binding media: proteinaceous materials give rise to luminescence spectra with dominant peaks at 457-60 nm, oils fall closer to 486 nm, and mixtures of egg and oil occur between 470-74 nm (Figure 5.32).⁶²³ Certain pigments, however, were found early on to influence the shape of luminescence spectra; Bittoroli and

⁶²² Mancuso and Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," 137.

⁶²³ Ibid., Bottiroli and Gallone, "La tecnica di microspettrofluorimetria applicata all'analisi dei leganti: La Pala di San Berndardino di Piero della Francesca," 91-5.

Gallone tested some of these effects beginning in the 1980s, but their reference paints consisted of only one pigment, making it difficult to draw comparisons to complex mixtures typically encountered in artworks (Figure 5.33).⁶²⁴ Subsequent studies have since pointed out additional factors that can influence the shape of luminescence spectra including “the wavelength of the excitation, temperature, ageing, sample source, and the presence of pigments or other interfering substances.”⁶²⁵ Furthermore, caution must be exercised when dealing with artworks that have suffered from extensive and complicated restoration campaigns, exemplified by histories associated with both Leonardo’s *Last Supper* and Giotto’s Scrovegni frescoes. Regarding the latter, Leonetto Tintori’s (an expert in wall painting conservation) 1963 examination of the fresco cycle revealed that egg or casein was likely used to globally consolidate the *a secco* paint layers during a nineteenth-century restoration.⁶²⁶ Although Tintori surmised that Giotto probably used egg tempera in his later additions, the presence of proteinaceous consolidant makes it difficult to characterize the original binding media using UV-vis spectrophotometry or any other analytical technique.⁶²⁷

⁶²⁴ Bottiroli, Gallone, and Masala, “Microspectrofluorometric analysis of organic binders,” 91-2; Bottiroli, Gallone, and Bernacchi, “Microfluorometric techniques as applied to the analysis of binding media and varnishes in color samples taken from paintings,” 168-71.

⁶²⁵ Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 114. See also Londa J. Larson, Kyeong-Sook Kim Shin, and Jeffery I. Zink, “Photoluminescence Spectroscopy of Natural Resins and Organic Binding Media of Paintings,” *Journal of the American Institute for Conservation* 30 (1991): 89-104 and Austin Nevin, Daniela Comelli, Gianluca Valentini, Demetrios Anglos, Aviva Burnstock, Sharon Cather, and Rinaldo Cubeddu, “Time-resolved fluorescence spectroscopy and imaging of proteinaceous binders used in paintings,” *Analytical Bioanalytical Chemistry* 388 (2007): 1897-1905 and Austin Nevin, Demetrios Anglos, Sharon Cather, and Aviva Burnstock, “The influence of visible light and inorganic pigments on fluorescence excitation emission spectra of egg-, casein-, and collagen-based painting media,” *Applied Physics A* 92 (2008): 69-76.

⁶²⁶ Leonetto Tintori, “The State of Conservation of the Frescoes and the Principal Technical Restoration Problems,” *Studies in Conservation* 8 (1963): 37-41, doi: 10.2307/1505277.

⁶²⁷ *Ibid.*, 37.

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Figure 5.33: Figure taken from Bittoroli et al.'s 2005 publication showing the luminescence reference spectra (from left to right) of azurite, azurite mixed with egg, and egg. The spectra clearly show that pigments can affect the shape and position of the spectral curves, complicating the identification of organic binders that may be present.⁶²⁸

additions, the presence of proteinaceous consolidant makes it difficult to characterize the original binding media using UV-vis spectrophotometry or any other analytical technique.⁶²⁹

⁶²⁸ Bottiroli, Gallone, and Masala, "Microspectrofluorometric analysis of organic binders," 93.

⁶²⁹ *Ibid.*, 37.

A similar case can be made for Leonardo's *Last Supper*; a review of consolidants that were frequently applied to frescoes reveals a wide range of materials including egg, glue, casein, calcium caseinate, shellac, oil, waxes, and acrylic resins.⁶³⁰

Compared to samples collected from frescoes, the UV-vis analysis of cross-sections from easel paintings may present scientists with fewer challenges particularly if the artwork is in good condition and the restoration history has been documented. Gallone's analysis of panel paintings by Piero della Francesca, Giovanni Bellini, Masaccio, and Masolino have generated some interesting results.⁶³¹ UV-vis spectrophotometry of samples collected from the Philadelphia Museum of Art's panels by Masolino (see Chapter 4, section 4.2.1) identified the presence of oil, results that were later corroborated with GC-MS and FTIR analysis (see Table 1 in Chapter 4 and Figure 5.34); however, one sample collected from St Paul's red cloak was found to contain a layer bound in animal glue that contained vermilion.⁶³² While

⁶³⁰ Ibid.; Alberto Felici, Serena Pini, and Andrea Vigna, "Il Chiostro Verde nel complesso di Santa Maria Novella a Firenze: storia e restauro," *OPD restauro: rivista dell'Opificio delle pietre dure e laboratorio di restauro di Firenze* 19 (2007): 13-48; Umberto Baldini et al., "Una storia complicata: gli affreschi del Camposanto Monumentale di Pisa," in *Sulle pitture murali: riflessioni, conoscenze, interventi: atti del convegno di studi, Bressanone 12-15 July, 2005 – Scienza e beni culturali*, 21, eds. Buido Biscontin and Guido Driussi (Marghera-Venezia: Arcadia ricerche, 2005), 12-27; Alexandru Ghillis, "Evaluarea unor sisteme adezive utilizate la consolidarea structurii picturilor degradate. Cinetica de consolidare (II)," *Revista muzeelor si monumentelor - Muzeu* 22 (1985): 36-46.

⁶³¹ Alexander and Galassi, "A study of Piero della Francesca's 'Sacra Conversazione' and its relationship to Flemish painting techniques," 9-12; Bittroli and Gallone, "La tecnica di microspettrofluorimetria applicata all'analisi dei leganti: La Pala di San Berdardino di Piero della Francesca," in *La Pala di San Berdardino di Piero della Francesca*, eds. Emanuela Daffra and Filippo Trevisani (Firenze: Quaderni di Brera, 1997), 91-5; Gallone, "Masaccio and Masolino Scientific Report –2001/2," Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art; Mancuso and Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials", 129-52.

⁶³² Gallone, "Masaccio and Masolino Scientific Report –2001/2," Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art. Note that no

the latter scenario is certainly possible, it was not common practice to apply warm distemper paint atop multiple layers of egg; a possible explanation is that the luminescence peak maximum was slightly shifted due to the presence of degradation components, pigments, and/or an additive to the paint.

Gallone's work in 2001 combined with the analytical results generated by the National Gallery London and the Philadelphia Museum of Art (in 1993 and 2002, respectively), helped scholars to determine that Masaccio likely completed the faces of Saints Paul and Peter (following Masaccio's untimely death in 1427) using oil as opposed to tempera. In addition, UV-vis spectrophotometry of the cross-sectional samples revealed an additional characteristic of the panel that neither FTIR or GC-MS was able to identify. In passages that were painted with tempera, Gallone indicates that both egg and oil were found in the layer directly above the ground corresponding to the underdrawing; it is possible that an oil-rich layer was applied before or after the underdrawing was executed, to reduce the absorbency of the gesso panel and/or seal in the underdrawing.⁶³³ Such a finding suggests that *both* Masaccio and Masolino employed drying oils into their painting practice, although Masaccio appears to have used it during the preparation of the panel as opposed to incorporating it into his pictorial layers. While this analytical finding was not reported in the 2002 publication *The Panel Paintings of Masaccio and Masolino: The Role of Technique*, it is a notion worth considering particularly as imaging techniques are being further developed to identify organic markers in paint cross-

amino acid analysis was performed during the 1993 and 2002 GC-MS analysis; the presence of egg tempera and/or oil was based solely on fatty acid ratios obtained by the different laboratories. For issues relating to the characterization of egg/oil paint systems using FTIR read the following paragraphs in this section; for challenges associated with GC-MS analysis see section 5.2.3.

⁶³³ Ibid.

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Figure 5.34: Schematic of *Saints Paul and Peter* (Masaccio and Masolino, c. 1427-8) at the Philadelphia Museum of Art summarizing the analytical results performed between 1993 and 2002 using GC-MS, FTIR, and UV-vis spectrophotometry. Potential reasons for the discrepancies noted between the 1993 and 2002 GC-MS results are addressed in section 5.2.3.⁶³⁴

⁶³⁴ Gallone, “Masaccio and Masolino Scientific Report –2001/2,” Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art; Kenneth Sutherland, “Masaccio and Masolino Scientific Report – 11 December, 2002” (Conservation file housed in the Paintings Conservation Department at the Philadelphia Museum of Art).

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Figure 5.35 (left) and 5.36 (right): Piero della Francesca's *Sacra Conversazione* (1472-4, Pinacoteca di Brera, Milan; left) and Giovanni Bellini and workshop's *Madonna and Child with St. John the Baptist* (c. 1490-1500, Indianapolis Museum of Art; right).

sections.⁶³⁵ As in the case of the Masolino-Masaccio panel, UV-vis spectrophotometry has identified similar “sealing” layers in cross-sections collected from other Quattrocento paintings. In Piero della Francesca's *Sacra Conversazione* (1472-74; Figure 5.35), Gallone and Bittoroli identified oil applied atop the ground while natural resin was found atop the ground in a painting attributed to Giovanni Bellini's workshop dated to 1490-1500 (Figure

⁶³⁵ See section 5.4 for more information relating to Masaccio and Masolino's technique.

5.36).⁶³⁶ It remains to be confirmed whether egg tempera paints (identified in samples from both paintings) would successfully adhere to a ground that has been coated with oil and/or resin to reduce the absorbency. If such layers were to be applied thinly it may not affect the handling of the tempera; however, thickly applied oil or resin would cause the initial applications of egg tempera to crawl and may eventually lead to poor adhesion. In order to determine whether sealing grounds with drying oils was commonly practiced by Quattrocento painters, it may be worth revisiting cross-sections from the aforementioned case studies using more sophisticated techniques such as ATR-FTIR (described in the following section).

Egg-oil paint systems have also been characterized using UV-vis spectrophotometry in Piero della Francesca and Giovanni Bellini's works.⁶³⁷ In Francesca's *Sacra Conversazione*, egg mixed with ultramarine was found in the Virgin's mantle while oil was determined to be the primary binder in the architectural paint; however, mixtures of binding media were identified in flesh tones (egg and oil) and St. John the Baptist's azurite robe (oil and resin).⁶³⁸ The latter raises additional questions as the authors conclude that the granular nature of

⁶³⁶ Alexander and Galassi, "A study of Piero della Francesca's 'Sacra Conversazione' and its relationship to Flemish painting techniques," 9-12; Bottiroli and Gallone, "La tecnica di microspettrofluorimetria applicata all'analisi dei leganti: La Pala di San Berndardino di Piero della Francesca," 91-5; Mancuso and Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," 129-52. Note that in 1987 Ingrid Alexander and Antonietta Gallone Galassi determined that glue was used to seal the gesso ground in Piero della Francesca's *Sacra Conversazione*. Ten years later, Bittiroli and Gallone instead claim that UV-vis detected an oil-rich layer. It is unclear from the literature why this assignment was changed.

⁶³⁷ Ibid.

⁶³⁸ Alexander and Galassi, "A study of Piero della Francesca's 'Sacra Conversazione' and its relationship to Flemish painting techniques," 9-12; Bottiroli and Gallone, "La tecnica di microspettrofluorimetria applicata all'analisi dei leganti: La Pala di San Berndardino di Piero della Francesca," 91-5.

azurite requires a “greater quantity of binding medium” as opposed to ultramarine, attributing the overabundance of darkened medium in St. John’s robe to Piero’s unfamiliarity with the oil technique.⁶³⁹ Practical experience with both ultramarine and azurite reveals that both pigments possess a granular quality and can be difficult to apply in even layers during the initial painting stages. On the other hand, azurite particles tend to be larger in size, creating paint films that are textural and replete with micro-fissures. It is equally likely that the brown, resinous medium present in the azurite robe represents embedded residues from previously applied oil-resin coatings, an observation that is frequently encountered in azurite-rich paint layers found on Old Master paintings.

The interpretation of egg-oil paint systems found in a group of paintings associated with Giovanni Bellini’s workshop should also be re-evaluated. UV-vis spectrophotometry was performed on several cross-sectional samples, revealing layers containing oil, egg, and/or *tempera grassa*.⁶⁴⁰ Mancuso and Gallone do acknowledge the problematic condition of some of these works; however, it is difficult to comprehend how they are able to differentiate between oil residues from overpaint not to mention whether small amounts of glue-based consolidants introduced to an oil paint layer would create luminescence spectra that simulate the presence of *tempera grassa*. Furthermore, the authors occasionally identify egg tempera “glazes” applied over oil-rich layers, again a technique that is not practical in terms of paint application (see Figure 5.37). Scientists typically do not have a first-hand knowledge of traditional art materials and their handling properties, a knowledge that can only be obtained by creating reconstructions of Old Master paintings using historically accurate materials (see

⁶³⁹ Alexander and Galassi, “A study of Piero della Francesca's ‘Sacra Conversazione’ and its relationship to Flemish painting techniques,” 11.

⁶⁴⁰ Mancuso and Gallone, , “Giovanni Bellini and His Workshop: A Technical Study of Materials,” 129-52.

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Figure 5.37: Luminescence spectra featured in Mancuso and Gallone's 2004 publication representing the various binders identified in a cross-section sample collected from the Virgin's red shirt in Giovanni Bellini and workshop's *Madonna and Child with St. John the Baptist* (c. 1490-1500, Indianapolis Museum of Art).⁶⁴¹

Figure 1.1 and 1.2). The suggestion that egg glazes were applied atop oil-rich layers, combined with the potential interference from pigments and degradation products, raises additional concerns regarding UV-vis spectrophotometry and its ability to concretely identify the presence of organic binders in multi-layered samples. While the technique has shed light on the complexities associated with Quattrocento paintings, UV-vis spectrophotometry is

⁶⁴¹ Ibid., 138.

perhaps best used in conjunction with more sophisticated analytical methods when attempting to characterize egg-oil paint systems.

Although UV-vis continues to be used to aid in the identification of organic pigments, it has been largely replaced in cultural heritage science with another spectroscopic technique. Fourier-Transform Infrared Spectroscopy (FTIR), has quickly become one of the most widely adopted methods used to characterize organic binding media in easel paintings.⁶⁴² Light from the mid-infrared (or near, as in the case of Raman spectroscopy) region is used to momentarily excite molecules within a paint sample; the stretching, bending, and vibrational energies associated with particular chemical bonds absorb infrared radiation to varying degrees, subsequently giving rise to characteristic FTIR spectra that can help with the identification of specific organic and inorganic materials (Figure 5.38).⁶⁴³ Robert L. Feller, a scientist at Carnegie Mellon University, first applied the technique to the analysis of art materials in 1954 (focusing on the characterization of natural resins) and his work was soon followed by other spectroscopic studies including articles published by scientists Manfred J. D. Low and Norbert S. Baer at New York University in the 1970s.⁶⁴⁴ During their testing,

⁶⁴² Jennifer Pilc and Raymond White, “The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings,” *National Gallery Technical Bulletin* 16 (1996): 73-84; Mills and White, *The Organic Chemistry of Museum Objects*, 2-20; Michele R. Derrick, Dusan Stulik, and James M. Landry, *Infrared Spectroscopy in Conservation Science* (Los Angeles: J. Paul Getty Trust, 1999), vii-x; Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 115-17.

⁶⁴³ Pilc and White, “The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings,” 73-76; Mills and White, *The Organic Chemistry of Museum Objects*, 2-20; Derrick, Stulik, and Landry, *Infrared Spectroscopy in Conservation Science*, 4-15; Mills and White, *The Organic Chemistry of Museum Objects*, 2-20.

⁶⁴⁴ Robert L. Feller, “Dammar and Mastic Infrared Analysis,” *Science* 120 (1954): 1069-70, accessed December 9, 2015. <http://www.jstor.org/stable/1681691>; Manfred J. D. Low and Norbert S. Baer, “Application of Infra-Red Fourier Transform Spectroscopy to problems in conservation. I. General Principles,” *Studies in Conservation* 22 (1977) 116–128, doi:

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Figure 5.38: Schematic from Derrick et al.'s 1999 publication demonstrating the spectral range represented by the infrared region and an example of an FTIR spectrum (top).⁶⁴⁵

10.2307/1505894.; —, “Dammar and Mastic Infrared Analysis,” in *Proceedings of ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1-8 October 1978* (Rotterdam: Bouwcentrum for the International Council of Museums, 1978), 78/16/5; —, “Advances in the infrared spectroscopic examination of pigments,” in *Proceedings of ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1-8 October 1978* (Paris: International Council of Museums, 1978), 78/20/3/1–5. See also James S. Olin, “The use of Infrared Spectrophotometry in the examination of Paintings and Ancient Artifacts,” *Instrument News* 17 (1966): 1 and Liliane Masschelein-Kleiner, Jos Heylen, and Frieda Tricot-Marckx, “Contribution à l’analyse des liants, adhesifs et vernis anciens,” *Studies in Conservation* 13 (1968) 105–121.

⁶⁴⁵ Derrick, Stulik, and Landrey, *Infrared Spectroscopy in Conservation Science, Infrared Spectroscopy in Conservation Science*, 5.

Low and Baer concluded that the direct comparison of fresh/aged reference samples to actual works of art proved challenging and noted that “many and perhaps most of the spectra of the normally complex mixtures used in the fine arts which have been recorded previously are inadequate and usable only for uncomplicated work.”⁶⁴⁶ As instrumental developments eventually led to improvements in sensitivity and resolution, it became evident that transmitted FTIR was not always able to successfully differentiate between original materials used by an artist or restoration. Analysis of Leonardo da Vinci’s *Last Supper* using FTIR in 1988 confirmed the presence of waxes, shellac, and gum Arabic, most of which were concluded by the authors to be associated with previous restoration campaigns rather than the original binding media.⁶⁴⁷ Two years later, in 1990, additional attempts were made to develop a more systematic approach to the study of Italian Renaissance using FTIR; a group of scientists based at MIT, Meilunas et al. published a number of detailed comparative spectra of fresh and aged (pigmented and un-pigmented) films of egg yolk, linseed oil, and mixtures of the two (egg-oil emulsions).⁶⁴⁸ While the authors concluded that their spectral results could be reliably used to identify original binding media, they also noted the following:

⁶⁴⁶ Low and Baer, “Dammar and Mastic Infrared Analysis,” 78/16/5; Francesca Casadio and Lucia Toniolo, “The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations,” *Journal of Cultural Heritage* 2 (2001): 71-8, [doi:10.1016/S1296-2074\(01\)01107-4](https://doi.org/10.1016/S1296-2074(01)01107-4).

⁶⁴⁷ Ibid; Pile and White, “The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Paintings,” 73; Elisabetta Galbiati and Giuseppe Zerbi, “Techniques of vibrational spectroscopy for the analysis of material in the work of art: the case of the last supper by Leonardo da Vinci” in *Proceedings of ICR, 2nd International Conference on non-destructive testing, microanalytical methods and environment evaluation for study and conservation of works of art, Perugia, 17-20 April 1988* (Rome: Istituto Centrale Per Il Restauro and Associazione Italiana Prove Non Distruttive, 1988), 6.1-17.

⁶⁴⁸ Raymond J. Meilunas, James G. Bentsen, and Arthur Steinberg, “Analysis of Aged Paint Binders by FTIR Spectroscopy,” *Studies in Conservation* 35 (1990): 33-51, doi:

[The] difficult problem of detecting egg in the presence of drying oil is complicated by the fact that triglyceride units composed of unsaturated fatty esters are common to both egg yolk and linseed oil.⁶⁴⁹

This observation unsurprisingly corroborates the early GC results published by Mills and White.⁶⁵⁰ During the late 1980s, cultural institutions were still amassing FTIR spectra associated with pigments, which may explain why Meilunas et al. placed considerable weight on the absence/presence of certain peaks for the characterization of binding media (Figure 5.39).⁶⁵¹ In light of more recent studies, scientists in 2016 would likely exercise greater caution, considering all potential peaks (or lack thereof) that may instead be attributed to pigment interference or influenced by materials from adjoining layers (e.g. animal glue from remnants of the ground, oil-containing varnish coatings, etc.). FTIR analyses of thin coatings or samples with simple stratigraphy often generate fairly straightforward spectra; however, interpretation of complex multi-layered paint samples can be challenging and heavily dependent on sample preparation. Currently there are generally three approaches to the preparation of samples for FTIR analysis:

10.2307/1506280; Casadio and Toniolo, “The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations,” 71-8; , doi: 10.2307/1506280.

⁶⁴⁹ Meilunas, Bentsen, and Steinberg, “Analysis of Aged Paint Binders by FTIR Spectroscopy,” 41.

⁶⁵⁰ Ibid.; Mills and White, “Analyses of Paint Media,” *National Gallery Technical Bulletin* 2 (1978): 72-3; —, “Analyses of Paint Media,” *National Gallery Technical Bulletin* 1 (1977): 57; Mills, “The Identification of Paint Media – An Introduction,” 69-71.

⁶⁵¹ Meilunas, Bentsen, and Steinberg, “Analysis of Aged Paint Binders by FTIR Spectroscopy,” 36-43. The authors place considerable weight on peaks (such as the N-H stretching peak at 3289 cm⁻¹ and the Amide II overtone at 3080 cm⁻¹) that are known to be potentially hampered/effected by the presence of certain pigments, degradation components, and sample preparation.

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Figure 5.39: FTIR spectra featured in Meilunas et al.'s 1990 publication demonstrating spectral differences observed between fresh egg yolk (top), aged egg yolk (middle), and aged egg yolk mixed with lead white (bottom).⁶⁵²

⁶⁵² Meilunas, Bentsen, and Steinberg, "Analysis of Aged Paint Binders by FTIR Spectroscopy," 40.

- 1) FTIR in transmitted mode (when infrared light is passed through the sample) requires that a sample be either dissolved in solution and placed between two transparent cells or crushed and thinly dispersed over a cell's surface.
- 2) FTIR in transmitted mode can also be applied to carefully prepared thin-sections cut from the surface of an embedded paint cross-section
- 3) FTIR in reflectance mode (when infrared is bounced off the surface of a sample) can be used on larger samples and intact paint cross-sections as long as the surface is fairly planar.⁶⁵³

Since Meilunas et al. prepared their samples using the first method, all stratigraphic information was likely lost, thus making it difficult to know whether oil restoration coatings and/or traces from the protein-containing glue ground may have been unintentionally incorporated into the samples and consequently affecting the FTIR spectra.⁶⁵⁴ Nevertheless, their analysis of two Italian paintings generated believable results; the authors analyzed samples collected from a painting attributed to Guariento di Arpo (c. 1350; Figure 5.40) and an *Enthroned Madonna* attributed to Antonio da Saliba (1480-97; Figure 5.41), claiming the latter to be “one of the first analyses of media from a painter so close to the origins of the

⁶⁵³ Meilunas, Bentsen, and Steinberg, “Analysis of Aged Paint Binders by FTIR Spectroscopy,” 35; Derrick, Stulik, and Landrey, *Infrared Spectroscopy in Conservation Science*, 28, 33; Casadio and Toniolo, “The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations,” 72.

⁶⁵⁴ Meilunas, Bentsen, and Steinberg, “Analysis of Aged Paint Binders by FTIR Spectroscopy,” 35; Townsend and Boon, “Research and Instrumental Analysis in the Materials of Easel Paintings,” 352-4. Townsend and Boon state the following regarding the reason for using reflectance mode over transmitted mode: The reflection mode is most often used when the integrity of the sample must be maintained for example in the analysis of multilayered composite materials like paint samples in a cross-section. Another form of reflection IR is the analysis of fluids or large surfaces using fibre-optic probes.

technique [oil] in Italy.”⁶⁵⁵ Unsurprisingly, egg tempera was identified in the fourteenth-century panel, and oil was found to be the primary binder in the late fifteenth-century painting (Figure 5.42). While Meilunas et al. were successfully able to draw conclusions based on

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Figure 5.40 (left) and 5.41 (right): Guariento di Arpo’s *Principatus Angel* (c. 1350, Fogg Art Museum, Harvard University; left) and Antonio da Saliba’s *Enthroned Madonna* (1480-97, Fogg Art Museum, Harvard University; right).

⁶⁵⁵ *Ibid.*, 45-7.

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Figure 5.42: FTIR spectra featured in Meilunas et al.'s 1990 publication demonstrating spectral results obtained from a fourteenth-century tempera (est.) painting (top; Figure 5.40) and a late fifteenth-century oil (est.) painting (middle and bottom; Figure 5.41). It is interesting to note the authors place considerable emphasis on peaks that appear almost negligible in the spectra. As more information has been collected on the FTIR analysis of pigments and degradation products (e.g. oxalates, metal soaps) it is likely that some of these earlier conclusions could be subjected to re-interpretation.⁶⁵⁶

⁶⁵⁶ Meilunas, Bentsen, and Steinberg, "Analysis of Aged Paint Binders by FTIR Spectroscopy," 45.

comparisons to reference samples, the authors stated that they were “not too optimistic” when faced with the accurate characterization of the aged egg-oil emulsion paints that might potentially be present in Italian Renaissance paintings.⁶⁵⁷

Throughout the 1990s, more museum laboratories began to invest in FTIR technology, prompting the formation of the Infrared and Raman Users Group (IRUG) in 1993, whose continued mission is:

[...] to improve and expand the spectroscopic data generated and shared within the international cultural heritage community through its collaborative database of reference spectra.⁶⁵⁸

During this period, cultural institutions began to routinely apply FTIR to the analysis of paintings while slowly transitioning away from older, less reliable/sophisticated techniques.⁶⁵⁹ In reviewing past and current literature relating to the analysis of egg- and/or oil-based paint systems encountered in Italian Renaissance paintings, the history behind the development of the scientific department at the National Gallery in London is especially relevant. Prior to the purchase of the FTIR in 1990, protein analysis at the National Gallery in London (NGL) was generally performed using ninhydrin tests (a compound that turns blue in the presence of

⁶⁵⁷ Ibid., 47.

⁶⁵⁸ “History of IRUG,” accessed January 28, 2016, <http://www.irug.org/about-us/history>.

⁶⁵⁹ Suzanne Q. Lomax, personal communication with the author, 20 April, 2009. Early techniques of medium analysis employed at the National Gallery of Art in Washington involved cross-sectional staining and HPLC methods developed by Susana Halpine. During this time, Suzanne Q. Lomax would generally perform fatty acid analysis using at least two different types of GC protocols (the GC was equipped with an FID detector). Since the arrival of the FTIR microscope in 2001, it has been consistently used at the NGA as a first step in characterization of binding media. Often if nothing could be deduced from the FTIR spectra due to pigment interference and/or sample size, the sample would then be analyzed with GC-MS. See also Liliane Masschelein-Kleiner, “Analysis of paint media, varnishes, and adhesives,” 189-92.

nitrogen), heating tests, or other stains.⁶⁶⁰ In their 1996 publication, Pilc and White discuss FTIR's inability to differentiate between various drying oils as well as sources of protein (egg white/yolk vs. animal glues).⁶⁶¹ Although the NGL scientists managed to develop a novel mounting system that allowed them to preserve the stratigraphy of cross-sections, this particular drawback of FTIR analysis makes it impossible to confirm whether a protein signal associated with an Italian painting is due to the presence of an egg-based medium (although glue-based mediums are certainly possible) or is attributed to contamination from glue-based materials (e.g. residues from glue-containing ground or glue-based adhesives used during previous restorations).⁶⁶² Pilc and White also warn about the challenges associated with the analysis of mixtures, stating that "the infra-red spectrum of a complex mixture contains so many individual bond absorptions that these overlap and merge into broad envelopes" and "paint which contains an emulsion of two components, for example, it is important to be aware of the limitations inherent in the precise definition of the measurement area."⁶⁶³

By 1999 the Getty Conservation Institute released a comprehensive guide to assist museums and scientists involved with the FTIR analysis of art materials, establishing the

⁶⁶⁰ Marika Spring, David Peggie, and Rachael Billinge, "Personal interview with Kristin deGhetaldi, 21 September, 2009," National Gallery, London. As with other chemical stains, ninhydrin tests do not always produce reliable results as nitrogen is present in many other types of materials encountered on easel paintings.

⁶⁶¹ Pilc and White, "The Application of FTIR-Microscopy to the Analysis of Paint Binders in Easel Painting," 81-2. Although analysis with FTIR pointed towards a protein-based binding medium in a sample collected from Dieric Bouts's *The Entombment*, a modified Ehrlich test was carried out in order to confirm the presence of animal glue.

⁶⁶² *Ibid.*, 78-80.

⁶⁶³ *Ibid.*, 75, 79.

technique as a standard form of analysis for cultural heritage studies.⁶⁶⁴ Like many institutions, the National Gallery in London often used FTIR as a preliminary form of analysis but began to encounter additional challenges as the sensitivity of the instrument continued to improve.⁶⁶⁵ Further research determined that degradation products such as the formation of oxalate-rich “crusts” on the surface of paintings and the presence of metal soaps could give rise to peaks in an FTIR spectrum that could easily be mistaken for a protein medium.⁶⁶⁶ Furthermore, the technology associated with the production of organic lake pigments could also give rise to similar amide peaks in a spectrum; these dyes were occasionally extracted from colored silks or woolen fabrics, both of which are proteinaceous fibers.⁶⁶⁷ Such pigments, when mixed with an oil medium, could give false positive results for protein,

⁶⁶⁴ See Derrick, Stulik, and Landry, *Infrared Spectroscopy in Conservation Science* (Los Angeles: J. Paul Getty Trust, 1999) for additional information on the development of FTIR for cultural heritage studies.

⁶⁶⁵ Jo Kirby, Marika Spring, and Catherine Higgitt, “The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate,” *National Gallery Technical Bulletin* 26 (2005): 71-87; Marika Spring and Catherine Higgitt, “Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media,” in *Medieval Painting in Northern Europe: Techniques, Analysis, Art History*, ed. Jilleen Nadolny (London: Archetype, 2006), 223-29; Catherine Higgitt, Marika Spring, and David Saunders, “Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-Tin Yellow,” *National Gallery Technical Bulletin* 24 (2003): 75-95.

⁶⁶⁶ Spring and Higgitt, “Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media,” 226. The origin and chemical reactions behind the formation of these crusts is not completely understood. They are thought to be associated with the degradation of proteins, carbohydrates, and/or lipid-containing materials. Metal soap formation, however, has been extensively studied and is thought to arise from the migration and interaction of free fatty acids with reactive metal cations associated with pigments (e.g. lead, copper, etc.).

⁶⁶⁷ Kirby, Spring, and Higgitt, “The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate,” 76-83.

leading analysts to conclude that an egg-oil emulsion was used by the painter. Spring and Higgitt summarize many of these challenges in their 2006 article “Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media” and provide detailed accounts of how these factors have led to erroneous conclusions in the past.⁶⁶⁸ While FTIR remains a commonly used technique in many institutions, many of these factors have likely led to misinterpretation of binding media analysis relating to Quattrocento paintings, something that should be considered when reviewing both past and current technical studies.

Improvements in FTIR technology eventually led to the development of attenuated total reflection FTIR (ATR-FTIR), a technique which allowed scientists to acquire spatially resolved “maps” that helped to reveal the location of pigments and binding media within embedded paint cross-sections.⁶⁶⁹ Spring et al. published their findings related to three paintings in the National Gallery London’s collection including Andrea del Verrocchio’s *The Virgin and Child with Two Angels* (c. 1450-80; Figure 4.23).⁶⁷⁰ A sample collected from the green lining of the Virgin’s robe generated rather compelling ATR-FTIR images (Figure 5.43); not only could the technique distinguish between the protein-rich medium and the particles of copper carbonate (malachite), but also small aggregates present in the lower

⁶⁶⁸ Spring and Higgitt, “Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media,” 223-9.

⁶⁶⁹ Jaap van der Weerd, H. Brammer, Jaap J. Boon, and Ron M. A. Heeren, “Fourier Transform Infrared Microscopic Imaging of an Embedded Paint Cross-section,” *Applied Spectroscopy* 56 (2002): 275-83, doi: 10.1366/0003702021954683; Townsend and Boon, “Research and Instrumental Analysis in the Materials of Easel Paintings,” 352-4.

⁶⁷⁰ Spring et al., “ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London,” 37-45; Mazzeo et al., “Attenuated total reflection micro FTIR characterization of pigment-binder interaction in reconstructed paint films,” 65-76.

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Figure 5.43: Excerpt from Spring et al.'s 2005 article demonstrating the application of ATR-FTIR imaging to the characterization of binding media present in a cross-sectional paint sample collected from the green lining of the Virgin's cloak in Andrea del Verrocchio's *The Virgin and Child with Two Angels* (Figure 4.23).⁶⁷¹

⁶⁷¹ Spring et al., "ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London," 39.

section of the paint layer were identified as copper carboxylates (copper soaps).⁶⁷² The authors point out that these results confirm that metal soap formation occurs not only in oil-rich paint films but in egg tempera as well (a phenomenon also observed by Mazzeo et al.):

Although drying oil is most commonly the source of fatty acids for copper carboxylate formation in paint samples, egg yolk also contains a high proportion of free fatty acids so the possibility that egg tempera can also react to form soaps must be considered, even though soaps have not so far been reported in samples from egg tempera paintings. It has recently been confirmed in the National Gallery laboratory (unpublished results) that test samples of red lead and lead tin yellow in egg tempera which had been artificially aged at high humidity contained lead fatty acid soaps. The location of the copper carboxylate in the sample determined by ATR-FTIR imaging suggests that here it is most likely to originate from the original materials rather than from conservation materials or surface coatings, supporting the hypothesis that it has formed through reaction of the pigment with the binding medium.⁶⁷³

While the technique of FTIR continues to be routinely used in cultural institutions to assist with the characterization of binding media in 2016, it should be stressed that ATR-FTIR (with or without imaging capabilities) may be better suited for the localization of certain materials within discrete paint and/or ground layers. The resolution of ATR-FTIR systems, however, is entirely dependent on the crystals that are pressed directly onto the surface of the sample; if there are multiple thin layers of paint/medium, for example, the crystal may not be able to distinguish one from another.⁶⁷⁴ Advancements in synchrotron radiation FTIR (SR-FTIR) now offer dramatic improvements in overall spatial resolution but as only a handful of

⁶⁷² Spring et al., “ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London,” 38-42. The authors attribute the peak at 1590 cm⁻¹ to be a “carbonyl stretching vibration from the copper salt of a carboxylic acid (copper soap, copper carboxylate).”

⁶⁷³ *Ibid.*, 41.

⁶⁷⁴ Townsend and Boon, “Research and Instrumental Analysis in the Materials of Easel Paintings,” 353.

facilities exist, the technique remains largely inaccessible to most cultural institutions.⁶⁷⁵ In summary, many of the issues discussed previously can still present challenges when interpreting FTIR spectra, despite whether the analysis has been gathered in reflectance mode (ATR) or transmitted mode. The fact that FTIR systems are not able to distinguish between protein sources (egg vs. animal glue) is particularly relevant to the identification of binding media encountered in Italian Renaissance paintings, an obstacle that has consequently inspired significant research efforts in the field of chromatography and mass spectrometry.

5.2.3 *Advancements in Chromatography and Mass Spectrometry*

Soon after Mills and White's pioneering research in gas chromatography during the 1960s and '70s, the field began to experience exponential improvements in technological advancements, data interpretation, and sample preparation. Chemical markers associated with particular classes of organic materials (e.g. resins, oils, proteins) became easier to identify as glass capillary tubes were eventually replaced with flexible fused silica columns.⁶⁷⁶ Yet despite these developments, the successful characterization of complex mixtures remained challenging. Before the adoption of mass spectrometers, the predominant method for the identification of an organic material was based on the duration of time it took for a compound to exit or elute from column (referred to as the "retention time"); however, certain chemical

⁶⁷⁵ Domenech-Carbo, "Novel analytical methods for characterising binding media and protective coatings in artworks," 116; Nati Salvado et al., "Advantages of the Use of SR-FT-IR *Microspectroscopy: Applications to Cultural Heritage* 77 (2005): 3444-51, doi: 0.1021/ac050126k.

⁶⁷⁶ Townsend and Boon, "Research and Instrumental Analysis in the Materials of Easel Paintings," 351; Mills and White, *The Organic Chemistry of Museum Objects*, 15-17.

compounds could exit the column simultaneously (co-elute) making it difficult to distinguish one from the other and the presence of certain pigments and restoration materials could also interfere with interpretation. Up until the late 1970s, most museum laboratories relied on not only retention times to assist with identification but also on the relative ratios of organic compounds. Ratios were calculated by manually cutting out peaks from the printed GC chromatograms and physically weighing them in order to determine the nature of the binding medium, a method that was later replaced with computerized technology. Once mass spectrometry (MS) methods began to be applied to cultural heritage studies in the early 1970s, scientists were able to develop more refined systems for the characterization of binding media in Quattrocento paintings.⁶⁷⁷

Perhaps more than of any other museum, the history of the National Gallery's scientific laboratory in London is intimately tied to the interpretation and study of fifteenth-century Italian paintings, due to the collection and the pioneering efforts of the scientific department. The National Gallery acquired their first gas-chromatography-mass spectrometry (GC-MS) system in 1979, a trend other cultural institutions would soon follow.⁶⁷⁸ The mass spectrometer enabled scientists to identify the chemical structures of various markers (or

⁶⁷⁷ Mills and White, *The Organic Chemistry of Museum Objects*, 24-6; Peggie, "The Chemistry and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century," 221-6. See also Maria Perla Colombini and Francesca Modugno, eds., *Organic Mass Spectrometry in Art and Archaeology*. (New York: John Wiley and Sons, 2009).

⁶⁷⁸ John S. Mills and Raymond White, "Organic Mass-Spectrometry of Art Materials: Work in Progress," *National Gallery Technical Bulletin* 6 (1982): 3-18; Suzanne Q. Lomax, e-mail message to author, 1 February, 2016. A Kratos MS25 gas-chromatography-mass-spectrometer was acquired by the National Gallery London as early as 1979. For comparison, the National Gallery of Art in Washington DC did not acquire their first mass spectrometer until the late 1980s/early '90s.

peaks in this instance) that appeared on a chromatogram with greater accuracy (Figure 5.44), reducing scientists' dependency on retention times.⁶⁷⁹ Simultaneously, the advent of computerized systems during the 1980s allowed for automated calculation of ratios between key chemical markers, a method that Mills and White initially adapted to distinguish between different types of drying oils present in aged paint films (linseed, walnut, and poppyseed) as well as the possible presence of "egg fats."⁶⁸⁰ In these early studies, the discrepancy between what the reader is advised against (making definitive conclusions regarding egg-oil paint systems) and the analytical findings that are reported (e.g. oil + egg, egg/oil, walnut with a trace of egg, etc.) should be noted.

Mills and White were forthcoming about the challenges posed by egg-oil paint systems, and they continued to work towards perfecting a method that relied on the use of fatty acid ratios for confirming whether or not egg tempera and/or drying oil was present in a paint sample. Such conclusions were largely based on the relative amounts of the free fatty acids palmitic (P) and stearic (S) as well as the amount/presence of dicarboxylic acids, namely azelaic (A), suberic (Sub), and sebacic acid (Seb).⁶⁸¹ After analyzing a considerable number of fresh and aged paint references, Mills and White found that relative ratios of these chemical markers could be used to characterize the binding medium found in a specific passage of an easel painting (Figure 5.10). This particular system remains in use to this day, as fatty acid

⁶⁷⁹ Mills and White, "Organic Mass-Spectrometry of Art Materials: Work in Progress," 3-18.

⁶⁸⁰ Mills, "The Gas Chromatographic Examination of Paint Media. Part 1. Fatty Acid Composition and Identification of Dried Oil Films," 92-107; —, "The Identification of Binding Media – An Introduction," 69-71; Mills and White, "The Identification of Paint Media from their Sterol Composition – A Critical View," 176-82; —, "The Organic Chemistry of Museum Objects, 171-2.

⁶⁸¹ Mills and White, "Organic Mass-Spectrometry of Art Materials: Work in Progress," 7; —, "The Organic Chemistry of Museum Objects, 171-2.

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Figure 5.44: Excerpt from Mills and White's 1982 article demonstrating the capabilities of the National Gallery London's new mass spectrometer. The red arrow indicates a peak in the gas chromatogram whose chemical composition was initially unknown. Subsequent application of mass spectrometry techniques determined which compounds in the database (two of which are shown in the bottom right) best fit the mass to charge (m/z) ratio of the unknown peak (eventually identified as the structure shown in the upper left, 6-Heptenoic acid).⁶⁸²

⁶⁸² Mills and White, "Organic Mass-Spectrometry of Art Materials: Work in Progress," 6.

(FA) ratios are currently be used to characterize the nature of drying oils (and whether they were pre-treated) as well as the possible presence of egg tempera.

The final chapter in Mills and White's *The Organic Chemistry of Museum Objects*, entitled "Analysis in Practice," summarizes the authors' approach to sample preparation, their interpretation of egg-oil systems, and the overall findings relating to Italian paintings from the fifteenth to the eighteenth centuries (Figure 5.45).⁶⁸³ Comparison of sample preparation and extraction protocols used in GC-MS analysis of binding media is a subject that is in great need of further study. Extraction of lipids, proteins, resins, and carbohydrates from a single paint sample can be exceptionally difficult; in recent years conservation scientists have developed elaborate protocols to tackle this challenge.⁶⁸⁴ A more common approach is to extract certain classes of organic materials from a single sample: for example fatty acids and resinous

⁶⁸³ Mills and White, *The Organic Chemistry of Museum Objects*, 169-72.

⁶⁸⁴ Koller, Fiedler, and Baumer, "Die Bindemittel auf Dürers Tafelgemälden," 102-119; —, "Vermeers Maltechnik – eine Mischtechnik. Untersuchung der Bindemittel auf dem Gemälde 'Bei der Kupplerin,'" 65-75; Anna Lluveras et al., "GC/MS Analytical Procedure for the Characterization of Glycerolipids, Natural Waxes, Terpenoid Resins, Proteinaceous and Polysaccharide Materials in the Same Paint Microsample Avoiding Interferences from Inorganic Media," *Analytical Chemistry* 82 (2010): 376-86, doi: 10.1021/ac902141m; Ilaria Bonaduce, Marcello Cito, and Maria Perla Colombini, "The development of a gas chromatographic-mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media," *Journal of Chromatography A* 1216 (2009): 5931-39, doi:10.1016/j.chroma.2009.06.033; Maria Perla Colombini et al., "Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry," *Accounts of Chemical Research* 43 (2010): 715-27, doi: 10.1021/ar900185f; Alessia Andreotti et al., "Combined GC/MS Analytical Procedure for the Characterization of Glycerolipid, Waxy, Resinous, and Proteinaceous Materials in a Unique Paint Microsample," *Analytical Chemistry* 78 (2006): 4490-500, doi:10.1021/issn.0003-2700. See also Kenneth Sutherland, ed, *MaSC 2007 GC-MS Workshop Handbook*, Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies, Users' Group for Mass Spectrometry and Chromatography, 2007.

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Figure 5.45: Table from Mills and White's *The Organic Chemistry of Museum Objects* showing a summary of recorded fatty acid ratios (palmitic/stearic or P/S) corresponding to Italian paintings dating from the fifteenth to the eighteenth centuries.⁶⁸⁵

⁶⁸⁵ Mills and White, *The Organic Chemistry of Museum Objects*, 172.

components are extracted from one paint sample while proteinaceous components are extracted from an additional sample. Mills and White were among the first to explore different sample preparation methods, particularly relating to the extraction and derivatization of fatty acids as well as the extraction and and trimethylsilylation of cholesterol present in egg tempera.⁶⁸⁶ Fatty acid extraction generally involves breaking down the paint sample using heat and/or solvents followed by esterification (a form of chemical “tagging”) of the free fatty acids with methyl groups; the most efficient procedures for creating these fatty acid methyl ester derivatives (FAMES) tend to involve base-catalyzed methods (Figure 5.46), reactions

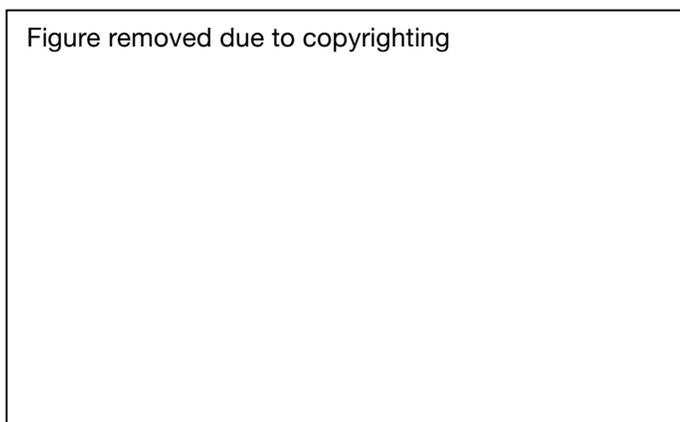


Figure 5.46: Schematic summarizing the transesterification (for intact triglycerides) and esterification (for free fatty acids/dicarboxylic acids) reactions that produce fatty acid methyl esters (FAMES) to ensure successful recovery and detection using GC-MS.⁶⁸⁷

⁶⁸⁶ Mills, “The Gas Chromatographic Examination of Paint Media. Part I. Fatty Acid Composition and Identification of Dried Oil Films,” 99; Mills and White, “Organic Mass-Spectrometry of Art Materials: Work in Progress,” 7-10.

⁶⁸⁷ “Dr. Yung Ka-Fu, Joseph,” accessed January 20, 2016, <http://www.polyu.edu.hk/~abct/en/staff-singledemo39e43.html?id=25>.

that are facilitated with the addition of “derivatizing” agents (alkylation derivatization reagents).⁶⁸⁸ While details concerning these various reagents and protocols may seem unrelated to the characterization of egg-oil paint systems, they are in fact intimately tied to our interpretation and understanding of binding media in Quattrocento paintings as they are frequently used and modified to successfully extract, detect, and quantify fatty acid markers in paint films.

By comparison, the detection of amino acids and cholesterol to confirm the presence of glues and egg-based paints has presented far more challenges for scientists than fatty acid analysis. While cholesterol is easily oxidized and prone to degradation, amino acids are far more resilient; however, the covalent bonds present in peptide chains often require harsh hydrolytic conditions usually in the presence of acidic solutions (Figure 5.47). Early attempts to perform quantitative analysis of amino acids seemed promising; however, some of these methods required extremely large paint samples, were inefficient and cost-prohibitive, and did not always involve steps to address pigment interference.⁶⁸⁹ Raymond White, for example, in

⁶⁸⁸ Mills, “The Gas Chromatographic Examination of Paint Media. Part I. Fatty Acid Composition and Identification of Dried Oil Films,” 99. Early on Mills and White and other organic chemists used reactions involving diazomethane to produce FAMES; however, as this reagent is both toxic and explosive, scientists eventually adopted other reagents for this purpose.

⁶⁸⁹ Sheldon Keck and Theodore Peters, “Identification of Protein-containing Paint Media by Quantitative Amino Acid Analysis,” 75-82; Liliane Masschelein-Kleiner, “Contribution to the Study of Aged Proteinaceous Media” 84-7; Raymond White, “The Characterization of Proteinaceous Binders in Art Objects,” *National Gallery of Art* 8 (1986): 5-14; Mills and White, “Organic Mass-Spectrometry of Art Materials: Work in Progress,” 7-10; Vallance, “Applications of Chromatography in Art Conservation: Techniques used for the Analysis and Identification of Proteinaceous and Gum Binding Media,” 75-81; Colombini and Modugno, “Organic Materials in Art and Archaeology,” 8; Mills and White, *The Organic Chemistry of Museum Objects*, 87-88; Boon et al., “Molecular Aspects of Mobile and Stationary Phases in Ageing Tempera and Oil Paint Films,” 39-49; Karpowicz, “Ageing and Deterioration of Proteinaceous Media,” 153-60; Katrien Keune, “Binding medium, pigments and metal soaps

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Figure 5.47: Schematic detailing the hydrolysis mechanism for reducing peptide chains into their constituent amino acids.⁶⁹⁰

1986 developed a multi-step procedure for the identification of amino acids in samples from works by Domenico Beccafumi (*Tanaquil*, c. 1519) and Giovanni Bellini (*Madonna of the Meadow*, c. 1500; Figure 5.48) using an ion-exchange mechanism, a procedure that, according to scientist Sarah Vallance, “requires a sample approximately three times the size of that for analysis of oil media, since the compensation should be made for losses incurred at every stage of the sample preparation.”⁶⁹¹ Vallance’s observation may account for why little work

characterised and localised in paint cross-sections” (PhD diss., University of Amsterdam, 2005), 33-34.

⁶⁹⁰ “Hydrolysis of Peptide Bond.” Accessed 25 January, 2016.
<https://www.boundless.com/physiology/textbooks/boundless-anatomy-and-physiology-textbook/the-digestive-system-23/chemical-digestion-224/mechanisms-of-chemical-digestion-1103-8914/>.

⁶⁹¹ White, “The Characterization of Proteinaceous Binders in Art Objects,” 5-14; Vallance, “Applications of Chromatography in Art Conservation: Techniques used for the Analysis and

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Figure 5.48: Giovanni Bellini, *Madonna of the Meadow* (c. 1500, National Gallery, London).

has been published on amino acid analysis in the *National Gallery Technical Bulletin* following White's 1986 publication.

Advancements in High Performance Liquid Chromatography (HPLC) eventually allowed for the analysis of smaller paint samples, a technique that was further adapted by Dr. Susanna Halpine at the National Gallery of Art in Washington during the 1980s/90s.⁶⁹²

Identification of Proteinaceous and Gum Binding Media," 77. White was able to identify glue in the ground layers of both paintings and loosely identified the priming layer atop the ground in Bellini's painting to be egg white (an unlikely assignment given what is now known about traditional painting techniques).

⁶⁹² David Erhardt et al., "A systematic approach to the instrumental analysis of natural finishes and binding media," in *American Institute for Conservation of Historic and Artistic Works Preprints, 6th Annual Meeting, Fort Worth, Texas, 1-4 June, 1988*, ed. Sarah Z. Rosenberg (Washington DC: American Institute for Conservation of Historic and Artistic Works, 1988), 67–84; Susana M. Halpine, "HPLC Applications in Art Conservation," in *Handbook of HPLC*, eds. Elena Katz, Roy Eksteen, and Peter Schoenmakers (New York: Marcel Dekker, 1999), 903–927; —, "Analyses of Artists' Materials Using High-performance Liquid Chromatography" in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, eds. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997), 21-28; —, "Investigation of Artists' Materials Using

Halpine's method involved subjecting samples to heat and hydrolysis (Figure 5.47) followed by derivatization using PITC (phenylisothiocyanate), a reagent that tagged the amino acids with a fluorophore group allowing for detection using a UV/Vis detector.⁶⁹³ Halpine found that she was able to improve upon an earlier HPLC method (which was only able to recover 8 amino acids) and warned about relying solely on fatty acid ratios "as some animal glue preparations can contain up to 10% of these non-drying oils, and a large enough sample could possibly be interpreted as egg yolk."⁶⁹⁴ Along with egg-based mediums, Halpine's comprehensive research identified a number of amino acids in non-proteinaceous materials (Figure 5.49), particularly natural resins (e.g. dammar and mastic) and gums (e.g. gum Arabic).⁶⁹⁵ Her findings presented additional challenges for scientists; natural resins have been frequently used to saturate the surface of paintings for hundreds of years while both natural resins and gum Arabic have been used as binders for retouching areas of loss and abrasion.

Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 29–69; —, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 22–38.

⁶⁹³ Ibid.

⁶⁹⁴ Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 23; Bengt Skans and Peter Michelsen, "Die Bedeutung von Fett in Tierleim für Malzweche," *Maltechnik-Restaur* 92 (1986): 63-71; Wilma G. Roelofs, "Some experiments with high performance liquid chromatography in analyzing binding media in objects of art," in *ICOM Committee for Conservation Preprints, 4th Triennial Meeting, Venice, 13-15 October 1975* (Paris: ICOM Committee for Conservation, 1975), 75/15/5.1-21.

⁶⁹⁵ Halpine, "Analyses of Artists' Materials Using High-performance Liquid Chromatography," 23-4; —, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 33, 39-41.

From an analytical standpoint, Halpine's publications focusing on the analysis of Quattrocento paintings are highly comprehensive and thorough, yet the reproducibility of the reported results remains questionable as subsequent studies focusing on amino acid analysis have not utilized the Pico-Tag method. Halpine's work incorporated both fresh and aged references of organic materials (something that is not always included in technical studies involving organic analysis), but only calcium and copper-containing pigments were used to examine possible interference problems.⁶⁹⁶ Copper pigments were ultimately found to to examine possible interference problems.⁶⁹⁷ Copper pigments were ultimately found to hamper the overall recovery of the amino acids, an observation that Halpine attributed to the pigment's potential to interfere with the hydrolysis of the amino acids.⁶⁹⁸ Vallance points out that recent analysis, however, has shown that metal ions form inorganic pigments like copper can form complexes with amino acids and can lead to further degradation, an observation that raises additional questions relating to Halpine's interpretation of samples collected from

⁶⁹⁶ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 35; —, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 32-3.

⁶⁹⁷ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 35; —, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 32-3.

⁶⁹⁸ Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 32-3.

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Figure 5.49: Table from Halpine's 1995 publication summarizing the amino acid composition of dammar resin and protein-based media. Results are reported as mole percent and were obtained from published literature as well as analysis of samples prepared at the National Gallery of Art, Washington.⁶⁹⁹

fifteenth-century Italian paintings.⁷⁰⁰ Halpine established that "comparison between the

⁶⁹⁹ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 33.

⁷⁰⁰ Vallance, "Applications of Chromatography in Art Conservation: Techniques used for the Analysis and Identification of Proteinaceous and Gum Binding Media," 78; Schilling et al., "Gas chromatographic analysis of amino acids in ethylchloroformate derivatives, Part I: Composition of proteins associated with art objects and monuments," 45; Maria Perla Colombini, Francesca Modugno, and Ambrogio Giacomelli, "Two procedures for suppressing interference from inorganic pigments in the analysis by gas chromatography-mass spectrometry of proteinaceous binders in paintings," *Journal of Chromatography A* 846

compositions of the water-soluble components in the supernatant and the insoluble components in the precipitate of a given sample” could be used to determine whether:

- a) an animal skin glue layer is adjacent to an egg yolk paint layer as a consolidant, an un-pigmented layer, or a paint/ground layer or
- b) whether the glue and egg are bound together, as in an emulsion paint or as a consequence of a glue lining.⁷⁰¹

In summary, the amino acids that are most easily extracted after soaking the sample with water for one hour are often determined to originate from glue proteins while insoluble amino acids are likely from egg tempera. Halpine also theorized that if the sole determining amino acid for animal glue (hydroxyproline) was found in the supernatant then glue must be present in the original binder; if present in the precipitant then glue was likely a product of the ground and/or due to an invasive glue-lining.⁷⁰² Halpine’s research pre-dates two relevant discoveries relating to the detection of proteins in traditional easel painting: 1) recovery of amino acids

(1999): 101-11, [doi:10.1016/S0021-9673\(99\)00344-1](https://doi.org/10.1016/S0021-9673(99)00344-1); Juana De la Cruz-Canizares, Maria Teresa Domenech-Carbo, Jose Vicente Gimeno-Adelantado, Rufino Mateo-Castro, Francisco Bosch-Reig, “Suppression of pigment interference in the gas chromatographic analysis of proteinaceous binding media in paintings with EDTA,” *Journal of Chromatography A* 1025 (2004): 277-85, doi: 10.1016/j.chroma.2003.10.118; Gwenaelle Gautier and Maria Perla Colombini, “Identification of proteins in wall painting samples: A fast procedure to remove copper-based pigment interferences,” *Talanta* 73 (2007) 95-102, doi: 10.1016/j.talanta.2007.03.008; Bonaduce et al., “The development of a gas chromatographic-mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media,” 5931–5939; Fang et al., “Influence of pigments and protein aging on protein identification in historically representative casein-based paints using enzyme-linked immunosorbent assay,” 203-15.

⁷⁰¹ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 35-39. The “supernatant” in this case refers to the solids at the bottom of the vial while hydrolyzed the “precipitant” are the hydrolyzed solids.

⁷⁰² Ibid, 41-53.

can be hampered by the formation of metal ion-amino acid complexes and 2) the production of lake pigments can inadvertently give rise to amino acids in the paint layer(s).⁷⁰³ This methodology may account for Halpine's findings relating to a large altarpiece by Agnolo Gaddi (*Madonna Enthroned with Saints and Angels*, c. 1380/90; Figure 5.50) in which separate colors were found to contain glue, tempera, and an emulsion of the two in an area of yellow paint (Figure 5.51).⁷⁰⁴ The use of an egg-glue emulsion during this time period would be both novel and impractical; glue must be applied as warm solution if used as a binding medium, a characteristic that applied as warm solution if used as a binding medium, a characteristic that would likely cause the egg yolk proteins to denature and eventually lead to a non-homogenous mixture.⁷⁰⁵ Halpine's deductions regarding two works by Andrea Mantegna seem more plausible. A sample collected from *Judith and Holofernes* (c. 1495; Figure 5.52) was found to contain egg yolk after "subtracting" the amino acid profile associated with dammar resin. On the other hand, analysis of a degraded sample collected

⁷⁰³ Kirby et al., "The Technology of Red Lake Pigment Manufacture: Study of the Dyestuff Substrate," 71-87. See note 586 for references on the formation of metal complexes with amino acids.

⁷⁰⁴ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 41-8.

⁷⁰⁵ This phenomenon would be best compared with egg being added to hot soups. While it is not impossible that Gaddi opted to use such an emulsion, it is perhaps more likely that the glue residue is from a contaminated brush during the painting process or even from later consolidants applied to the face of the painting.

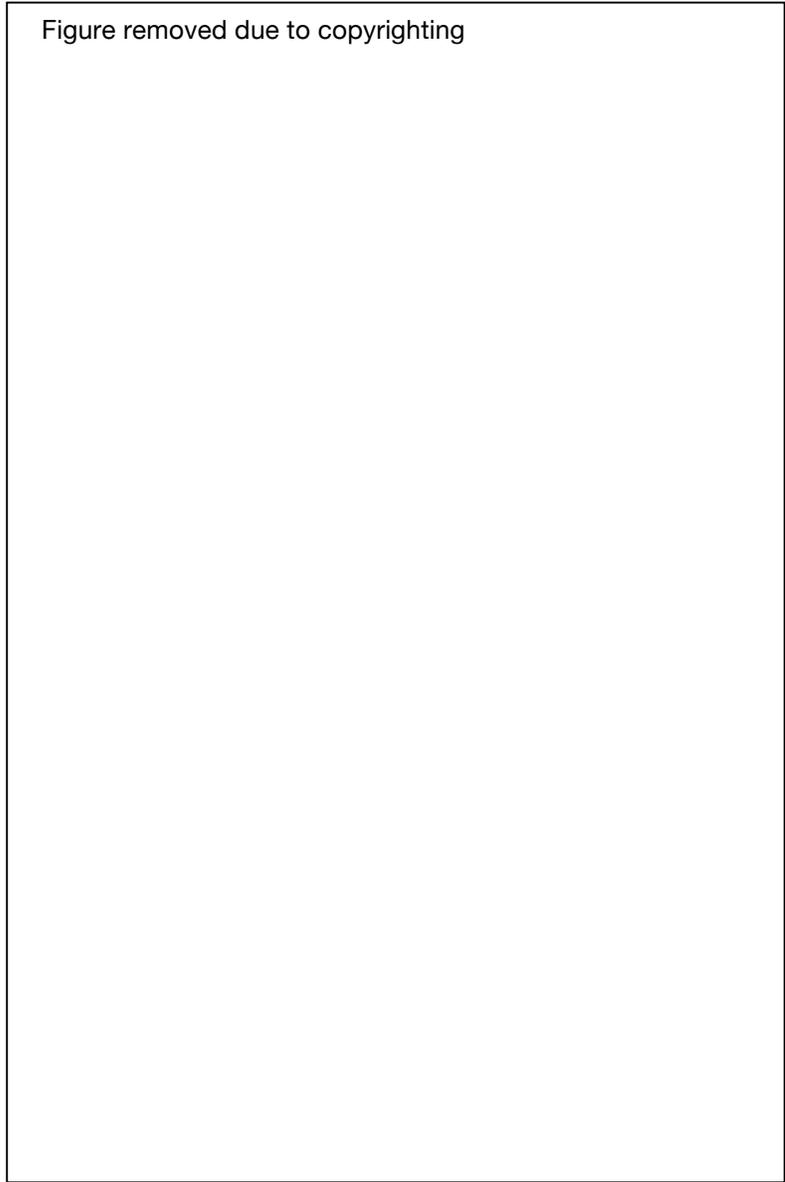


Figure 5.50 (top) and 5.51 (bottom): Agnolo Gaddi's *Madonna Enthroned with Saints and Angels* (c. 1380/90, National Gallery of Art, Washington DC; top). The bottom table, from Halpine's 1995 publication, lists the calculated amino acid composition of four samples collected from Agnolo Gaddi's *Madonna Enthroned with Saints and Angels*.⁷⁰⁶

⁷⁰⁶ Halpine, *Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure*, 42-3.

from Mantegna's *Christ Child Blessing* (c. 1480/90; Figure 5.53), a delicate painting on canvas, proved to be more complicated. Halpine concluded that the binder is likely egg-based, attributing the small amount of hydroxproline to the glue in the gesso ground and/or residue from the lining; however, in this instance Halpine opts to normalize the amino acid profile of the sample to that of animal glue but not dammar (Figure 5.55), a curious decision as the canvas clearly contains significant residues left behind by previous varnishing campaigns.⁷⁰⁷ Such residues could certainly contribute to the amino acid profile of a paint sample, and possibly even lead to incorrect assumptions.



Figure 5.52 (left) and 5.53 (right): Andrea Mantegna's *Judith and Holofernes* (c. 1495, National Gallery of Art, Washington DC; left) and *Christ Child Blessing* (c. 1480/90, National Gallery of Art, Washington DC; right).

⁷⁰⁷ Ibid., 51-2.

Halpine's conclusion that Mantegna used egg tempera as a binder in this instance is not unfounded. A survey conducted by Andrea Rothe in 1992 identified egg, glue, and casein in a number of Mantegna's canvas paintings while analysis of canvas paintings at the Louvre and National Gallery London also confirmed that egg was likely the primary binding medium.⁷⁰⁸ Furthermore, a cross-section (Figure 5.54) collected from the *Christ Child Blessing* demonstrates the presence of a thin gesso ground, an observation that corresponds with reports published by both Dunkerton and Andrea Rothe; however, with such thinly applied paint layers it seems nearly impossible to avoid extracting glue residues from the ground layer during analysis.⁷⁰⁹ Certainly, other laboratories were faced with a similar problem when analyzing Mantegna's canvas paintings: the Louvre utilized cross-sectional

⁷⁰⁸ Andrea Rothe, "Andrea Mantegna's 'Adoration of the Magi,'" in *Historical Painting Techniques, Materials, and Studio Practice: Preprints of a Symposium, University of Leiden, the Netherlands, 26-29 June 1995*, eds. Arie Wallert, Arie, Erma Hermens, and Marja F.J. Peek (Los Angeles: Getty Publications, 1995), 111-16; —, "Mantegna's Paintings in Distemper," in *Andrea Mantegna*, ed. Jane Martineau (London & New York: The Royal Academy of Arts and The Metropolitan Museum of Art, 1992), 80-8; Jill Dunkerton, "Mantegna's Painting Techniques" in *Mantegna and 15th Century Court Culture*, eds. Frances Ames-Lewis and Anka Bednarek (London: Birkbeck College, 1993), 26-38; Caroline Villers, "Paintings on Canvas in Fourteenth Century Italy" in *Zeitschrift für Kunstgeschichte* 58 (1995): 347, doi: 10.2307/1482818; Suzanne Boorsch and Keith Christiansen, *Andrea Mantegna* (New York: Metropolitan Museum of Art, 1993), 80-8; Delbourgo et al., "L'analyse des peintures du Studiolo d'Isabelle d'Este au Laboratoire de Recherche des Musées de France. II - Étude analytique de la matière picturale," 21-8. Susana M. Halpine, "Andrea Mantegna Scientific Report –1990." Scientific report housed in the Paintings Conservation Department at the Philadelphia Museum of Art. Halpine identified the use of egg tempera on Mantegna's *The Christ Child Blessing* (on canvas) using HPLC while scientists at the Getty Conservation Institute found glue to be the predominant binder used in his paintings on fabric. Dunkerton has also expressed doubt as to whether the artist actually used casein as a binder based on the analytical methods used to confirm the presence of the material (see Chapter 5, section 5.2.3).

⁷⁰⁹ Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 50-53; Dunkerton, "Mantegna's Painting Techniques," 33; Rothe, "Mantegna's Paintings in Distemper," 80-8.

staining and fatty acid analysis using GC (neither of which are able to confirm the presence of egg tempera), the National Gallery on fatty acid analysis alone (using GC-MS), while the Getty Conservation Institute relied on solubility tests, the detection of phosphorous, and amino acid/fatty acid analysis performed with GC-MS.⁷¹⁰ Like HPLC, GC-MS is one of the few techniques that can reliably be used to confirm the presence of protein (a technique that will be described in detail in the following paragraphs); however, neither technique is able to successfully locate egg and/or glue within thinly applied paint layers. The technical notes published in the 2003 Catalogue also seem to convey a sense of skepticism regarding the analysis of Mantegna's *Christ Child Blessing*:

Technical analysis indicates that the binding medium is egg tempera, but it is possible that the artist also employed glue, since he frequently used distemper (tempera and glue) on unprimed canvas. Technical analysis confirmed the presence of glue but could not determine whether it was an artifact of the glue lining or part of the tempera layer. [...] Due to the extreme thinness of the ground, the paint has soaked into the cloth support and the surface has been further flattened through the relining of the canvas, which may have been trimmed slightly at the top and bottom. The flesh tones in particular are abraded, resulting in a darkened appearance, and the ground is too thin and transparent to hide the brown of the old canvas, which shows through. Here and in the rest of the picture the dark tonality is also due to successive layers of discolored varnish.⁷¹¹

As mentioned previously, copper pigments can be especially problematic when attempting to recover amino acids from a degraded paint sample, an issue that Halpine encountered during her 1992 examination of a panel painting by Cosme Tura (*The Annunciation with Saint Francis and Saint Louis of Toulouse*, c. 1475; Figure 5.56). Copper ions are known to form

⁷¹⁰ Dunkerton, "Mantegna's Painting Techniques," 35-37; Rothe, "Mantegna's Paintings in Distemper," 82; —, "Andrea Mantegna's 'Adoration of the Magi,'" 111; Delbourgo et al., 21-8.

⁷¹¹ Miklos Boskovits and David Alan Brown, eds. *Italian Paintings of the Fifteenth Century*. (Washington DC: Oxford University Press and the National Gallery of Art, 2003), 428.

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Figure 5.54 (top) and 5.55 (bottom): The top image is a cross-section collected from the *Christ Child Blessing* (Figure 5.53) featured in Halpine's 1995 publication while the bottom table summarizes the amino acid profiles found in samples collected from the paintings shown in Figures 5.53 and 5.54.⁷¹²

⁷¹² Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 49, 52.

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Figure 5.56: Cosme Tura's *Annunciation with Saint Francis and Saint Louis of Toulouse* (c. 1475, National Gallery of Art, Washington DC).

metal complexes with amino acids; however, the physical nature of malachite and azurite particles can pose additional challenges from a practical standpoint. Malachite and azurite pigments lose their brilliant color the finer they are ground, accounting for their granular appearance that can still be observed with the naked eye in many Quattrocento paintings. Such passages are prone to darkening, flaking, crumbling, and other issues, since residues of surface coatings containing oil and/or varnish, surface grime, and glues from consolidants and/or facings can become imbibed within the rough surface created by these pigments. Conclusions based on Halpine's 1992 assessment of the panels seem credible; egg tempera was identified in nearly all of the samples save for three collected from blue passages (two

from the sky in the St. Francis panel and another from the blue robe of St. Toulouse) that were found to contain animal glue (Figure 5.57).⁷¹³ While Halpine had not yet discovered the potential contributing effects of materials such as dammar, she carefully considered the restoration history of the panels and avoided sampling from damaged areas of the painting (e.g. the blue robe of the *Madonna*; Figure 5.58). A detail shown in Figure 5.58 reveals the rough and uneven surface of the sky on the St. Francis panel with exposed areas of the glue ground throughout, a characteristic often associated with degraded azurite paint films in azurite paint films in Quattrocento paintings. As Halpine's findings were later corroborated with non-destructive imaging techniques (discussed in Section 5.3.2); it appears that she was able to avoid inadvertently collecting residues from the ground during sampling.⁷¹⁴ In summary, Halpine's HPLC method is perhaps worth re-visiting as a reliable method for the general recovery of amino acids in aged paint films; however, Halpine herself alluded to the challenges associated with samples containing multiple layers as well as the difficulties imposed by previous restoration campaigns, scenarios that would require further analytical investigation to confirm the layers of ground and paint:

Careful evaluation of the data showed that the glue found in association with the blue-pigmented areas of the painting was apparently the binding medium although, because of the age of the panels, a consolidant used in previous treatments may also have been present. Amino acid analysis alone cannot determine whether the animal glue found in samples is the pigment binder, a consolidant, or part of the ground layer.⁷¹⁵

⁷¹³ *Ibid.*, 28-34.

⁷¹⁴ Kathryn A. Dooley, Damon M. Conover, Lisha D. Glinsman, and John K. Delaney, "Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting," *Angewandte Chemie International Edition* 53 (2014): 13775-79, doi: 10.1002/anie.201407893.

⁷¹⁵ *Ibid.*, 34.

Figure removed due to copyrighting

Figure 5.57: Table from Halpine's 1992 publication summarizing the amino acid profiles of samples collected from panels shown in Figure 5.56.⁷¹⁶

⁷¹⁶ Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 29.

Figure removed due to copyrighting

Figure 5.58: Cosme Tura's *Madonna* panel (c. 1475, National Gallery of Art, Washington DC; left) as seen after removal of varnish and heavily applied overpaint and a detail (right) of the abraded azurite paint layer in the background of Cosme Tura's *St Francis* panel from the same series.⁷¹⁷

Since the time of Halpine's work in the 1990s, much of the HPLC analysis performed on samples collected from fifteenth-century paintings has focused on the identification of

⁷¹⁷ "Cosme Tura – 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" Conservation File housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC.

dyestuffs rather than on amino acids, while GC-MS research has witnessed an exponential growth in the field of cultural heritage.⁷¹⁸ Certainly HPLC today offers a greater level of sensitivity when compared with other chromatography techniques like GC-MS; however, recent studies seem to neglect the earlier findings reported by Halpine and others that amino acids and associated proteinaceous markers can arise from other sources (such as natural resins).⁷¹⁹ Meanwhile, a common goal shared by GC-MS operators was to develop a multiple-step extraction protocol that would allow for the detection of a wide range of organics (e.g. waxes, oils, proteins, resins, gums, etc.) from a single, tiny paint sample. Witold Nowik, a scientist at the Laboratoire de Recherche des Monuments Historiques in Paris, developed a technique for GC analysis in 1995 that allowed for the simultaneous detection of fatty acids and amino acids using a derivatizing agent ethyl chloroformate (following hydrolysis and treatment with an ethanol pyridine solution), a reagent that was also adopted by Dr. Michael Schilling during his work on proteins the following year in 1996 (see Figure 5.59).⁷²⁰ Schilling et al. used a similar method to identify which amino acids remained

⁷¹⁸ Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 123-8.

⁷¹⁹ Karin Groen, “Investigation of the Use of Binding Medium by Rembrandt: Chemical Analysis and Rheology,” 76-81, 90. Groen has reported the presence of amino acids encountered in Rembrandt’s lead white paint using HPLC, inferring that the lack of copper (which Halpine found problematic) in this instance further confirms that the artist added egg yolk/whole egg to his paints; however, Groen also states the following in Note 30, indicating that the particular method used may not have successfully recovered all possible amino acids: Although the important amino acids proline and hydroxyproline, present in animal glue, cannot be demonstrated with this technique as used by DSM Research, the method was employed nonetheless.

⁷²⁰ Witold Nowik, “Acides amines et acides gras sur un même chromatogramme: un autre regard sur l’analyse des liants en peinture,” *Studies in Conservation* 40 (1995): 120-6, doi: 10.2307/1506511; Schilling, Khanjian, and Souza, “Gas chromatographic analysis of amino acids in ethylchloroformate derivatives, Part I: Composition of proteins associated with art objects and monuments,” 45–59; Schilling and Khanjian, “Gas chromatographic Analysis of

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Figure 5.59: Table of chloroformate derivatizing reagents (MCF, ECF) and silylating reagents (BSTFA, MSTFA, and MTBSTFA) as well as their corresponding products formed during amino acid analysis. Note that while it is possible to add two silyl groups (SiCH_3) to the nitrogen of an amino acid, common conditions used in most procedures involving the analysis of paint samples are more likely to add a single silyl group instead.⁷²¹

Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media,” 123-44; —, “Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part III: Identification of Proteinaceous Binding Media by Interpretation of Amino Acid Composition Data,” 211-19; Dr. W. Christian Petersen, e-mail message to author, 7 April, 2016.

⁷²¹ Yunping Qiu and Deborah Reed, “Gas Chromatography in Metabolomics Study.” In *Advances in Gas Chromatography*, ed. Xinghua Guo (CC BY 3.0 License: Yunping Qiu and

recoverable and intact after extensive aging in paint and reference samples (Figure 5.5), the effects caused by certain pigments, and the characterization of proteins in a wide range of organic materials (Figure 5.11).⁷²² Presumably it was this technique that was used to identify amino acids in samples collected from a number of Mantegna's paintings on canvas based on a survey performed in the early 1990s.⁷²³ In reviewing Rothe's summary of the analytical findings, it appears that the Getty scientists were likely faced with a problem very similar to that which faced by Halpine during her analysis of Mantegna's *Christ Blessing Child* in 1995; complete separation of the thinly applied paint was likely challenging and not always possible.⁷²⁴ As with Halpine's research, many of the conclusions were based on the relative amount of hydroxyproline encountered in paint samples; if hydroxyproline was absent the painting was determined to contain egg or casein binders, if present the medium was declared to be glue or a combination of egg and glue if present in small quantities.⁷²⁵ Unfortunately, all three conclusions are based on problematic scientific methods. Certainly these paintings are extremely challenging to sample, so if a small amount of hydroxyproline is present it is likely from the glue ground while larger amounts suggest either a distemper medium and/or

Deborah Reed, 2012), 83-101, accessed January 10, 2016, <http://cdn.intechopen.com/pdfs-wm/46061.pdf>.

⁷²² Ibid.

⁷²³ Rothe, "Mantegna's Paintings in Distemper," 82; —, "Andrea Mantegna's 'Adoration of the Magi,'" 111.

⁷²⁴ Rothe, "Mantegna's Paintings in Distemper," 82; —, "Andrea Mantegna's 'Adoration of the Magi,'" 111; Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 29-69.

⁷²⁵ Rothe, "Mantegna's Paintings in Distemper," 81-2.

significant ground contamination.⁷²⁶ If it is absent then it is possible Mantegna employed egg tempera as his primary binder or possibly casein; however, Dunkerton points out potential problems with the Getty's method for the identification of the latter.⁷²⁷ Rothe states that the presence of phosphorous indicates that casein was employed as a binding medium, yet Dunkerton states that phosphorous can be found in bone black, red lakes, residues from egg yolk, and even glue if the collagen is extracted from bones.⁷²⁸ While the National Gallery's reliance on fatty acids alone is fraught with problems, the detection of casein in this instance warrants further research.

Eventually scientists began to utilize different types of reagents designed for gas chromatography, particularly those that remained stable for longer periods and proved more effective at producing FAMES (Figure 5.46) and amino acid markers (Figure 5.59). By 1995, the National Gallery in London began to routinely use m-trifluoromethylphenyl trimethylammonium hydroxide (today referred to as "Meth-Prep II") for the analysis of fatty acids via esterification (Figure 5.46).⁷²⁹ Schilling followed suit, using the same reagent for fatty acid analysis while designing an additional protocol (Figure 5.60) that seems especially appropriate for egg-oil paint systems as it allows for the detection of both fatty acids and amino acids from a single paint sample.⁷³⁰ For amino acid identification, Schilling's protocol

⁷²⁶ The problems associated with combining hot solutions of egg and glue have already been discussed.

⁷²⁷ Rothe, "Mantegna's Paintings in Distemper," 82; Dunkerton, "Mantegna's Painting Techniques," 34.

⁷²⁸ Ibid.

⁷²⁹ Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 16 (1995): 85.

⁷³⁰ Ibid.; Michael Schilling, "Procedure for Quantitative GC-MS Analysis of Amino Acids, Fatty Acids, and Glycerol as (t-butyl-dimethylsilyl) Derivatives," in *MaSC 2007 GC-MS*

involves the addition of the silylating MTBSTFA (N-tert-butyltrimethylsilyl- N-methyltrifluoroacetamide) following acid hydrolysis, a compound that has been found to be more stable and less prone to damage from moisture than other reagents (Figure 5.59).⁷³¹

Based on the fatty acid ratios and/or the amino acid profiles that are obtained, both protocols can theoretically assist in determining:

- a) whether a proteinaceous material is present
- b) the origin of the protein source (e.g. egg, glue) if present
- c) whether a drying oil is present
- d) its nature and origin (e.g. pre-treated vs. non, linseed vs. walnut, etc.) of the drying oil if present

Unfortunately there have not been subsequent publications comparing the two protocols directly. Samples from fresh and aged reference samples (as well as from actual artworks) should be tested in order determine whether the two protocols outlined in Figure 5.60 generate similar results.⁷³² With regard to egg-oil paint systems this issue is particularly relevant, as fifteenth-century Italian paintings are often characterized based on fatty acid ratios (egg vs. oil, vs. emulsion) even if amino acids have been identified. This topic that will be further explored in Chapter 6 (section 6.5) based on actual results obtained from Quattrocento paintings.

Workshop Handbook, ed. Kenneth Sutherland (Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies. Users' Group for Mass Spectrometry and Chromatography, 2007).

⁷³¹ Schilling, "Procedure for Quantitative GC-MS Analysis of Amino Acids, Fatty Acids, and Glycerol as (t-butyl-dimethylsilyl) Derivatives," *Ibid*.

⁷³² Kristin deGhetaldi, "The Organic Analysis of Artworks: Early Challenges and Future Directions," *Western Association for Art Conservation* 34 (September 2012): 12-17, accessed November 12, 2105, <http://www.cool.conservation-us.org/waac/wn/wn34/wn34-3/wn34-304.pdf>.

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Figure 5.60: The flow chart pictured above represents a sample preparation protocol developed by conservation scientist Michael Schilling at the Getty Conservation Institute. Scientists can choose between extracting fatty acids alone (left) or amino acids and glycerol in addition (right) from a given paint sample.⁷³³

Beginning in the late 1990s, additional efforts were being carried out at the Doerner Institut in an attempt to characterize every class of organic binder that could potentially reside within a single sample.⁷³⁴ While this particular protocol shared certain aspects with those proposed by Schilling, it required a greater number of extractions and used TMSH (trimethylsulfonium hydroxide) as its derivatizing agent for fatty acids (Figure 5.61).⁷³⁵ Of

⁷³³ Ibid.

⁷³⁴ Koller, Fiedler, and Baumer, “Die Bindemittel auf Dürers Tafelgemälden,” 102–19.

⁷³⁵ Ibid; Ursula Baumer, Johann Koller, Patrick Dietemann, and Irene Fiedler, “Extraction Procedure,” in *MaSC 2007 GC-MS Workshop Handbook*, ed. Kenneth Sutherland

Figure removed due to copyrighting

Figure 5.61: The flow chart pictured above represents a sample preparation protocol developed by conservation scientists at the Doerner Institut. This six-step extraction procedure is designed to characterize resins, waxes, oils, gums, and proteins that may reside within a single sample.⁷³⁶

greater interest is the extraction step listed in number 4 in Figure 5.61; unless fatty acids are detected during this stage of the analysis (extraction with oxalic acid) it is assumed that no metal soaps are present, suggesting that the artist used either egg tempera (if proteins are detected) or that the artist “first ground his pigments with egg as a binding medium and only added linseed oil as a painting medium on the palette.”⁷³⁷ The latter possibility, while

(Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies. Users’ Group for Mass Spectrometry and Chromatography, 2007).

⁷³⁶ Baumer, Koller, Dietemann, and Fiedler, “Extraction Procedure,” 2.

⁷³⁷ Ibid; Stephanie Dietz et al., “Studying the ‘Graue Passion’ by Hans Holbein the Elder” in

intriguing, is not practical in terms of traditional painting practice. Pigments cannot effectively ground into an egg yolk and/or white medium, as the aqueous binder evaporates quickly and can form coalesced aggregates of pigment that are not ideal for paint application. While the addition of oil may help to break up these dried aggregates, this step seems somewhat superfluous for those who have at least some familiarity with oil painting techniques. Furthermore, the assumption that extractable fatty acids in step 4 (Figure 5.61) correspond only with metal soaps associated with drying oils is difficult to prove; analysis using ATR-FTIR imaging (Figure 5.43) has demonstrated the formation of metal soaps in an egg-based paint medium from a sample collected from Verrocchio's *The Virgin and Child with Two Angels* (Figure 4.23) in addition to reference paints.⁷³⁸

Similar deductions have been made regarding Leonardo da Vinci's *Madonna of the Carnation* (1478-80; Figure 4.26) in Munich based on results obtained in 2006 from two small

Studying Old Master Paintings: Technology and Practice - National Gallery Technical Bulletin 30th Anniversary Conference Postprints, ed. Marika Spring (London: Archetype Publications, 2010), 94; Dietemann, et al., "A Colloidal Description of Tempera and Oil Paints, Based on a Case Study of Arnold Böcklin's Painting 'Villa am Meer II' (1865)," 29-46; Koller and Baumer, " 'Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.' Leonardos Rolle in der frühen italienischen Ölmaleri," 155-71; Koller, Fiedler, and Baumer, "Die Bindemittel auf Dürers Tafelgemälden," 102-19; —, "Vermeers Maltechnik – eine Mischtechnik. Untersuchung der Bindemittel auf dem Gemälde 'Bei der Kupplerin,'" 65-75. Recent analyses carried out by the Doerner Institut have identified small amounts of egg present in oil-based paints in works by Vermeer, Rembrandt, Stefan Lochner, Albrecht Dürer, and Leonardo da Vinci as well as a number of late medieval Cologne paintings using the aforementioned protocol. Further analysis is needed in order to confirm which paint and/or ground layers possess amino acid and fatty acid markers.

⁷³⁸ Spring et al., "ATR-FTIR imaging for the analysis of organic materials in paint cross-sections: case studies on paint samples from the National Gallery, London," 37-45; Mazzeo et al., "Attenuated total reflection micro FTIR characterization of pigment-binder interaction in reconstructed paint films," 65-76.

samples that were collected from the edge of the painting.⁷³⁹ The same extraction method outlined in Figure 5.61 was used for the characterization of drying oils in addition to ion-exchange chromatography for the identification of proteinaceous components (e.g. glue, egg yolk, etc.); however, neither method can effectively identify materials residing in individual paint and/or ground layers. Nevertheless, a sample from the Madonna's blue robe (from the bottom to the top) was reported to contain the following:

- 1) yellowish priming consisting of glue with traces of oil towards the top of the layer
- 2) an *imprimatura* layer consisting of lead white in linseed oil
- 3) brown intermediate layer containing walnut oil and an unidentified natural resin
- 4) black paint layer consisting of carbon black and lead white bound in walnut oil (possibly some resin) with additions of linseed oil and egg protein
- 5) blue paint layer containing lapis lazuli bound in walnut oil, linseed oil, an unidentified natural resin, and traces of egg protein and
- 6) a varnish layer (restoration coating) containing dammar.⁷⁴⁰

While similar results were found with a sample collected from the brown paint, other experts who have examined and analyzed works by Leonardo have cast doubt on the reported findings.⁷⁴¹ Dunkerton suggests that the presence of linseed oil may be due to the application

⁷³⁹ Koller and Baumer, “ ‘Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.’ Leonardos Rolle in der frühen italienischen Ölemalerei,” 155-174. See Chapter 4 for more information regarding medium analysis of paintings by da Vinci and associated painters.

⁷⁴⁰ Ibid.

⁷⁴¹ Ibid.; Jill Dunkerton, “Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence,” *National Gallery Technical Bulletin* 27 (2011): 31. For the brown sample collected from the *Madonna of the Carnation*, the composition of each layer save the glue-gesso ground (from the bottom to the top) is described as the following: 1) yellowish priming consisting of glue with traces of oil towards the top of the layer 2) *imprimatura* consisting of lead white in linseed oil 3) brown intermediate layer containing walnut oil and/or an

of unoriginal oil-containing materials (e.g. paints, varnishes) as the National Gallery London has only identified walnut oil in Leonardo's *The Virgin of the Rocks* (Figure 4.27).⁷⁴² On the other hand, Doerner scientists Johann Koller and Ursula Baumer state that linseed oil was likely added to speed the drying rate of the walnut oil medium (a material that Leonardo describes in his own writings; see Chapter 3, section 3.3), a characteristic that also prompted the artist to use it as the binder in the lower *imprimatura* layer(s).⁷⁴³ Conversely, Koller and Baumer attribute these additions to Leonardo's desire to speed the drying rate of his walnut oil medium and identify linseed oil as the primary binder in the lower *imprimatura* layer(s).⁷⁴⁴ Regarding the presence of protein, the authors again provide a questionable explanation

unidentified natural resin with traces of glue and egg-based proteins 4) varnish layer (restoration coating?) containing dammar, mastic, and walnut oil.

⁷⁴² Dunkerton et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery* (New Haven: Yale University Press, 1994), 203-4; Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 17 (1996), 96-102; Larry Keith, Ashok Roy, Rachel Morrison, and Peter Scade, "Leonardo da Vinci's 'Virgin of the Rocks': Technique and the Context of Restoration," *National Gallery Technical Bulletin* 32 (2011): 42, 48; Dunkerton, "Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence," 31. In "Leonardo in Verrocchio's Workshop: Re-examining the Technical Evidence," Dunkerton summarizes the analytical results in note 53 of the *Madonna of the Carnation* as the following: The results of analysis of two small samples from the edge of the painting are complicated. In addition to the walnut oil, which is clearly the principal binder, small amounts of linseed oil were found in the upper blue layer. Leonardo might have added some linseed oil to his paints (and seems to have used linseed oil for the first white *imprimatura* layer) but another possibility is that it is present as a result of contamination by later oil-varnish layers. Traces of egg proteins were also reported, with the suggestion that they might be related to the preparation of the blue pigment.

⁷⁴³ Koller and Baumer, " 'Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.' Leonardos Rolle in der frühen italienischen Ölemalerei," 155-174; Jean Paul Richter, *The Literary Works of Leonardo da Vinci*, vol. 1 (London: Sampson Low, Marston, Searle & Rivington, 1883), 319-22.

⁷⁴⁴ Koller and Baumer, " 'Er [...] erprobte die seltsamsten Methoden, um Öle zum Malen [...] zu finden.' Leonardos Rolle in der frühen italienischen Ölemalerei," 155-174.

stating that since amino acids (and therefore egg and/or glue) have been found in other oil paintings dating to the Medieval and Renaissance periods, proteinaceous materials must have been occasionally added both during the preparation of pigments as well as the painting process.⁷⁴⁵ While it is not impossible that such practices were adopted, the authors neglect to consider the other possible origins for amino acids, namely natural resins. Furthermore, there is often a higher probability of encountering residues from previous restoration campaigns and even contamination when sampling along the outer edges of a painting, an issue that the Doerner also encountered during the analysis of Antonello da Messina's *St. Sebastien* (Figure 4.8), also claimed to have been painted using egg-oil emulsions and even egg white based on the presence of amino acids.⁷⁴⁶

The main benefit offered by the Doerner method for GC-MS analysis is reflected in its ability to successfully extract wide range of chemical markers from a single sample, an approach that is not often embraced in other analytical laboratories equipped with GC-MS

⁷⁴⁵ Ibid.

⁷⁴⁶ Andreas Henning, "Il 'San Sebastiano' di Antonello da Messina a Dresda. Iconografia e restauro," in *Antonello da Messina: L'opera completa*, ed. Mauro Lucco (Milano: Silvana Editoriale S.p.A., 2006), 85-87; — and Gunter Ohlhoff, *Antonello da Messina: Der Heilige Sebastian* (Dresden: Staatliche Kunstmmlungen, 2005), 61-67. Initial results performed with Fourier-Transform Infrared Spectroscopy (FTIR) pointed towards the presence of an oil-based medium; however, subsequent analysis performed using more sophisticated chromatography methods suggested the presence of egg yolk and/or whole egg and even egg white in three paint samples, with a fourth sample testing positive for animal glue. It is worth noting that the conservator Andreas Henning, who carried out the restoration of the painting, states that the problematic interpretation may be due to where the team was allowed to collect samples, shedding light on some of the realistic challenges often facing conservation scientists. Henning concludes that since all four samples were collected from the edge may not provide an accurate representation of the entire picture it is possible the artist employed drying oils in other sections of the composition. The suggestive use of egg white as a primary binding medium is highly unlikely in this case based on what has been deduced from the analysis of hundreds of Italian Renaissance panel paintings.

instrumentation. The method has recently generated intriguing and fairly credible results relating to the analysis of nineteenth-century works, paintings whose restoration history is either known or less problematic and can be tied to written anecdotal and/or primary sources describing the artist's use of binding media.⁷⁴⁷ While the method may be ill-suited in determining the location and origin of specific organics within minute, multi-layered paint samples collected from fifteenth-century paintings, it is able to confirm the presence of protein rather than merely relying on FTIR and fatty acid ratios produced by GC-MS. The latter approach summarizes the methods used by scientists at the National Gallery London when faced with possible egg-oil paint systems in Renaissance paintings. A recent example can be demonstrated by a sample collected from the Virgin's blue mantle in *The Virgin of the Rocks*.⁷⁴⁸ While FTIR analysis pointed towards the presence of protein in the ultramarine paint, GC-MS produced surprisingly low amounts of azelaic acid indicating that egg is likely not present in the binder (see Figure 5.10).⁷⁴⁹ For whatever reason, the authors opted not to perform amino acid analysis to provide absolute confirmation that protein was not present in the sample, assigning the protein peaks in the FTIR to the possible presence of calcium oxalates and associating the low amount of azelaic acid instead to walnut oil as the primary binding medium.⁷⁵⁰ Furthermore, the authors also describe problems encountered with the

⁷⁴⁷ Dietemann et al., "A Colloidal Description of Tempera and Oil Paints, Based on a Case Study of Arnold Bocklin's Painting 'Villa am Meer II' (1865)," 29-46.

⁷⁴⁸ White and Pilc, "Analyses of Paint Media," 96-102; Keith et al., "Leonardo da Vinci's 'Virgin of the Rocks': Technique and the Context of Restoration," 42, 48.

⁷⁴⁹ Keith et al., "Leonardo da Vinci's 'Virgin of the Rocks': Technique and the Context of Restoration," 42, 48.

⁷⁵⁰ Ibid. For more information on lead soaps found in Old Master paintings see the following: Jaap J. Boon et al., "Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych," in *Proceedings of the Sixth Infrared and Raman Users Group, Florence, 29 March – 1 April 2004*, ed. Marcello

sample collected from the flesh of St. John, pointing out that lead soaps (identified using FTIR) in the paint may have altered the ratio of fatty acids (calculated from the GC-MS

Picollo (Il Prato: Padova, 2004), 66–74; Jaap J. Boon, Frank Hoogland, and Katrien Keune, “Chemical process in aged oil paints affecting metal soap migration and aggregation,” in *AIC Paintings Specialty Group Postprints, 34th Annual Meeting in Providence, Rhode Island, 16–19 June 2006*, ed. Helene Mar Parkin (Washington DC: American Institute for Conservation, 2007), 18–25; Higgitt, Spring, and Saunders, “Pigment-medium interactions in oil paint films containing red lead or lead tin yellow,” 75–95; Keune et al., “Comparative study of the effect of traditional pigments on artificially aged oil paint systems using complementary analytical techniques,” 833–42; Petria Noble and Jaap J. Boon, “Metal soap degradation of oil paintings: aggregates, increased transparency and efflorescence,” in *AIC Paintings Specialty Group Postprints, 34th Annual Meeting in Providence, Rhode Island, 16–19 June 2006*, ed. Helene Mar Parkin (Washington DC: American Institute for Conservation, 2007), 1–9; Petria Noble, Jaap J. Boon, and Jorgen Wadum, “Dissolution, aggregation and protrusion: lead soap formation in 17th century grounds and paint layers,” *Art Matters: Netherlands Technical Studies in Art 1* (2002): 46–61; Petria Noble, Annalies van Loon, and Jaap J. Boon, “Chemical changes in Old Master paintings II: darkening due to increased transparency as a result of metal soap formation,” in *ICOM Committee for Conservation Preprints, 14th Triennial Meeting, The Hague, 12-16 September 2005*, ed. Isabelle Verger, vol. II (London: James & James, 2005), 496-503; David Saunders, Marika Spring, and Catherine Higgitt, “Color change in red lead-containing paint films,” in *ICOM Committee for Conservation Preprints, 13th Triennial Meeting Preprints, Rio de Janeiro, 22–27 September 2002*, ed. Roy Vontobel, vol. II (London: James & James, 2002), 455-63; Annelies van Loon, “Color Changes and Chemical Reactivity in Seventeenth-Century Oil Paintings.” PhD diss., University of Amsterdam, 2008; — and Jaap J. Boon, “Characterization of the deterioration of bone black in the 17th century Oranjezaal,” *Spectrochimica acta, Part B*” *Atomic spectroscopy 59* (2004): 1601-9; —, Petria Noble, and Jaap J. Boon, “The formation of complex crusts due to the degradation of lead white and smalt in seventeenth-century oil paintings: dissolution, depletion, diffusion, deposition” (Poster presented at the conference SEM and Microanalysis in the Study of Historical Technology, Materials and Conservation, British Museum, 9–10 September 2010, London, 2010); Jaap van der Weerd et al. “Chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented paint layers of 17th century paintings,” *Zeitschrift für Kunsttechnologie und Konservierung 16* (2002): 36–51; Jaap J. Boon et al., “Mechanical and chemical changes in Old Master paintings: dissolution, metal soap formation and remineralization processes in lead pigmented ground/intermediate paint layers of 17th century paintings,” in *ICOM Committee for Conservation Preprints, 13th Triennial Meeting Preprints, Rio de Janeiro, 22–27 September 2002*, ed. Roy Vontobel, vol. II (London: James & James, 2002), 401-6.

results).⁷⁵¹ These complexities, amongst other reasons, beg the question as to when binding media analysis is actually considered feasible. Such challenges account for the hesitation to perform destructive sampling of precious works especially if they have undergone multiple restoration campaigns. Medium analysis was not carried out during a 2011 restoration treatment of a “re-discovered” Leonardo, possibly due to the compromised condition of the picture (Figure 5.62).⁷⁵²

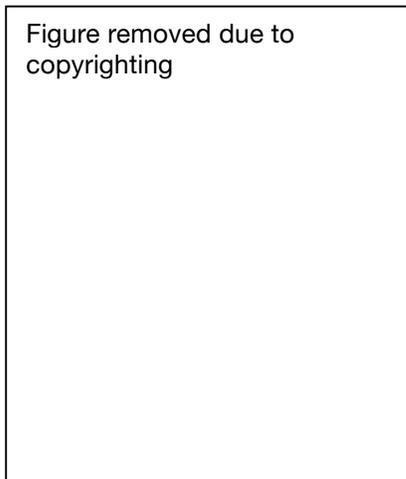


Figure 5.62: Leonardo da Vinci, *Salvator Mundi* (c. 1490-1510, private collection, New York City).

⁷⁵¹ Ibid.

⁷⁵² During a one-day symposium on February 18, 2012 at the Institute of Fine Arts in New York, Dianne Dwyer Modestini presented her work on a “re-discovered” painting attributed to Leonardo da Vinci. Questions posed by the audience members to the panel of conservators, art historians, and scientists revealed that no medium analysis had been performed to determine whether egg and/or oil is present (although today the work is presented as an oil painting). During Modestini’s presentation she showed the audience an image of the painting after the removal of overpaint and discolored varnishes and the composition exhibited several areas that had suffered extensive paint loss and abrasion, presenting possible complications if GC-MS analysis were to have been carried out; however, no efforts were made to perform ATR-FTIR on the cross-sections that were collected.

In light of these observations, caution must be exercised when reviewing information relating to binding media analysis in previous publications found throughout the *National Gallery Technical Bulletin* series as many conclusions appear to have been based on fatty acid ratios which previous sections have demonstrated to be unreliable; contamination from restoration materials, the possible presence of more than one type of drying oil and/or *tempera grassa*, and pigment-binder interactions (metal soaps) can all lead to misinterpretation of these ratios. More recently, scientists and conservators from the National Gallery have summarized their concerns regarding the reliability of ratios, FTIR, cross-sectional staining, and other methods that have been commonly used to characterize binding media.⁷⁵³ The realization that metal soap formation could easily influence fatty acid ratios was formally reported by National Gallery scientists in 2003, in an article that described a direct correlation between the presence of metal soaps and enhanced palmitate and stearate levels.⁷⁵⁴ In 2015, National Gallery scientist David Pegg offered this synopsis specifically relating to the difficulties involved with the interpretation of fatty acid ratios associated with samples collected from Quattrocento paintings:

There are several reasons why an intermediate A-P ratio might be obtained. The first is when both egg and oil are indeed present in the sample. Since the whole sample is derivatised and submitted for chromatographic analysis, the larger the sample required, the greater the likelihood that it may contain several layers of paint. Furthermore, no information will be obtained regarding the spatial distribution of the

⁷⁵³ Spring and Higgitt, "Analyses Reconsidered: The Importance of the Pigment Content of Paint in the Interpretation of the Results of Examination of Binding Media," 223-29; Pegg, "The Chemistry and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century," 223-26; Dunkerton, "Antonello da Messina and oil painting in the 15th century," in *Around Antonello da Messina: Reintegrating Quattrocento Culture*, eds. Michael W. Kwakkelstein and Bette Talvacchia (Firenze: Centro Di, 2014), 35, 46-47.

⁷⁵⁴ Higgitt, Spring, and Saunders, "Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-Tin Yellow," 75-95.

different media, i.e. whether they are present in different layers of the paint structure or within the same layer.

There is also the possibility that any oil detected may not be an original component of the medium. It is extremely rare that the entire conservation history of a work is known and since a paint film might contain coarsely ground pigment particles such as malachite or azurite, the surface may be uneven and/or porous. Any oil observed may therefore be from surface layers, coatings or oil-containing varnishes which have become trapped in the paint texture and not been removed during cleaning.

Another situation which might result in an intermediate A-P ratio being obtained is when a constituent of the paint, such as the pigment or another additive, interferes with the oil binder in some way, altering the expected A-P ratio. [...] This [lead soap formation] results in a lower than expected A-P ratio, suggesting the presence of two binders (egg and oil) when only oil is actually present.⁷⁵⁵

Peggie's last sentence is particularly compelling since earlier publications put forth by the National Gallery London cite multiple Quattrocento paintings that were either completely or partially painted using an egg-oil emulsion or *tempera grassa*.⁷⁵⁶ Jill Dunkerton formally introduced the term to the conservation community as early as 1996, likely inspired by her earlier work on nineteenth-century painting practices and earlier Italian publications; although Dunkerton states that the latter are "scarcely based on any form of scientific analysis."⁷⁵⁷ The

⁷⁵⁵ Peggie, "The Chemistry and Chemical Investigation of the Transition from Egg Tempera Painting to Oil in Italy in the 15th Century," 223-25.

⁷⁵⁶ Jill Dunkerton, Carol Christensen, and Luke Syson, "The Master of the Story of Griselda and Paintings for Sienese Palaces," *National Gallery Technical Bulletin* 27 (2006): 37; Catherine Higgitt and Raymond White, "Analysis of Paint Media: New Studies of Italian Paintings of the Fifteenth and Sixteenth Centuries," *National Gallery Technical Bulletin* 26 (2005): 90-1; Ashok Roy, Marika Spring, and Carol Plazzotta, "Raphael's Early Work in the National Gallery Paintings before Rome," *National Gallery Technical Bulletin* 25 (2004): 7-8; Jill Dunkerton, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," in *Early Italian Paintings, Techniques and Analysis: Proceedings of the Symposium held at the Stichting Restauratie Atelier Limburg, Maastricht, 9-10 October 1996*, ed. Tonnie Bakkenist, René Hoppenbrouwers, and Hélène Dubois (Maastricht: Limburg Conservation Institute, 1997): 29-34; Jill Dunkerton, et al., *Giotto to Dürer: Early Renaissance Painting in the National Gallery*, 197.

⁷⁵⁷ Jill Dunkerton, "Technical Note: Joseph Southall's Tempera Paintings," in *Joseph Southall 1861-1944 Artist-Craftsman*, ed. Dennis Farr (Birmingham: Birmingham Museums &

term has since been widely adopted in publications focusing on the transition for egg to oil painting in fifteenth-century Italy and Quattrocento painting practice.⁷⁵⁸ Much like David Peggie's testament in 2014, Dunkerton also appears to have become more hesitant when faced with interpretation of binding media encountered in Renaissance paintings; some of these concerns were expressed during an international conference on Antonella da Messina in 2012, although curiously Dunkerton's presentation still maintained the infallibility of GC-MS's ability to characterize drying oils and/or egg-oil emulsion based on fatty acid ratios:

An analytical technique such as GC-MS (gas-chromatography-mass-spectrometry) can give remarkably precise results from very small paint samples, distinguishing drying oils from egg tempera and other proteinaceous media, determining the type of oil, whether linseed or walnut, and revealing whether it has been pre-treated by heating (heat-bodied oil). In recent years, however, it has become apparent that when interpreting the results of such analysis, and also those from techniques such as the staining of cross-sections with marker stains that indicate the presence of drying oil, insufficient account has been taken of the interrelationship between pigments and binding media. Even with early Netherlandish painting the occasional use of protein-based media, often apparently in an emulsion with the drying oil, has been reported, especially when results are based on the staining of cross-sections. We now know that lead soaps (formed by a reaction between the oil binder and the lead in a lead-containing pigment such as lead white, lead-tin yellow and red lead) will produce a false positive when stained for protein; that many red lakes were made from the clippings of woollen fabrics died with madder or kermes, resulting in the detection of protein in the wool by sensitive analytical techniques, and that paint films containing ultramarine in oil can generate fatty acid ratios which in the past led to the misidentification of the medium as egg tempera. At the National Gallery the recent acquisition of the imaging technique of ATR-FTIR, which can be used to distinguish the presence of oils and proteins in separate paint layers in cross-section,

Gallery, 1980), 18-24; —, "Modifications to traditional egg tempera techniques in fifteenth-century Italy," 31. See also Umberto Baldini, *Primavera*, trans. Mary Fitton (Sidgwick and Jackson: London, 1984), 48-52.

⁷⁵⁸ See the following: Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Art Press, 2004); Carl Strehlke and Cecilia Frosinini, eds., *The Panel Paintings of Masaccio and Masolino: The Role of Technique* (Milan: 5 Continents Editions srl, 2002).

has already proved invaluable, especially when used in conjunction with the results by GC-MS.⁷⁵⁹

Dunkerton's summary provides an interesting glimpse into the vast and complicated history associated with the scientific laboratory at the National Gallery London, one that I have already demonstrated to be inextricably tied to our current understanding (and misconceptions) regarding Quattrocento painting technique. When directly compared to Peggie's statement, it appears that there are outstanding questions and even disagreements over the weight that continues to be assigned to fatty acid ratios and what they are able to tell us as far as what an artist originally may have used. In either case, both Peggie and Dunkerton's accounts are informative regarding the drawbacks associated with chromatography techniques (particularly GC-MS) as such methods are unable to pinpoint the precise location of oil and egg markers within a multi-layered paint sample, requiring more sophisticated imaging techniques that will be discussed in the following section.

Since the beginning of the twenty-first century, a number of scientists have tackled many challenges associated with the analysis of artworks using GC-MS, seeking ways to work around some of the variables that can alter ratios and hamper detection of organic binders. Based at the University of Pisa, Dr. Maria Perla Colombini and her colleagues have made significant contributions to chromatography-mass spectrometry studies in cultural heritage, publishing one of the first comprehensive texts on the subject in 2009.⁷⁶⁰ Nearly three times the length of Mills and White's seminal textbook (*The Organic Chemistry of Museum Objects*), Colombini and Dr. Francesca Modugno's *Organic Mass Spectrometry in*

⁷⁵⁹ Dunkerton. "Antonello da Messina and oil painting in the 15th century," 35. It should be noted that I also presented at this conference on October 19-20, 2012 and thus had the privilege of attending Jill Dunkerton's presentation.

⁷⁶⁰ See Maria Perla Colombini and Francesca Modugno, eds., *Organic Mass Spectrometry in Art and Archaeology* (New York: John Wiley and Sons, 2009).

Art and Archaeology is a physical testament to the exponential growth in scientific advancements that has occurred since the late 1980s/early 1990s. Directly related to the analysis of egg-oil paint systems, Colombini has been able to demonstrate and quantify the extent to which certain pigments interfere with the recovery of amino acids, building upon past research conducted by Halpine and other scientists.⁷⁶¹ Furthermore, Colombini has also developed one of the more complex multi-step extraction processes for the analysis of organic compounds, much like the protocols designed at the Getty Conservation Institute and the Doerner Institut (Figure 5.63).⁷⁶² Finally, her work has also revealed problems regarding the relationship that is often drawn between the relative amounts of dicarboxylic acids (azelaic,

⁷⁶¹ Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse,'" 22–38; Halpine, "Investigation of Artists' Materials Using Amino Acid Analysis: Introduction of the One Hour Extraction Procedure," 29–69; Vallance, "Applications of Chromatography in Art Conservation: Techniques used for the Analysis and Identification of Proteinaceous and Gum Binding Media," 78; Sarah L. Vallance et al., "The Analysis of Proteinaceous Artist's Media by High Performance Liquid Chromatography," *LC-GC International* 10 (1997): 48-53; Colombini, Modugno, and Giacomelli, "Two procedures for suppressing interference from inorganic pigments in the analysis by gas chromatography–mass spectrometry of proteinaceous binders in paintings," 101-11; Gautier and Colombini, "GC–MS identification of proteins in wall painting samples: A fast clean-up procedure to remove copper-based pigment interferences," 95-102; Bonaduce, Cito, and Colombini, "The development of a gas chromatographic–mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media," 5931-39; Lluveras et al., "GC/MS Analytical Procedure for the Characterization of Glycerolipids, Natural Waxes, Terpenoid Resins, Proteinaceous and Polysaccharide Materials in the Same Paint Microsample Avoiding Interferences from Inorganic Media," 376-86; Maria Perla Colombini and Francesca Modugno, "Characterisation of proteinaceous binders in artistic paintings by chromatographic techniques" *Journal of Separation Science* 27 (2004): 147-60, doi: 10.1002/jssc.200301625.

⁷⁶² Andreotti et al., "Combined GC/MS Analytical Procedure for the Characterization of Glycerolipid, Waxy, Resinous, and Proteinaceous Materials in a Unique Paint Microsample," 4490-500; Colombini et al., "Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry," 715-27; Lluveras et al., "GC/MS Analytical Procedure for the Characterization of Glycerolipids, Natural Waxes,

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Figure 5.63: The flow chart pictured above (from Lluveras et al., 2010) represents a sample preparation protocol developed by conservation scientists at the University of Pisa. This multi-step extraction procedure is meant to characterize resins, waxes, oils, gums, and proteins that may reside within a single sample using an additional step (OMIX C4 purification) to address possible interference from reactive pigments (e.g. copper-containing, lead-containing, etc.).⁷⁶³

Terpenoid Resins, Proteinaceous and Polysaccharide Materials in the Same Paint Microsample Avoiding Interferences from Inorganic Media,” 376-86.

⁷⁶³ Lluveras et al., “GC/MS Analytical Procedure for the Characterization of Glycerolipids, Natural Waxes, Terpenoid Resins, Proteinaceous and Polysaccharide Materials in the Same Paint Microsample Avoiding Interferences from Inorganic Media,” 379.

suberic, and sebacic) and whether an oil is pre-treated using heat.⁷⁶⁴ The various methods of refining oils include a wide range of processes aside from heat (such as water-washing, sun bleaching, etc.) and the presence of driers, pigments, and even natural aging processes can lead to unforeseen deviations in fatty acid ratios.⁷⁶⁵ Dr. Jaap Boon and his colleagues have taken Colombini's research even further, carrying out several studies that expose the inconsistencies associated with the successful recovery of dicarboxylic acids in oil-based paints and thus questioning preconceived notions involving the identification of "heat-bodied" and "partially-heat bodied" oils.⁷⁶⁶

All of these recent efforts have begun to offer a more in-depth picture of the challenges scientists face with when they are attempting to characterize and identify original binding media present in aged paint films. Colombini's work has helped shed light on additional factors that can alter expected and measurable trends in amino acid/fatty acid ratios (such as biological/fungal growth on wall paintings, the presence of restoration materials, etc.) when dealing with Italian wall and easel paintings dating from the thirteenth to the seventeenth centuries. The incorporation of chemometrics (using computer modeling and

⁷⁶⁴ Bonaduce et al., "New Insights into the Ageing of Linseed Oil Paint Binder: A Qualitative and Quantitative Analytical Study," e49333. It appears that different ratios have been used (azelaic/sebacic vs. azelaic/suberic vs. azelaic/sum of dicarboxylic acids) to determine whether or not an oil has been pre-treated, an inconsistency that causes problems when comparing analytical results obtained from different laboratories.

⁷⁶⁵ Ibid.

⁷⁶⁶ Ferreira, van der Horst, and Boon, "Chemical aspects of the binding media of the Oranjezaal ensemble: an insight into 17th century Netherlandish materials and methods," 12-16; Keune et al., "Comparative Study of the Effect of Traditional Pigments on Artificially Aged Oil Paint Systems using Complementary Analytical Techniques," 833-42.

algorithms to help discriminate between related protein sources for example) has quickly found its way into cultural heritage studies, and constitutes an important feature of Colombini's work involving the differentiation between glue, casein, and egg. Using principal component analysis (PCA), plots are generated that can assist in identification by collecting data from dozens of known references (see section 5.3.3 for more information regarding PCA); Colombini and Gwenaëlle Gautier (a former PhD student under Colombini) applied this method to demonstrate the efficacy of their purification step when dealing with copper pigments, showing an improved recovery and therefore correlation of their paint samples to the cluster groups on the PCA plot (Figure 5.64).⁷⁶⁷ Despite these recent advancements in sample preparation, there still appear to be problems when Colombini's methods have been applied to actual works of art. Initial attempts to characterize the wall paintings present within the cemetery in Pisa (which includes frescoes spanning time periods from 1300 to 1700 by a number of artists including Taddeo Gaddi and Benozzo Gozzoli) identified the presence of glue and casein.⁷⁶⁸ Unfortunately, these particular frescoes had suffered from exposure to the elements during World War II, necessitating their detachment and re-attachment using a casein-based adhesive as well as applications of other adhesives to the front of the paintings with facing tissue (see section 5.2.2 for additional information on consolidants applied to

⁷⁶⁷ Gautier and Colombini, "GC-MS identification of proteins in wall painting samples: A fast clean-up procedure to remove copper-based pigment interferences," 95-102.

⁷⁶⁸ Maria Perla Colombini, "GC MS in the Characterisation of Protein Paint Binders," *Science and Technology for Cultural Heritage* 7 (1998): 49-58, doi: 10.1002/jssc.200301625; Maria Perla Colombini et al., "Characterization of Proteinaceous Binders in Wall Painting Samples by Microwave-Assisted Acid Hydrolysis and GC-MS Determination of Amino Acids," *Studies in Conservation* 43 (1998): 33-41, doi: 10.1179/sic.1998.43.1.33; Colombini et al., "Two procedures for suppressing interference from inorganic pigments in the analysis by gas chromatography-mass spectrometry of proteinaceous binders in paintings," 101-11.

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Figure 5.64: PCA score plots of paint samples taken from Gautier and Colombini's 2007 publication (A=casein, B=egg tempera, C=glue) shown together with cluster groups representing reference materials (clear diamonds; grouped into three categories). The A, B, and C samples lie farther outside the designated cluster groups in the left score plot due to pigment interference while the samples shown in the right score plot have been purified and align more closely with their corresponding cluster group. Such techniques can be used to help with identification when several factors must be considered simultaneously.⁷⁶⁹

frescoes).⁷⁷⁰ While Colombini et al. were able to improve their extraction method by reducing the interference caused by the porous and degraded nature of the paint (presumably *a secco*

⁷⁶⁹ Gautier and Colombini, "GC-MS identification of proteins in wall painting samples: A fast clean-up procedure to remove copper-based pigment interferences," 99-100.

⁷⁷⁰ Colombini et al., "Characterization of Proteinaceous Binders in Wall Painting Samples by Microwave-Assisted Acid Hydrolysis and GC-MS Determination of Amino Acids," 34-5. Colombini et al. state the following: Unfortunately, the fact that these frescoes were exposed to the external environment for about five centuries, the bombing during the Second World

additions in this instance) proved too problematic to confirm the original nature of the binding media. On the other hand, analysis of Giotto's *a secco* paints collected from frescoes in the Chapel of the Magdalena at the National Museum of the Bargello (c. 1335) produced more successful results; four samples were found to contain egg tempera while the fifth contained animal glue.⁷⁷¹ The interpretation of the latter is of particular interest as Gautier attributes this phenomenon in her thesis to the presence of calcium oxalates (determined with FTIR), an indication that biological growth on the plaster has led to the formation of hydroxyproline.⁷⁷² If this is the case, then presence of oxalates on wall paintings (or even easel paintings) should be noted when performing protein analysis since these degradation products apparently give rise to the one amino acid that is only found in animal glue.

Colombini and her colleagues have yet to characterize the amino acid profiles associated with additional artists' materials (with the exception of garlic found as an ingredient in a mordant used for gilding).⁷⁷³ Surprisingly, amino acids that can be found in gums and natural resins (identified in studies carried out by both Schilling and Halpine) have

War which destroyed the northern wall and caused a big fire and, above all, human carelessness have caused such damage to the precious frescoes that some parts have been lost for ever. At the end of the last century, therefore, these frescoes were detached from the walls and relocated, using a mixture of milk and casein binder with calcium carbonate in a ratio of 1:3 approximately. After this operation, the frescoes were still not preserved in appropriate conditions and casein degradation made the situation worse. The layers of paint appeared whitened, dusty and corroded by mould and efflorescence, caused above all by the effects of sea air and dampness on casein. They were there-fore detached again and suitably treated for casein removal.

⁷⁷¹ Gautier, "A reliable analytical procedure for the characterization and identification of proteinaceous binding media in wall paintings," 165-9.

⁷⁷² *Ibid.*, 168.

⁷⁷³ Colombini et al., "Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry," 722.

not been factored into Colombini's PCA plots, materials that have been and continue to be used during the restoration of wall and easel paintings. This omission raises additional questions regarding the manner in which mixtures of organic binders are characterized.⁷⁷⁴ Colombini identified the presence of both egg and drying oil in Raphael's *Girl with a Unicorn* (c. 1505-6; Figure 5.65) while "tempera grassa" was found in three works by Lorenzo Lotto (with a fourth identified as egg tempera; Figure 5.66).⁷⁷⁵ While there is no mention of amino

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Figure 5.65: Raphael's *Girl with a Unicorn* (c. 1505-6, Galleria Borghese).

⁷⁷⁴ See Figure 5.11. Hydroxyproline, for example, has been detected in human saliva (often used for cleaning), fruit gums (e.g. almond, cherry, apricot), gum arabic (found in watercolors and/or gouache paints used for retouching), and gum tragacanth.

⁷⁷⁵ Maria Perla Colombini, et al., "A GC-MS study on the deterioration of lipidic paint binders," *MicroChemical Journal* 73 (2002): 175-85, [doi:10.1016/S0026-265X\(00\)00075-8](https://doi.org/10.1016/S0026-265X(00)00075-8); Kamilla B. Kalinina et al., "An analytical investigation of the painting technique of Italian Renaissance master Lorenzo Lotto," *Journal of Cultural Heritage* 13 (2012): 259-74, [doi:10.1016/j.culher.2011.11.005](https://doi.org/10.1016/j.culher.2011.11.005).

acids possibly originating from additional sources, the problematic condition of many of these works makes it impossible to confirm whether these artists originally used both types of media or whether these markers are associated with surface coatings and/or adhesives applied when several were transferred from panel to canvas.⁷⁷⁶ Many of the cross-sections collected from the four Lotto paintings show multiple layers of paint some of which would be impossible to isolate during sample preparation before performing GC-MS analysis.⁷⁷⁷ Taking into account that hydroxproline was found in all samples (meaning that glue was present) as well as the presence of reactive pigments, additional research/analysis is needed to confirm whether these paintings can still be accurately identified as *tempera grassa* or even egg alone (*Rest on the Flight into Egypt with St. Justine*; Figure 5.66).⁷⁷⁸ It is curious that fatty acid/amino acid ratios are used to dictate what Lotto and Raphael originally used as paint binders as Colombini herself warns in an earlier publication against weighing too heavily on

⁷⁷⁶ Kamilla B. Kalinina et al., “An analytical investigation of the painting technique of Italian Renaissance master Lorenzo Lotto,” 259-74. Note that Raphael’s painting has been transferred from panel to canvas as well as Lotto’s *Christ Leading the Apostles to Mount Tabor* (1511/12) and *Rest on the Flight into Egypt with St. Justine* (1529/30).

⁷⁷⁷ Ibid.

⁷⁷⁸ Ibid. The authors state the following regarding Lotto’s technique: Lotto selected a *tempera grassa* technique throughout most of his creative life, although not continuously (*Rest on the Flight into Egypt with St. Justine* was painted using an egg tempera). The addition of a drying oil to egg to make a binding mixture commonly referred to as *tempera grassa* enabled very interesting optical and physical properties of the binder to be obtained. Egg tempera dries very quickly, making it impossible to mix the colours on the palette, and thus, requiring the preparation of each colour shade separately. As a consequence, the paint was commonly applied in several layers by means of small brush strokes. The egg tempera paint is characterised by intensely bright and matt colours. By adding oil to egg, the drying time of the binder increased greatly, allowing the artist to mix the colours on the palette and to apply the paint in homogeneous layers. In addition, it was possible to create layers with an adjustable transparency and of higher colour saturation.

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Figure 5.66: Sample locations collected for analysis from Lorenzo Lotto's *Christ Leading the Apostles to Mount Tabor* (1511/12, top left), *Family Portrait* or *The Portrait of a Married Couple* (1523-24; top right), *Rest on the Flight into Egypt with St. Justine* (1529/30; bottom left), and *The Madonna della Grazie* (1524; bottom right) housed at the State Hermitage Museum in St. Petersburg.⁷⁷⁹

⁷⁷⁹ Kalinina et al., "An analytical investigation of the painting technique of Italian Renaissance master Lorenzo Lotto," 261.

certain markers when faced with possible egg-oil mixtures:

The ratio between the amounts of palmitic and stearic acids (P/S) has been proposed as a possible index for differentiating between drying oils. The ratio is considered constant over time since these two saturated monocarboxylic acids are less subject to degradation during curing and aging. Typical P/S ratio values are reported as 1.4-2.4 for linseed oil, 2-4.5 for walnut oil, 3-8 poppy seed oil, and 2.5-3.5 for egg. However, evaluating this parameter is particularly delicate because of the possible presence of mixtures of different lipid materials, as in “tempera grassa”, and the contribution of fatty acids from other sources, such as natural waxes. [...] Moreover, fatty acids, and especially palmitic and stearic acids, are abundant in the environment and may contaminate the paint layer (hand contact, residues of burning vegetable oils and animal fats for lighting, etc.). Microorganisms can also alter the P/S values of those expected for pure materials. Another important aspect is that fatty acids react with metal cations in paint films thus forming metal soaps. Different reactivity, speed, and solubility of the metal carboxylates in the paint media and in the cleaning solvents could alter the amounts of acids that are recovered in the analysis. Lastly, it is known that fatty acids can sublime over time, altering the ratios between the saturated acids with a different number of carbons, that is, palmitic and stearic acids.⁷⁸⁰ As a result of all these factors, the widely used P/S parameter should be very carefully considered, and in our opinion, further research is needed to define the criteria for reliably identifying the botanical source of a drying oil in a paint sample.⁷⁸⁰

Aside from revealing important information regarding the deleterious effects that pigments can have on binding media analysis, Colombini’s group has also helped to demonstrate yet another problem when comparing the results of one laboratory with another. As outlined throughout this chapter, it is evident that each scientific department in cultural institutions utilizes the resources that are available to them, developing unique methods of sample preparation and extraction processes. This aspect of cultural heritage science makes it increasingly difficult to compare the analytical findings that are associated with a single artist, workshop, or period in art. Results from a “round robin exercise” (where a number of institutions participate in a blind test) were published in 2011; all eleven laboratories reported

⁷⁸⁰ Colombini et al., “Analytical Strategies for Characterizing Organic Paint Media Using Gas Chromatography/Mass Spectrometry,” 722-24; Colombini and Modugno, “Organic Materials in Art and Archaeology,” 9.

slightly different results, with some identifying components that were not actually present in the sample that had been prepared by Colombini's lab (Figure 4.67).⁷⁸¹ Such exercises confirm that a set of guidelines may be needed to move forward in the organic analysis of artworks, establishing a clearer summary of the pros and cons associated with each technique

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Figure 5.67: Analytical results of the round-robin exercise performed in 2011. The unknown sample (aged and unaged) comprised of a mixture containing plaster, beeswax, colophony, pine resin, galbanum resin, pig suet, olive oil, and silver litharge. Each laboratory reported different results with a few instances of false positives (materials shown in italics where not actually present in the sample). This exercise further demonstrates a need for a standardized approach to the organic analysis of artworks.⁷⁸²

⁷⁸¹ Maria Perla Colombini et al., "A Round Robin Exercise in Archaeometry: Blind Analysis of a Sample Reproducing a Seventeenth Century Pharmaceutical Ointment," *Analytical Bioanalytical Chemistry* 401 (2011): 1847-1860, doi: 10.1007/s00216-011-5105-1.

⁷⁸² Colombini et al., "A Round Robin Exercise in Archaeometry: Blind Analysis of a Sample Reproducing a Seventeenth Century Pharmaceutical Ointment," 1858.

and its related protocols. The summary of GC-MS results obtained by the National Gallery London and the Philadelphia Museum of Art relating to Masaccio/Masolino's paintings (Figure 5.34) is an excellent example of this issue; however, Gautier's dissertation in 2006 was perhaps one of the first scientific studies that provided a detailed comparison between a variation of Schilling's GC-MS protocol (Figure 5.60) with Colombini's protocol (Figure 5.63).⁷⁸³ Gautier found that both methods were similar in their abilities to identify and characterize proteins in paint films as long as a purification step was used to suppress the effects of reactive pigments.⁷⁸⁴ Work is still needed in order to assess and compare various protocols and analytical approaches, especially if we are to successfully characterize egg-oil paint systems in Quattrocento paintings. While GC-MS and other chromatographic techniques (e.g. Pyrolysis-GC-MS) are powerful tools, a review of the literature reveals that they are not well suited for multi-layered paint samples and are perhaps best used in conjunction with instruments that are equipped with imaging capabilities.

5.3 Future Prospects: Overcoming Challenges and New Applications

5.3.1 Advancements in Mass Spectrometry-Based Techniques

As noted in the first two sections of this chapter, the increased sensitivity of today's instruments has led to a greater awareness of the complexities associated with the analysis of Quattrocento paintings and the presence of egg, oil, or a mixture of the two. The previous

⁷⁸³ Gautier, "A reliable analytical procedure for the characterization and identification of proteinaceous binding media in wall paintings," 177-8; See section 5.2.2 for more information on the analysis of Masaccio and Masolino's paintings.

⁷⁸⁴ *Ibid.*

sections of this chapter have demonstrated the impact that science has had on our understanding of organic materials found in paintings, compelling scientists to embrace alternative methods in an attempt to address the analytical challenges related to the characterization of degraded paint films. Consequently, recent initiatives in cultural heritage science have focused on improving the identification of proteinaceous materials (e.g. glue, egg yolk, etc.), maintaining the stratigraphy of the multi-layered paint samples during analysis, using non-destructive imaging to detect organic binders, and the potential application of multivariate analysis. The following sections will highlight how each of these areas has been applied to the characterization of egg-oil paint systems encountered in Italian Medieval and Renaissance works of art.

As stated in the previous section, Colombini and Modugno's *Organic Mass Spectrometry in Art and Archaeology* in 2009 demonstrated the ever-growing number of mass spectrometry-based techniques that continue to be used in the identification of organic materials in traditional easel and wall paintings; however, only a handful appear to offer improvements relating to the characterization of egg-oil paint systems. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has been used in recent times to detect peptide fragments in protein sources as opposed to relying solely on the recovery of amino acids. This not only provides unambiguous results regarding protein classification (e.g. egg yolk, casein, glue, etc.) but it can also occasionally confirm the origin of the proteinaceous material (e.g. bone glue, fish glue, hide glue, etc.).⁷⁸⁵ To carry out this method, an enzyme,

⁷⁸⁵ Daniel P. Kirby et al., "Protein Identification in Artworks by Peptide Mass Fingerprinting," in *ICOM Committee for Conservation Preprints, 16th Triennial Meeting, Lisbon, 19-23 September, 2011*, ed. Janet E. Bridgland (Almada: Critério Produção Gráfica, LDA, 2011), 1-10, accessed February 20, 2016, <http://bh1.fpc.pt/winlib/winlibimg.aspx?skey=24ABA9ADFDD94ABEB9B67FB4D9642350&doc=13853&img=3664&save=true.sers/kristindeghetaldi/Downloads/34fa43e0a0304cec8026692c0e399bdd.pdf>; Kirby, Phillips, and Khandekar, "Implementation of MALDI mass

such as trypsin, is applied to the sample (which may or may not be in cross-sectional form) to cleave the intact peptide chains at specific linkages on the chain, a process referred to as digestion.⁷⁸⁶ The resulting fragments consist of amino acids that are linked together in unique sequences, patterns that can then be used to identify the source of the protein using MALDI or another analytical technique (Figure 5.68).

The analysis of a number of Quattrocento easel and wall paintings using MALDI-based techniques was reported beginning around 2006 and in the immediate years that followed.⁷⁸⁷ Due to the nature of this analytical method, it is virtually impossible to obtain

fingerprinting in a museum laboratory for the identification of proteins in works of art,” accessed February 17, 2016, <http://www.ndt.net/article/art2011/papers/KIRBY%20-%20M%201.pdf>; Stepanka Kuckova, Radovan Hynek, and Milan Kodicek, “MALDI-MS Applied to the Analysis of Protein Paint Binders,” in *Organic Mass Spectrometry in Art and Archaeology*, eds. Maria Perla Colombini and Francesca Modugno (Sussex: John Wiley & Sons, 2009), 166-87; —, “Identification of proteinaceous binders used in artworks by MALDI-TOF mass spectrometry,” *Analytical Bioanalytical Chemistry* 388 (2007): 201-6, doi: 10.1007/s00216-007-1206-2; Radovan Hynek et al., “Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry as a tool for fast identification of protein binders in color layers of paintings,” *Rapid Communications in Mass Spectrometry* 18 (2004):1896-1900, doi: 10.1002/rcm.1570; Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 120-1.

⁷⁸⁶ Samples are typically dissolved in a solvent and mixed with a matrix, a mixture of crystallized molecules. Once the solvent is evaporated the matrix absorbs radiation and assists desorption and ionization of compounds from the sample without excessive decomposition.

⁷⁸⁷ Caroline Tokarski et al., “Identification of Proteins in Renaissance Paintings by Proteomics,” *Analytical Chemistry* 78 (2006): 1494-502, doi: 10.1021/ac051181w; Gabriella Leo et al., “Proteomic strategies for the identification of proteinaceous binders in paintings,” *Analytical Bioanalytical Chemistry* 395 (2009): 2269-280, doi: 10.1007/s00216-009-3185-y; Cosima D. Calvano et al., “Fingerprinting of egg and oil binders in painted artworks by matrix-assisted laser desorption ionization time-of-flight mass spectrometry analysis of lipid oxidation by-products,” *Analytical Bioanalytical Chemistry* 400 (2011): 2229-240, doi: 10.1007/s00216-011-4919-1; van der Werf et al., “A simple protocol for Matrix Assisted Laser Desorption Ionization – time of flight – mass spectrometry (MALDI-TOF-SIMS) analysis of lipids and proteins in single microsamples of paintings,” 1-10,

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Figure 5.68: Schematic diagram outlining the various stages of sample preparation, detection, and interpretation of proteinaceous materials used during analysis using matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS).⁷⁸⁸

false positives (as has been found with other techniques such as cross-sectional staining) unless the sample becomes contaminated; if animal glue peptides are detected then they are likely to be present somewhere within the paint and/or ground. On the other hand, it appears that pigment interference remains a problem. While some attempts have been made to address

doi:10.1016/j.aca.2011.12.056; Kirby, Narayan Khandekar, Julie Arslanoglu, and Ken Sutherland, "Protein Identification in Artworks by Peptide Mass Fingerprinting," 1-10.

⁷⁸⁸ "Quantitative Proteomics," accessed February 21, 2016, <https://www.thermofisher.com/us/en/home/life-science/protein-biology/protein-biology-learning-center/protein-biology-resource-library/pierce-protein-methods/quantitative-proteomics.html>.

this issue during sample preparation, it seems that more research is needed in order to confirm how effective certain methods are at recovering proteinaceous markers in the presence of pigments.⁷⁸⁹ Furthermore, scientists have postulated that the presence of synthetic consolidants can also prevent digestion from occurring.⁷⁹⁰ After testing various methods that would help to facilitate protein digestion, scientists from the Universities of Perugia and Naples were unable to identify any proteins in samples collected from fresco fragments from Giotto and Cimabue's frescoes in the upper church in the basilica of St. Francis in Assisi, wall paintings that had been coated with Paraloid B-72 consolidant during previous restoration campaigns.

As with other techniques, interference from pigments or restoration materials can lead to misinterpretation of the binders present in fourteenth and fifteenth-century Italian paintings when MALDI is applied. Analysis of five fourteenth-century Italian altarpieces at the Harvard Art Museum found traces of egg in only six out of nineteen samples (Figure 5.69).⁷⁹¹ One sample revealed the presence of only animal glue and egg white, findings that could lead to the erroneous conclusion that egg white was the primary binder in this particular instance.⁷⁹² Egg white proteins (as well as egg yolk) were also identified in Benedetto Bonfigli's triptych

⁷⁸⁹ Leo et al., "Proteomic strategies for the identification of proteinaceous binders in paintings," 2269-280.

⁷⁹⁰ Ibid. It should be noted that Liquid Chromatography-Mass Spectrometry (LC-MS) with Electrospray Ionization (ESI) was used to analyze the samples as opposed to MALDI; however, both techniques involve protein digestion during sample preparation.

⁷⁹¹ Kirby et al., "Protein Identification in Artworks by Peptide Mass Fingerprinting," 7-8.

⁷⁹² Ibid., 7.

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Figure 5.69: Table from Kirby et al.'s 2012 publication summarizing the analytical results obtained using MALDI on nineteen samples collected from five fourteenth-century Italian altarpieces. The fact that trace amounts of egg yolk (the traditional binder used by fourteenth-century painters) were identified in only a few samples suggests that pigments likely interfere with the detection of peptides.⁷⁹³

⁷⁹³ Ibid.

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Figure 5.70: Benedetto Bonfigli, *The Virgin and Child, St. John the Baptist, St. Sebastian* (mid-1400s, Petit Palais Museum, Avignon).⁷⁹⁴

(mid-1400s, *The Virgin and Child, St. John the Baptist, St. Sebastian*; Figure 5.70) and Niccolo di Pietro Gerini's *Virgin and Child* (1300s).⁷⁹⁵ In comparing both case studies, it seems that egg white proteins may be easier to recover during the digestion process; traces of egg white would certainly accompany egg yolk during the preparation of traditional tempera, and whole egg could also be used as a binder although more research is needed to explore this theory.

⁷⁹⁴ Tokarski et al., "Identification of Proteins in Renaissance Paintings by Proteomics," 1500.

⁷⁹⁵ Ibid., 1494-1502.

While MALDI can concretely identify proteins from specific sources it has not yet been used to generate spatial information, locating protein markers in discrete paint and ground layers on a cross-section. Again this has led to possible misinterpretation of binders used by Italian painters as contamination from the application of surface coatings (e.g. egg white varnishes, oil-resin varnishes) and consolidants (e.g. animal glue) can complicate data processing. Tokarski et al. concluded that both Niccolo di Pietro Gerini and Benedetto Bonfigli used *tempera grassa* since MALDI identified egg proteins while oil was detected using “preliminary histochemical and heating tests” (see section 5.1.1 on the problems associated with chemical/heating tests).⁷⁹⁶ Bartolomeo Vivarini’s *Madonna with Child and St. Bernard, St. Nicholas, St. Vito, and St. John the Baptist* (1490, Figure 5.71) was also

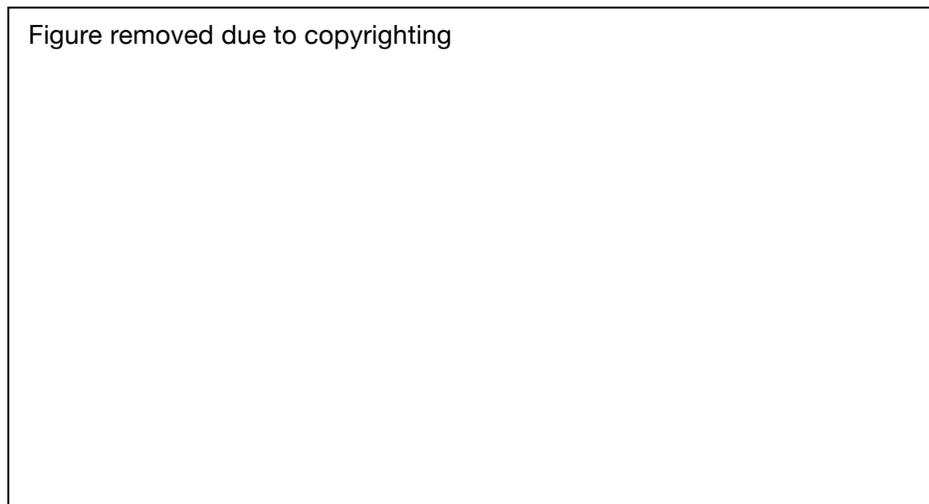


Figure 5.71: Bartolomeo Vivarini, *Madonna and Child and St. Bernard, St. Nicholas, St. Vito, and St. John the Baptist* (1490. Santa Maria Assunta-Polignano a Mare, Italy).

⁷⁹⁶ Ibid., 1501.

determined to have been painted using an egg-mixture; MALDI identified the presence of egg while A/P ratios obtained using Pyrolysis-GC-MS suggested the presence of oil.⁷⁹⁷ As discussed in the previous sections of this chapter, such determinations can be made only when the original stratigraphy of a paint cross-section remains intact during analysis and spatial imaging techniques are applied. It is likely that MALDI will be able to provide such information in the future, but until that time it is a technique that is best used in conjunction with other analytical methods when performing binding medium analysis of easel paintings.

Since 2004, imaging systems associated with Secondary-Ion Mass Spectrometry (e.g. ToF-SIMS) have shown great potential as a characterization tool for organic binders present in artworks.⁷⁹⁸ Secondary ion mass spectrometry (SIMS) is a technique used for spatially

⁷⁹⁷ Calvano et al., “Fingerprinting of egg and oil binders in painted artworks by matrix-assisted laser desorption ionization time-of-flight mass spectrometry analysis of lipid oxidation by-products,” 2229-240. The authors also claim that egg was found in a sample collected from the red bole based on the relative amount of phospholipids. Bole was traditionally prepared using animal glue, not egg, and it is unclear in the paper whether egg proteins were also identified. Glair (egg white) was occasionally used as an adhesive to attach gold leaf to the surface of panels but it was not admixed with bole. As the authors did not test for the presence of glue it is likely that the sample did consist of traditional glue-bound bole.

⁷⁹⁸ Katrien Keune and Jaap J. Boon, “Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden,” *Analytical Chemistry* 76 (2004): 1374–85, doi: 10.1021/ac035201a; Boon, Keune, and Zucker, “Imaging Analytical Studies of Lead Soaps Aggregating in Preprimed Canvas Used by the Hudson River School Painter F.E. Church,” 444–5; Boon et al., “Image analytical studies of lead soap aggregates and their relationship to lead and tin in 15th C lead tin yellow paints from the Sherborne triptych,” 66–74; Jaap J. Boon et al., “Imaging Microspectroscopic, Secondary Ion Mass Spectrometric and Electron Microscopic Studies on Discoloured and Partially Discoloured Smalt in Cross-sections of 16th Century Paintings,” *Chimia* 55 (2001): 952–60, accessed January 25, 2016, <http://www.ingentaconnect.com/udel.idm.oclc.org/search/article?option1=tka&value1=Imaging+Microspectroscopic%2c+Secondary+Ion+Mass+Spectrometric+and+Electron+Microscopic+Studies+on+Discoloured+and+Partially+Discoloured+Smalt+in+Cross-sections+of+16th+Century+Paintings&pageSize=10&index=1>; Annemie Adriaens and Mark G. Dowsett, “Applications of SIMS to Cultural Heritage Studies,” *Applied Surface Science*

Figure removed due to copyrighting

Figure 5.72: Schematic demonstrating the ionization process (using gallium, bismuth, cesium, or other ion beams) used in time-of-flight secondary ion mass spectrometry to collect both organic and inorganic molecular and elemental maps from the exposed surface of embedded paint cross-sections.⁷⁹⁹

resolved organic mass spectrometric analysis, which makes it ideal for medium analysis of layers in paint cross-sections. SIMS is an ultra-high vacuum technique and because of the pulsed nature of the ionization process, ions are generally analyzed on the basis of their time of flight (ToF); the larger the size of the molecule the longer it takes to reach the detector during the ionization process (Figure 5.72). ToF-SIMS systems have a wide-mass range

252 (2006): 7096–101, doi:10.1016/j.apsusc.2006.02.193; Vincent Mazel and Pascale Richardin. “ToF SIMS Study of Organic Materials in Cultural Heritage,” in *Organic Mass Spectrometry in Art and Archaeology*, eds. Maria Perla Colombini and Francesca Modugno (New York: Wiley, 2009), 433–57.; Domenech-Carbo, “Novel analytical methods for characterising binding media and protective coatings in artworks,” 130.

⁷⁹⁹ “Analytical Instrument Facility,” accessed February 39, 2016, <https://www.aif.ncsu.edu/equipment/time-of-flight-secondary-ion-mass-spectrometry/>.

(above 10,000 Daltons), which makes them suitable for analysis of larger polymers as well as smaller molecules that are associated with inorganic pigments. The probe technique analyzes the upper nanometers of exposed paint cross-sections, thus requiring a clean, uncontaminated surface.⁸⁰⁰

With respect to cross-sectional paint samples, imaging ToFSIMS offers four main advantages:⁸⁰¹

- 1) the instrument can be used to simultaneously collect chemical information (both elemental and molecular) from inorganic and organic materials.
- 2) ToF-SIMS is capable of performing both high mass-resolution and high spatial-resolution chemical imaging since the primary ion beam can be focused to less than 1 μm (Figure 5.73). This enables the simultaneous, unambiguous identification of both organic and inorganic species present in discrete areas within a sample, specifically those located in individual layers or as distinct particles.

⁸⁰⁰ Mazel and Richardin, “ToF SIMS Study of Organic Materials in Cultural Heritage,” 433–57. See also Keune, “Binding medium, pigments and metal soaps characterised and localised in paint cross-sections,” (PhD diss., University of Amsterdam, 2005).

⁸⁰¹ Keune and Boon, “Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden,” 1374–85; Pascale Richardin et al., “Identification of Different Copper Green Pigments in Renaissance Paintings by Cluster-TOF-SIMS Imaging Analysis,” *Journal of the American Society for Mass Spectrometry* 22 (2011):1729–36, doi: 10.1007/s13361-011-0171-3; Jana Sanyova et al., “Unexpected materials in a Rembrandt painting characterized by high spatial resolution cluster-TOF-SIMS Imaging,” *Analytical Chemistry* 83 (2011): 753-60, doi: 10.1021/ac1017748; Ester, B. Ferreira, Rachael Morrison, and Jaap J. Boon, “Imaging Chemical Characterisation of Preparatory Layers in Fifteenth and Sixteenth-century North European Panel Paintings,” in *Preparation for Painting: The Artist’s Choice and its Consequences*, eds. Joyce Townsend, Tiarna Doherty, Gunnar Heydenreich & Jacqueline Ridge (London: Archetype Publications, 2008), 50–9.

3) cross-sectional samples can be retained for future analysis. In addition, new organic information can be obtained using cross-sections that have been stored in museums for several decades.

4) ToF-SIMS is one of the few mass spectrometric techniques that allows the user to analyze directly the surface of the unmodified solid sample, which is not subjected to an extraction protocol prior to analysis, nor to the addition of a chemical matrix (as is done with MALDI).

ToF-SIMS imaging not only assists with identification of the materials and techniques used by the artist, but also with identification of compounds associated with pigment/binder alteration or non-original materials that may be present from previous restoration campaigns. While some of the issues discussed above (such as sample contamination) are also

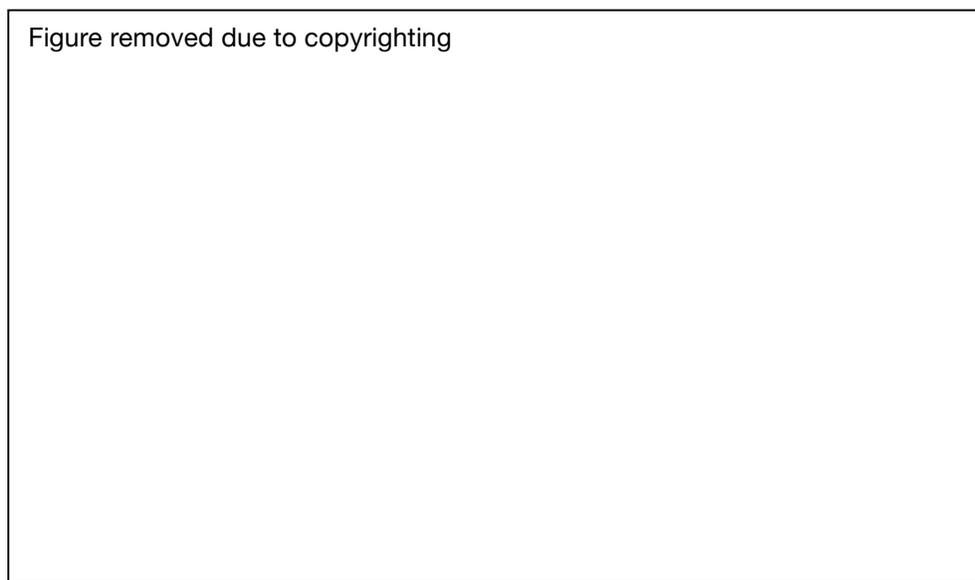


Figure 5.73: Detail of a mass spectrum representing an animal glue reference, demonstrating ToF-SIMS's ability to generate high resolution mass spectra. Mass fragments that bear similar mass to charge ratios (m/z) are more easily differentiated and therefore identified using the soft ionization method.

encountered using ToF-SIMS, the technique has the benefit of providing spatial maps to help distinguish between unoriginal/original materials and to characterize discrete layers. Previous studies have published molecular ion maps corresponding to compounds of interest found in paint cross-section samples: blood has been identified on the surface of African sculptures and protein and starch-containing materials have been located in a paint cross-section collected from Rembrandt van Rijn's *Portrait of Nicolaes van Bambeek* (1641, Figure 5.74). Unfortunately, most of these early applications of ToF-SIMS to the analysis of artworks proved relatively unsuccessful at detecting markers for proteins, particularly those associated

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Figure 5.74: Image of a paint cross-section (left) collected from Rembrandt van Rijn's *Portrait of Nicolaes van Bambeek* (1641, Royal Museum of Fine Arts, Brussels) and the corresponding organic and inorganic materials identified using ToF-SIMS (right).⁸⁰²

⁸⁰² Sanjova et al., "Unexpected materials in a Rembrandt painting characterized by high spatial resolution cluster-TOF-SIMS Imaging," 753, 755.

with egg-based materials.⁸⁰³

As a part of this dissertation project, several samples collected from Italian panel paintings were analyzed using ToF-SIMS. Egg proteins were successfully identified for the first time using this technique in paint cross-sections as well as ion fragments associated with fatty acids (see Chapter 6, section 6.6). The co-localization of certain amino acids and fatty acids within a sample is interpreted as representing egg tempera while the absence of amino acids and presence of fatty acids suggests the presence of drying oil along. When hydroxyproline is identified it often is present in the ground layers but has also been identified in a restoration layer (presumably applied as a consolidant; Figure 5.75) in a paint cross-section collected from an Italian seventeenth-century oil on canvas painting. The ability to map these chemical markers to discrete paint, ground, and varnish layers enables scientists to

⁸⁰³ Boon et al., “Chemical Process in Aged Oil Paints Affecting Metal Soap Migration and Aggregation” 18-25; —, “Imaging Microspectroscopic, Secondary Ion Mass Spectrometric and Electron Microscopic Studies on Discoloured and Partially Discoloured Smalt in Cross-sections of 16th Century Paintings,” 952-60; Boon, Keune, and Zucker, “Imaging Analytical Studies of Lead Soaps Aggregating in Preprimed Canvas Used by the Hudson River School Painter F.E. Church,” 444-5; Keune and Boon, “Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden,” 1374-85; Katrien Keune and Jaap J. Boon, “Analytical Imaging Studies Clarifying the Process of the Darkening of Vermilion in Paintings,” *Analytical Chemistry* 77 (2005): 4742-50, doi: 10.1021/ac048158f; Beatrice Marino et al., “Imaging TOF-SIMS and NANOSIMS Studies of Barite-celestite Particles in Grounds from Paintings by Van Gogh,” *e-Preservation Science* 3 (2006): 41-50, accessed February 12, 2016, <http://www.morana-rtd.com/e-preservation-science/2006/Marino-06-11-06.pdf>; Ferreira et al., 50-9; Katrien Keune et al., “Evaluation of the ‘Added Value’ of SIMS: A Mass Spectrometric and Spectroscopic Study of an Unusual Naples Yellow Oil Paint Reconstruction,” *International Journal of Mass Spectrometry* 284 (2009): 22-34, doi:10.1016/j.ijms.2008.10.016; Keune et al., “Comparative Study of the Effect of Traditional Pigments on Artificially Aged Oil Paint Systems using Complementary Analytical Techniques,” 833-42; Adriaens and Dowsett, “Applications of SIMS to Cultural Heritage Studies,” 7096-101; Mazel and Richardin, “ToF SIMS Study of Organic Materials in Cultural Heritage,” 433-57; Sanyova et al., “Unexpected materials in a Rembrandt painting characterized by high spatial resolution cluster-TOF-SIMS Imaging,” 753-60.

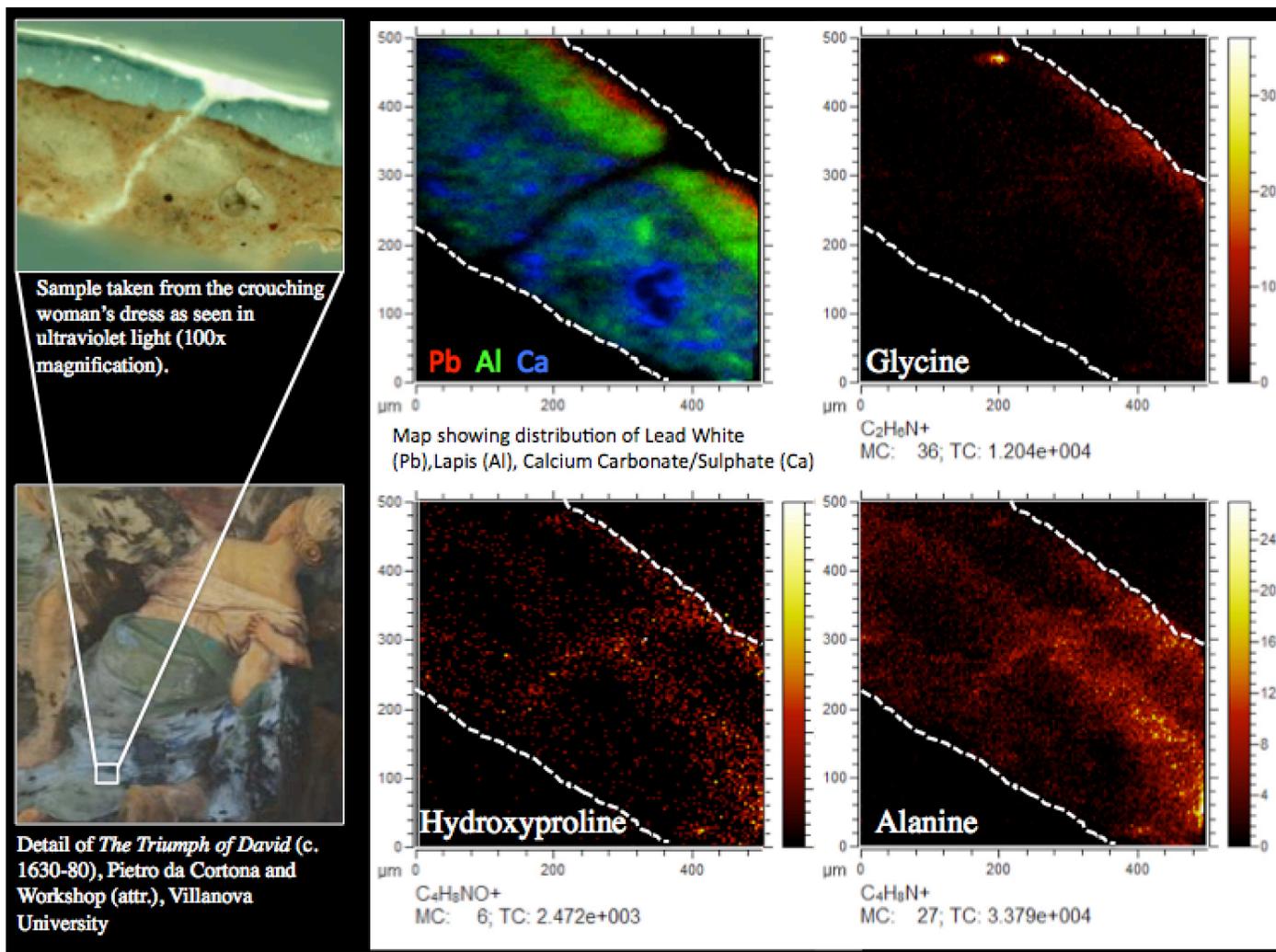


Figure 5.75: ToF-SIMS analysis of a paint cross-section (upper left) collected from *The Triumph of David* (attr. to Pietro da Cortona and Workshop, c. 1630-80, Villanova University). The ToF-SIMS images demonstrate the spatial distribution of elements associated with inorganic pigments (lead white, lapis lazuli, and calcium-containing pigments) as well as the presence of amino acids (shown above are glycine, hydroxyproline, and alanine) that originate from the surface coating. As this layer is shown penetrating the crack in the cross-section, this coating (identified as glue based on the maps above) was applied as part of a later restoration campaign, presumably to consolidant insecure or flaking paint in this section of the composition. This further demonstrates the ability of ToF-SIMS to differentiate between proteinaceous materials (e.g. egg vs. glue) in addition to providing spatial information that can be used to characterize original organic materials from those that were applied during subsequent restorations.

distinguish between original and nonoriginal materials and to develop a better understand of organic binders present in multi-layered paint systems.

As with any technique, ToF-SIMS is not able to answer all questions relating to Quattrocento painting practice. ToF-SIMS (as with MALDI and other chromatography methods) is still unable to concretely identify *tempera grassa* within a paint layer for similar reasons that have been summarized in the previous sections. An interesting discovery was the clear pattern noted in some samples that revealed a significant amount of fatty acid depletion (Figure 5.76). In tempera paint films and/or degraded samples, a lower amount of fatty acids was present along the surface of the uppermost paint layers. This depletion pattern is perhaps (Figure 5.76). In tempera paint films and/or degraded samples, a lower amount of fatty acids was present along the surface of the uppermost paint layers. This depletion pattern is perhaps due to volatilization, previous restoration campaigns, environmental factors, pigment-medium interactions, or some combination thereof, a phenomenon that may also explain why samples collected from the same painting occasionally generate different fatty acid ratios. As with all techniques, ToF-SIMS is best used in conjunction with other analytical methods (e.g. SEM-EDS, GC-MS) in order to ensure that all of the relevant ion fragments are accounted for during data collection. It is also recommended that samples which have already been subjected to ToF-SIMS analysis are re-microtomed before carrying out any subsequent imaging analysis in order to avoid complications that may arise due to potential beam damage.⁸⁰⁴ Finally, recent efforts have combined multivariate analysis (see section 5.3.3), HPLC, and ToF-SIMS techniques (although without imaging capabilities) to successfully identify a glue-based consolidant on a fresco by Ambrogio Lorenzetti in Siena (1331-38,

⁸⁰⁴ The ToF-SIMS system outlined in Chapters 5 and 6 can potentially generate beam damage that extends no more than 3 microns from the outer surface of the cross-section.

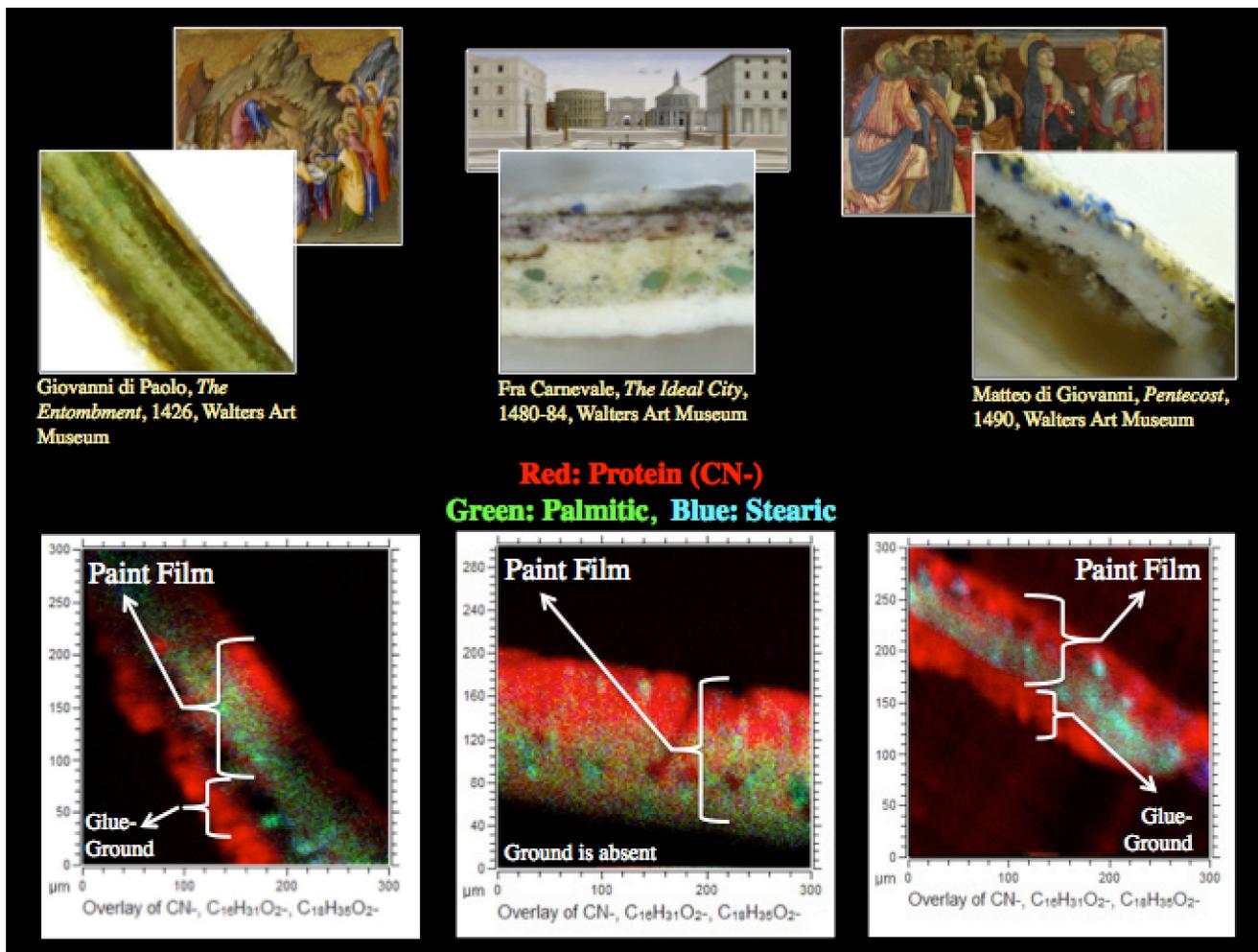


Figure 5.76: Three paint cross-sections (top) collected from Italian paintings at the Walters Art Museum and their corresponding ToF-SIMS images (bottom). Note the depletion pattern observed with the fatty acid signals (palmitic and stearic) mapped against the red signal for proteinaceous materials (CN-).

Madonna and Child enthroned with Saints), further demonstrating the potential of this technique.⁸⁰⁵

⁸⁰⁵ Francesca Benetti et al., "ToF-SIMS characterization of proteinaceous binders in the wall painting 'Madonna and Child enthroned with Saints' by Ambrogio Lorenzetti in the St. Augustine Church (Siena, Italy)," *International Journal of Mass Spectrometry* 392 (2015): 111-17, doi: 10.1016/j.ijms.2015.09.018.

5.3.2 Recent Developments in Non-Destructive Imaging

Over the past decade, technological advancements in non-destructive imaging have allowed scientists to “map” the distribution of certain pigments and organic binders present in painted artworks.⁸⁰⁶ The basic premise of these techniques is to “excite” or illuminate the materials with various wavelengths of light and then record their absorption and/or reflectance spectra using sophisticated detectors, filters, and spectrometers. Hyperspectral imaging performed in the near infrared region (1650-2500 nm) is one such example, a technique that has been recently used to map binders in Quattrocento panel paintings, frescoes, and illuminated manuscripts by collecting vibrational features associated with organic compounds.⁸⁰⁷ While these imaging systems are used to map larger regions of a work,

⁸⁰⁶ Dooley et al., “Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting,” 13775-79; Paola Ricciardi et al., “Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts,” *Angewandte Chemie International Edition* 51 (2012): 5607-10, doi: 10.1002/anie.201200840; Francesca Rosi et al., “Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach,” *Analytical Bioanalytical Chemistry* 395 (2009): 2097-2106, doi: 10.1007/s00216-009-3108-y; Manuela Vagnini et al., “FT-NIR Spectroscopy for non-invasive identification of natural polymers and resins in easel paintings,” *Analytical Bioanalytical Chemistry* 395 (2009): 2107-18, doi: 10.1007/s00216-009-3145-6; Costanza Miliani et al., “Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings,” *Applied Spectroscopy* 61 (2007): 293-99, doi: 10.1366/000370207780220840.

⁸⁰⁷ Dooley et al., *Ibid.*, “Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting,” 13775-79; Ricciardi et al., “Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts,” 5607-10; Rosi et al., “Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach,” 2097-2106; Miliani et al., “Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings,” 293-99.

scientists can also obtain higher-resolution spectra at specific sites (with a spot size measuring around 3 mm) using Fiber Optic Reflectance Spectroscopy (FORS) to confirm the presence of certain pigments and/or binders. Information obtained with FORS can then be used to better inform the scientists when they are mapping larger areas on the same painting as additional features can be recorded using the following spectral ranges:⁸⁰⁸

- 1) the visible range (400-750 nm; predominantly used for pigment identification)
- 2) the near IR range (750-1700 nm; typically used for the identification of hydroxy inorganic pigments like azurite and organic binders)
- 3) further into the near IR range (1700-2500 nm; used to collect features associated with carbonate functional groups and organic binders).

The main benefit of hyperspectral/FORS imaging is that both inorganic and organic information can be obtained without sampling the artworks; however, complex mixtures, the presence of restoration materials, abraded paint films, and other factors can complicate interpretation.

As this type of imaging is quickly being adopted by conservation laboratories, it is worth reviewing recent case studies involving Italian Quattrocento paintings as well as reference paints bound in glue, egg yolk, and drying oil.⁸⁰⁹ Reflectance spectra of lead white

⁸⁰⁸ Ricciardi et al., "Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts," 5607-8; Dooley et al., "Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting," 4839-41.

⁸⁰⁹ Ibid. Ricciardi et al. summarize the particular functional groups that are used to identify binding media: Proteic media are characterized by features associated with amide and carbonyl groups, whereas oils and fats by methylene, methyl and ethenyl functional groups. While vibrational features are weaker in strength than their corresponding features in the mid-IR, working in the NIR relieves the stress on the technical requirements of the imaging spectrometer and light levels on the artwork. I prepared some of the paint references used for

and vermilion reference paints (bound with varying amounts of egg yolk and/or linseed oil) are shown in Figures 5.77 and 5.78.⁸¹⁰ In both sets of reference paints, there is a distinctive shift in the position of the prominent peak centered at around 2300 nm, moving slightly to the right as the percentage of protein (egg yolk) increases. While some of the labeled peaks in the diagrams are spectral features that correspond to the organic binder, other peaks (such as the shoulder at around 2345 nm in the vermilion paints) appear to correspond to the inorganic pigment; however, in considering mixtures of the two pigments, interpretation becomes increasingly more difficult. For example, mixing vermilion, lead white, and egg tempera to create a pink paint may generate a dominant peak centered at 2310 nm, a spectral feature that could easily be misinterpreted as representing a mixed egg-oil binder. Certainly with aged, degraded paint films that involve more than one pigment (in addition to restoration materials) can lead to misinformed conclusions, requiring the analyst to possess an acute awareness of the artwork's condition and restoration history.

Vagnini et al. (scientists from the University of Perugia) specifically describe the complexities involved with characterizing egg-oil paint systems using this technique.⁸¹¹ Relying heavily on multivariate analysis, subsequent studies appear to have successfully overcome some of these challenges, identifying mixed media (egg and oil) in panel paintings

both studies; the same egg-oil paint gradients (see Chapter 6, section 6.1) were also used to test the efficiency of FTIR, GC-MS, and cross-sectional staining techniques.

⁸¹⁰ FORS spectra collected in 2010 by Dr. John Delaney at the National Gallery of Art, Washington using a fiber optic probe spectral radiometer (ASD FS3). I am grateful to Dr. Delaney for sharing this information.

⁸¹¹ Vagnini et al., "FT-NIR Spectroscopy for non-invasive identification of natural polymers and resins in easel paintings," 2110.

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Figure 5.77: Reflectance spectra corresponding to vermilion reference paints bound in egg and/or oil (collected by Dr. John Delaney using an ASD F3 fiber optic probe spectral radiometer).

as well as distinguishing between egg yolk and animal glue.⁸¹² Scientists from the National Gallery of Art in Washington include a FORS spectrum representing Carlo Crivelli's

⁸¹² Vagnini et al., "FT-NIR Spectroscopy for non-invasive identification of natural polymers and resins in easel paintings," 2107-18; Ricciardi et al., "Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts," 5607-8; Dooley et al., "Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting," 4839-41.

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Figure 5.78: Reflectance spectra corresponding to lead white reference paints bound in egg and/or oil (collected by Dr. John Delaney using an ASD F3 fiber optic probe spectral radiometer).

Madonna and Child Enthroned with Donor (c. 1470, Figure 5.79) in their 2012 publication to demonstrate the presence of egg tempera in the binder; however, analysis using FTIR and GC-MS performed in 2007 revealed that both egg and oil are potentially present in throughout the painting.⁸¹³ The scientific report states that amino acids and fatty acids were detected

⁸¹³ Ricciardi et al., “Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts,” 5609; Suzanne Q. Lomax, “Carlo Crivelli Scientific Report – 3 December, 2007,” Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC. FORS spectra collected in 2010 by Dr. John Delaney at the National Gallery of Art, Washington using a fiber optic probe spectral radiometer (ASD FS3).

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Figure 5.79: Reflectance spectra corresponding to various regions found on Carlo Crivelli's *Madonna and Child Enthroned with Donor* (collected by Dr. John Delaney using an ASD F3 fiber optic probe spectral radiometer).

(hydroxyproline was present in both samples suggesting that the ground was inadvertently sampled) although it was impossible to know whether the egg and oil markers were from different paint layers.⁸¹⁴ Although certain sections of the composition were undoubtedly

⁸¹⁴ Lomax, "Carlo Crivelli Scientific Report – 3 December, 2007," Scientific report file housed in the Paintings Conservation Department at the National Gallery of Art, Washington, DC.

painted with egg tempera, the unpublished FORS spectra (Figure 5.79) of the painting appear to reflect some of the confusing results obtained with FTIR and GC-MS. When mixtures of certain pigments are present (as discussed earlier) it seems impossible to confirm whether or not small additions of oil are present, either as a superficial glaze, residues from an old oil-resin coating/overpaint, or mixed directly into the tempera binder. The spectrum associated with the marbled area is of particular interest. Visual examination of this area of the composition using high magnification does reveal transparent glazes throughout this section with very little evident brushwork. While the spectrum appears to reflect certain features that are visible in the 100% oil-lead white spectrum shown in Figure 5.78, the peak at 2056 nm seems to indicate that egg tempera may also be present. Like most techniques, FORS is not able to successfully confirm where these markers exist throughout a multi-layered paint system unless cross-sectional samples have been prepared and analyzed with other techniques (such as ATR-FTIR or ToF-SIMS).

National Gallery scientists have also recently applied these techniques to a series of paintings attributed to Cosme Tura (see Figures 5.56 and 5.58), revealing the “use of distemper (animal skin glue) in the blue paints, egg yolk tempera for the red paints, and a mixture of the two for the other regions.”⁸¹⁵ These particular paintings were subjected to protein analysis using HPLC in 1992 (see section 5.2.3), which also found that egg tempera and glue were used for different passages.⁸¹⁶ Hyperspectral imaging (near infrared) was used to obtain reflectance spectra of reference samples to help identify characteristic peaks associated with lipids (present in egg yolk) and protein (present in both egg and glue-based mediums).

⁸¹⁵ Dooley et al., “Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting,” 4839.

⁸¹⁶ Halpine, “Amino Acid Analysis of Proteinaceous Media from Cosima Tura's *The Annunciation with Saint Francis and Saint Louis of Toulouse*,” 22–38.

Reference spectra were then compared with a spectra collected from a rather degraded azurite-containing robe of Lorenzo Monaco's *Madonna and Child*, a passage that was likely painted in egg tempera (1413, Figures 5.80 and 5.81).⁸¹⁷ In comparing the azurite-egg tempera spectrum to reference spectra (Figures 5.77 and 5.78), the scientists were then able to better characterize the reflectance spectra obtained from the Cosme Tura panels.

Again with FORS, the team was reliant on the appearance of lipid and protein-related features in the reflectance spectra (see the peaks designated "l" and "p" in Figures 5.77 and 5.78). The absence of some lipid peaks was found to be a result of pigment interference (as in the case of azurite which can mask the "l" peaks at around 2309 and 2347 nm), forcing the scientists to rely on the position of other lipid peaks between 1690 and 1760 nm to distinguish between glue or egg yolk (see Figures 5.82 and 5.83). In some instances, the decision to assign binders to specific reasons appears rather arbitrary, especially as FORS was able to detect "a lipidic component in spectra from all regions, even though the lipidic features were much less intense for regions of the blue sky and blue robe where the binder was identified as animal skin glue."⁸¹⁸ For example, the scientists were not able to effectively map the lipid components in the areas painted with earth pigments, suggesting that while egg tempera is likely the binder in areas containing brown there is "less lipid is present" in the brown (e.g.

⁸¹⁷ Visual examination of the robe under high magnification reveals the darkened, degraded nature of the azurite paint film. Using this particular painting as a comparative reference may lead to unforeseen complications due to the condition of the blue robe as well as the likely presence of oil and/or resin residues imbibed in the paint layer. In this case, traces of oil-containing residues from previous coatings and/or oil paint could very easily give rise to weak lipidic peaks in a reflectance spectrum making it difficult to determine whether such features correspond to egg yolk or drying oil.

⁸¹⁸ Dooley et al., "Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting," 4846.

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Figure 5.80 (top left), 5.81 (top right), 5.82 (lower left) and 5.83 (lower right): Lorenzo Monaco's *Madonna and Child* (1413, National Gallery of Art, Washington) and a detail of the darkened, degraded azurite robe (top right). Fiber-optic reflectance spectra from Dooley et al.'s 2013 publication demonstrating lipid and protein features found in reference materials (lower left) and a comparison of spectra corresponding to azurite in egg tempera (collected from Lorenzo Monaco's *Madonna and Child*; Figure 5.80) and azurite bound in glue (right).⁸¹⁹

⁸¹⁹ Dooley et al., "Complementary Standoff Chemical Imaging to Map and Identify Artist Materials in an Early Italian Renaissance Panel Painting," 4841.

the landscape in the foreground and the hair of the figures; see Figures 5.84 and 5.85).⁸²⁰ Is this also possible for other areas of the painting? For the Madonna's blue ultramarine robe, the scientists explain that they were able to observe a weak lipid feature at 2309 nm much like the spectrum shown in Figure 5.83. Instead of assigning this feature to egg tempera (as was done with other colors), it is instead dismissed as possible contamination from restoration materials such as MS2A varnish (2315 nm) and wax (2312 nm).⁸²¹ It seems impossible then to be able to characterize *any* areas on these panels as egg tempera, if these restoration materials are present.

Based on these decisions, the Madonna's robe was ultimately identified as animal glue-bound paint as were the areas of blue sky painted with azurite. While these areas may very well be painted in animal glue (hydroxyproline was identified using HPLC in 1992), the azurite pigment can create a rather granular paint film and depending on where the FORS spectrum was collected the ground is exposed in several areas (see Figure 5.58).⁸²² If the glue ground is visible in any manner it could in fact give the impression that the paint film is also bound with glue (again the spot size of FORS is limited to around 3 mm). Granular paint films can also lead to potential problems when dealing with diffuse reflectance; with increased particle size, the depth of penetration of incident radiation (light) increases, leading to a decrease in overall reflectance and possibly accounting for the weak signals associated with lipid features. While these features can be seen in the spectrum collected from the azurite robe in the Lorenzo Monaco panel (Figure 5.83), the condition of this painting is much different

⁸²⁰ Ibid., 4841-2.

⁸²¹ Ibid., 4846.

⁸²² Halpine, "Amino Acid Analysis of Proteinaceous Media from Cosima Tura's The Annunciation with Saint Francis and Saint Louis of Toulouse," 22–38.

Figure removed due to copyrighting

Figure 5.84 (left) and 5.85 (right): Cosme Tura's *Angel Gabriel* (c. 1475, National Gallery of Art, Washington) and a hyperspectral map of the painting (right) denoting areas bound in glue (blue and green) and egg tempera (red and yellow).⁸²³

⁸²³ Ibid., 4842.

from the condition of the Tura panels. The darkened robe is presently covered with multiple coatings (e.g. MS2A and/or wax) and likely contains imbibed residues of fatty acids from past applications of oil paint and/or oil-resin varnishes, residues that may occasionally account for peaks corresponding to lipidic features in the reflectance spectra (Figures 5.80, 5.81, 5.82, and 5.83). Using FORS techniques it is almost impossible to account for the precise degree of degradation, the distribution of particle size, the presence of coatings, and/or thickness of the film, all of which are factors that can potentially influence the resulting reflectance spectra. While the preliminary results of this study demonstrate great promise in the field of non-destructive imaging, FORS/hyperspectral imaging is best applied in tandem with other techniques when used to characterize binding media particularly relating to the analysis of painted artworks. Analysis of cross-sectional paint samples using imaging ToF-SIMS (see section 5.3.1 and Chapter 6, section 6.6) has revealed depletion patterns associated with fatty acid distribution in certain instances; paint films that are especially aged/degraded, thin, and/or contain larger-sized pigment particles may contain much lower amounts of free fatty acids. Conversely, significant amounts of fatty acids seem to co-localize when lead white is present. It appears that Dooley et al. observed similar results during their analysis of Cosme Tura's panels, although the inability of the hyperspectral system to detect fatty acid signals is instead attributed to the presence of glue instead of egg tempera. This is readily apparent in Figures 5.86 and 5.87, where fatty acids are only mapped to the thickly applied lead white highlights in contrast to the underlying paint layers (containing iron oxides and calcium-based pigments; see the x-radiograph in Figure 5.88) that are so thinly applied that the ground is clearly visible in areas of the face. The authors conclude that these regions are instead painted with animal glue as opposed to considering the impact that layer thickness has on the

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Figure 5.86 (top left), 5.87 (top right), and 5.88 (bottom): A detail of Cosme Tura's *Angel Gabriel* (Figure 5.84) and a hyperspectral map of the painting (bottom) denoting areas presumably bound in glue (blue and green) and egg tempera (red). Note that the glue-ground is easily visible throughout significant areas of the flesh. The bottom image is an x-radiograph of Gabriel's head, demonstrating the thinly applied paint in areas of the face and hair as compared to the lead-white highlights.⁸²⁴

reflectance spectra (as well as the fact that the earth pigments do not appear to generate strong lipid features to allow for effective mapping). There are many factors that may account for the weak lipid features detected in certain areas on these panels, problems that may be addressed

⁸²⁴ Ibid., 4844.

in future studies that involve aged, degraded reference samples that also account for varying levels of paint thickness.

5.3.3 *Chemometrics and Data Processing*

Chemometrics is a technique that is appearing more and more in technical studies of artworks, particularly those involved with the characterization of binding media found in traditional easel and wall paintings. Several examples have already been mentioned in section 5.2.3; therefore, it is worth briefly summarizing what these methods involve and how scientists are applying them to the study of Quattrocento paintings.⁸²⁵ Beginning in the 1990s, advancements in computer programming coupled with multivariate statistical analysis (MVA) facilitated the extraction of meaningful information from complicated datasets, much like those that are often associated with the organic analysis of paint binders.⁸²⁶ These statistical methods offer the possibility of revealing “hidden” relationships when comparing a single sample to an existing set of samples obtained from reference paints while simultaneously accounting for a number of variables such as the presence of pigments, aged vs. fresh samples, etc. Such variables are examples of issues that are impossible to control or predict, adding unwanted complications when dealing with questions relating to identification of artists materials. One particular MVA technique known as Principal Component Analysis

⁸²⁵ Multivariate analysis was also employed to generate the hyperspectral maps shown in Figures found throughout section 5.3.2.

⁸²⁶ Up until this period, statistical analysis used in the study of artworks was limited to the use of descriptive statistical terminology (i.e. averages), comparative methods (i.e. correlation), and various forms of hypothesis testing (i.e. t-tests). While such methods can provide important information regarding experimental design and reproducibility, they may not be sufficient when characterizing the complex mixtures frequently encountered in easel paintings

(PCA) can be used to overcome some of these challenges. Thanks in part to Maria Perla Colombini's work at the University of Pisa (as described in section 5.2.3), PCA has become more frequently applied when mass spectrometry techniques are used to identify organic binding media in paint samples.⁸²⁷

As mentioned in the beginning of this chapter, conservators and scientists are interested in the relative amounts (and presence) of amino acids, fatty acids, and dicarboxylic acids when characterizing potential egg-oil paint systems in Quattrocento paintings. If only one variable is considered during an experiment this is typically not enough data to reveal a pattern. For instance, if the only variable recorded is the ratio of palmitic to stearic (P/S) acid, it becomes increasingly difficult to determine whether or not egg might be present; however, if all possible ratios between organic markers are considered, a pattern may begin to emerge. The relationship between these variables (called *covariance*) can be used to reduce large, complicated sets of data into a manageable number by defining new variables, or *principal components*. These are linear combinations of the initial variables which are subsequently used to generate a visual aid in the form of a PCA score plot (Figures 5.89 and 5.90). Depending on the data and the experimental design, these first few principal components generally account for a large percentage of the variance and thus take into account the most important "features" of a given data set. For example, scientists from the University of Perugia, the Getty Conservation Institute, and the British Museum were able to better characterize the protein binders present in *a secco* paints from fresco reference samples by removing the first principal component (t1) that was highly dependent on the presence of inorganic pigments and fillers. By making a new score plot that focused on the second and

⁸²⁷ Rosi et al., "Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach," 2097-2106.

fourth principal components (labeled as t2 and t4; t3 likely corresponded to a pattern found to bear little significance), the scientists were able to generate a better visual guide for assessing possible protein binders present in actual fresco paint samples (Figures 5.89 and 5.90). In this sense, PCA allows scientists to account for any underlying patterns or relationships that may be otherwise difficult to detect (particularly when samples from actual artworks are limited in number and pigment interference plays a role), generating score plots that can even be used as predictive tools for the identification of binding media.

PCA has also been used to reveal the limitations associated with a given analytical technique in addition to variables that may inadvertently lead to misinterpretation of paint media. Regarding the former, Rosi et al. and Miliani et al. compared samples from a fresco by Pietro Perugino (1531, Figure 5.91) to known references using FTIR and UV-vis reflectance.⁸²⁸ After analyzing dozens of fresco reference paint samples from the Tintori collection, PCA plots demonstrated the potential issues caused by the presence of the carbonate plaster when attempting to identify the organic binders in Perugino's fresco paints.⁸²⁹ Furthermore, both studies encountered difficulty resolving peaks and/or patterns associated with reference samples that were bound in egg tempera.⁸³⁰ Both cases prove that PCA is only as robust as a) the technique being used b) the reference data set and c) the condition of the artwork. For this particular fresco cycle, the scientists were still challenged by

⁸²⁸ Ibid.; Miliani et al., "Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings," 293-99.

⁸²⁹ Ibid., 2102; Miliani et al., "Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings," 295.

⁸³⁰ Rosi et al., "Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach," 2101; Miliani et al., "Fiber-Optic Fourier Transform Mid-Infrared Reflectance Spectroscopy: A Suitable Technique for in Situ Studies of Mural Paintings," 296.

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Figure 5.89 (left) and 5.90 (right): PCA score plots in Rosi et al.'s 2009 study showing *a secco* paint reference samples analyzed with mid-FTIR reflectance spectroscopy. The left image shows that much of the variance when plotting t1 vs. t2 is attributed to the spectral features associated with pigments. Plotting different principal components (t2 vs. t4) for the same data set (right image) allows scientists to group the references according to their binding media (the circled data point represents an outlier, as it falls closer to the *tempera grassa* cluster rather than the egg cluster).⁸³¹

the presence of a casein-based consolidant (that had been applied globally across the surface) as well as significant areas of retouching.

⁸³¹ Rosi et al., "Non-invasive identification of organic materials in wall paintings by fiber optic reflectance infrared spectroscopy: a statistical multivariate approach," 2101.

Figure removed due to copyrighting

Figure 5.91: Pietro Perugino, *Adorazione dei Magi* (1531, Madonna della Lacrime, Trevi, Italy).

Variables can also be removed from data sets, helping to reveal hidden patterns when characterizing binding media. Gwenaëlle Gautier (mentioned in section 5.2.3) provides a nice example of this in her doctoral thesis as three amino acid markers were found to be irrelevant (methionine, lysine, and tyrosine are known to degrade over time) and were subsequently removed from the PCA data set.⁸³² The differences in the score plots before and after this modification helped to improve classification of unknown samples into groups that corresponded to various proteinaceous binders (Figures 5.92 and 5.93). While Gautier's research demonstrates some of the benefits associated with PCA and MVA techniques in general, caution should be exercised when reviewing case studies that are reliant on these methods. As with any type of statistical data analysis, decisions must be made while carefully keeping the context of the original data set and experimental design in mind. One of the strengths of PCA is that it is able to compare multiple variables that are not measured using the same units (i.e. location, temperature, ppm, etc); however, there are times when PCA can "fail" or may not be applicable.⁸³³ Finally, other complications can arise if the data set is handled and manipulated incorrectly (e.g. giving the impression that patterns exist where they do not), something that may compel the researcher or analyst to seek consultation from an experienced statistician. In the case of egg-oil painting techniques used in Quattrocento Italy, it has become apparent that pigments and restoration materials still very much effect the outcome of analytical results even after PCA has been applied.

The history of media analysis in conservation is a topic that is not often discussed; this

⁸³² Gautier, "A reliable analytical procedure for the characterization and identification of proteinaceous binding media in wall paintings," 67-70.

⁸³³ For example, if it turns out that much of the variance in the data set is spread evenly between components, as can occur with high dimensional data sets, PCA may not be beneficial or even possible.

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Figure 5.92 (left) and 5.93 (right): PCA score plots of three *a secco* paint references (green circle = casein, purple triangle = glue, yellow diamond = egg). The top plot was obtained using 14 quantitated amino acids while the bottom relied on 11. Note that the three references are better aligned with their respective cluster groups in the bottom score plot.⁸³⁴

history should be considered when assessing the literature relating to the evolution of oil painting in Renaissance Italy. The success of any given analytical technique depends on its ability to detect (and in some cases quantify) key chemical markers found in egg tempera- and oil-bound paints. Instrumentation and analytical methods (i.e. sample preparation) have greatly improved since the early efforts of Mills and White. Over the years massive spectral libraries representing artists' materials have been developed and organized, giving scientists access to searchable databases. But as with most technological improvements, unforeseen complications can arise. Many instruments, notably techniques involving mass spectrometry,

⁸³⁴ Ibid., 68, 70.

have become more refined and thus able to detect far more compounds than in the past. Conservation scientists now have the daunting task of selecting the most appropriate protocol for sample preparation before bringing the sample to the actual instrument. Finally, numerical references (such as fatty acid and amino acid ratios) that were once used to confirm the presence of *tempera grassa*, egg tempera, and various drying oils have been found to be affected by the presence of restoration materials, pigments, degradation components, and other factors. In moving forward, more research is needed to address these issues including pigment interactions with organic binders, the analysis of complex mixtures, detection limits, and the comparison of analytical protocols and instrumentation. For egg-oil paint systems, analysis with imaging ATR-FTIR and ToF-SIMS has helped to improve our understanding of these complex, multi-layered paint systems as they allow for the detection of inorganic and organic components present throughout intact cross-sectional paint samples. In surveying previous technical studies performed on Italian easel and wall paintings it seems that these techniques can offer significant insight into the evolution of oil painting. While past assumptions regarding egg-oil paint systems require re-examination, the increased sensitivity of today's instruments offers exciting new prospects for scientists, conservators, and art historians who are working in tandem to develop a better understanding of Renaissance painting techniques.

Chapter 6

ANALYSIS IN PRACTICE: USING HISTORICAL RECONSTRUCTIONS AND ACTUAL ARTWORKS TO EVALUATE CURRENT ANALYTICAL METHODS

As instruments have become more sophisticated, we can no longer rely on generic reference materials when it comes to the analysis of easel paintings. Interactions between substrates, ground layers, pigments, surface coatings, and restoration materials must all be considered not to mention the effects of aging. It is important to evaluate paint references that are artificially and/or naturally aged; such samples often exhibit different chemical and physical properties than freshly prepared materials. Work is still needed to assess and compare various protocols and analytical approaches. There are many variables to consider, some of which can prove overwhelming, time consuming, and even impossible to simulate during the organic analysis of art materials. While references will never serve as accurate substitutes for samples collected from actual artworks, they can still be used to assess and compare various protocols and analytical approaches used in cultural institutions. Over the past two decades, paint reconstructions have been used to distinguish historically prepared lead white from its modern counterpart, to explore previous assumptions concerning the pigment “copper resinate,” and to test whether our instruments can successfully detect organic binders/materials present in complex paint systems.⁸³⁵ As most scientists have little time to

⁸³⁵ Kristin deGhetaldi, “The Organic Analysis of Artworks: Early Challenges and Future Directions,” *Western Association for Art Conservation* 34 (September 2012): 12-17, accessed November 12, 2105, <http://www.cool.conservation-us.org/waac/wn/wn34/wn34-3/wn34-304.pdf>; Joyce H. Townsend, Jacqueline Ridge, and Stephen Hackney, *Pre-Raphaelite Painting Techniques* (London, Tate Publishing, 2004): 62-5, 77-8; Margareit Van Eikema Hommes, “Interpreting Historical Sources on Painting Materials and Techniques: The Myth

devote to preparing historically representative paint samples, this is an area where conservators can often offer their service and expertise. Throughout this dissertation, a concerted effort was made to create a series of paint references that represented a range of egg-oil paint systems, using historically accurate pigments and ground materials that were employed by Quattrocento painters. Analytical results of these references provided a basis for comparison when similar analytical techniques were applied to Italian panel paintings dating from the fourteenth to the sixteenth century. The benefits and drawbacks associated with these paint references will be discussed in an analytical context followed by relevant case studies involving the examination of Italian Renaissance paintings. A major goal of this chapter is to stress the important role that paint references can play when assessing current methods of organic analysis applied to traditional easel paintings; analytical protocols used for the identification of binding media can be improved only when their limitations are thoroughly tested and explored.

6.1 Preparation of Paint References

of ‘Copper Resinate’ and the Reconstruction of Indigo Oil Paints,” in *Art of the Past - Sources and Reconstructions*, eds. Mark Clarke, Joyce H. Townsend, and Ad Stijnman (London: Archetype Publications, 2005), 16-23; Leslie Carlyle, “Exploring the Grammar of Oil Paint through the Use of Historically Accurate Reconstructions,” in *The Conservation of Easel Paintings*, eds. Joyce H. Stoner and Rebecca Rushfield (London: Routledge, 2012), 33-38; Amber Kerr, Kristin deGhetaldi, Brian Baade, Zachary Voras, and Christian Petersen, “Deconstructing the Stratigraphy of Color and Design in the Artistic Works of Henry Ossawa Tanner,” in *ICOM Committee for Conservation, 17th Triennial Meeting, Melbourne, 15-19 September 2014*, ed. Janet E. Bridgland, Art. 1306. (Paris: International Council of Museums, 2014), 1-8, accessed January 11, 2016, https://www.academia.edu/14365674/Deconstructing_the_stratigraphy_of_color_and_design_in_the_artistic_works_of_Henry_Ossawa_Tanner.

Using historically accurate raw materials, a series of paint references was created with the intent to re-evaluate analytical procedures that are being used in museum laboratories worldwide. Paint references, or reconstructions, offer the analyst unlimited sampling opportunities; however, caution must be exercised when comparing analytical results obtained from references to those obtained from actual works of art. While accelerated aging can ensure that paint films are completely cured, it cannot truly simulate the effects of natural aging. In addition, pollution, the detrimental effects of light exposure, damage related to fluctuations in humidity and temperature, as well as previous restoration campaigns can all contribute to the natural aging processes and thus the material changes that ensue. In this study, references were created in order to assess the efficacy of different analytical procedures, namely cross-sectional staining, Fourier-Transform Infrared Spectroscopy (FTIR), Gas Chromatography-Mass Spectrometry (GC-MS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

To prepare the reference paints, raw materials and layering methods were based on paint cross-sections that have been published and/or collected from Italian Renaissance paintings. Supports consisted of traditionally prepared gesso grounds (glue mixed with calcium sulfate) applied atop glass or tulip poplar. Pigments representing a range of reactivity, color, and composition were chosen as the primary colorants (lead white, yellow ochre, vermilion, and azurite). Binder formulations were prepared using a stepwise procedure (outlined in Appendix D) in order to create a series of paints ranging from pure egg yolk, to mixtures of egg and linseed oil (*tempera grassa*), to pure linseed (see Figures 6.1 and 6.2). Red lake (brazilwood) and lapis lazuli (refined ultramarine) oil glazes were also applied over the vermilion and azurite paint gradients, respectively, as these multi-layered paint systems are frequently encountered in Renaissance paintings.

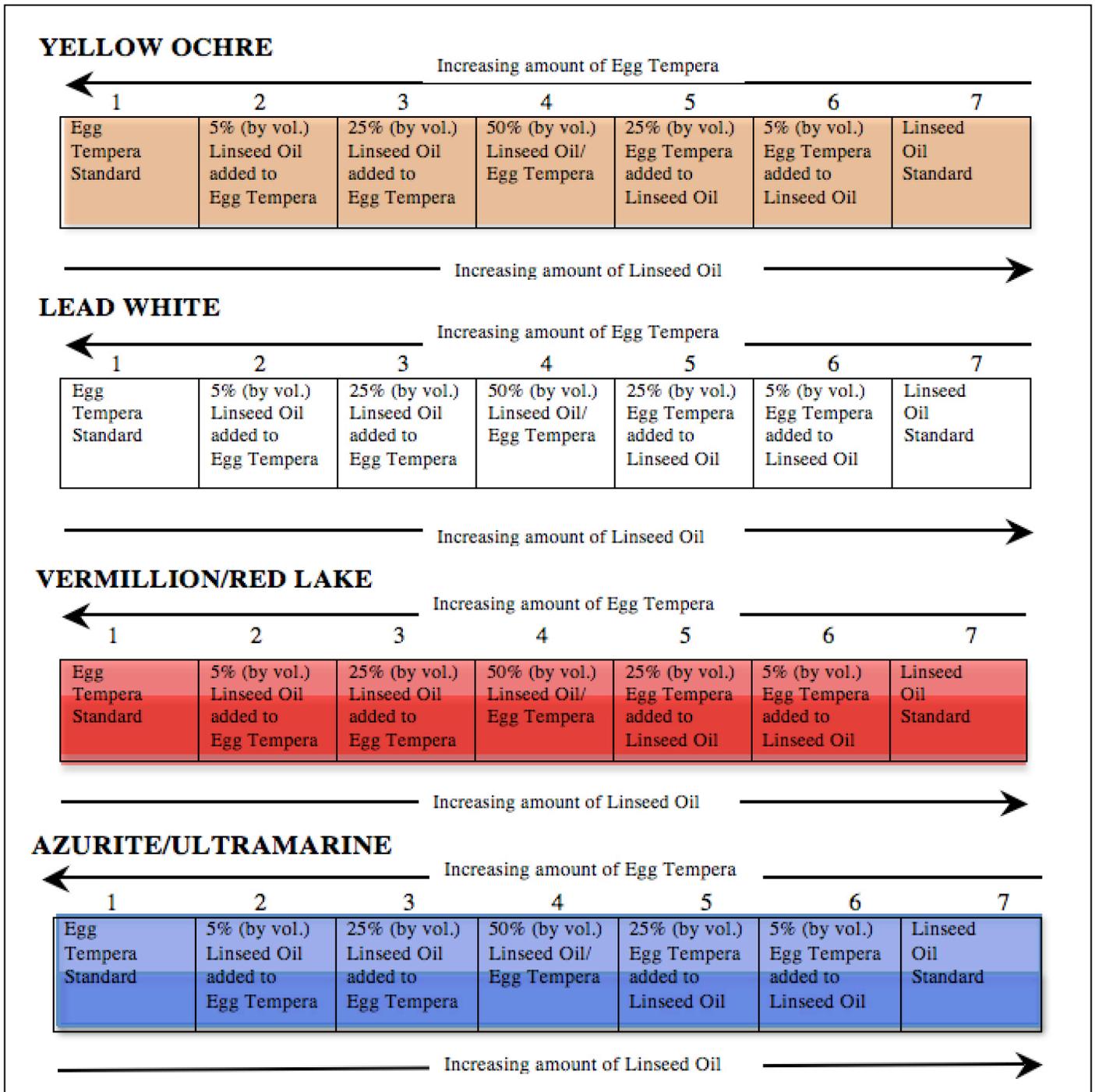


Figure 6.1: Schematic representations of the egg-oil paint gradients shown in Figure 6.2. Two additional sets were prepared on glass substrates to serve as aged and un-aged references.

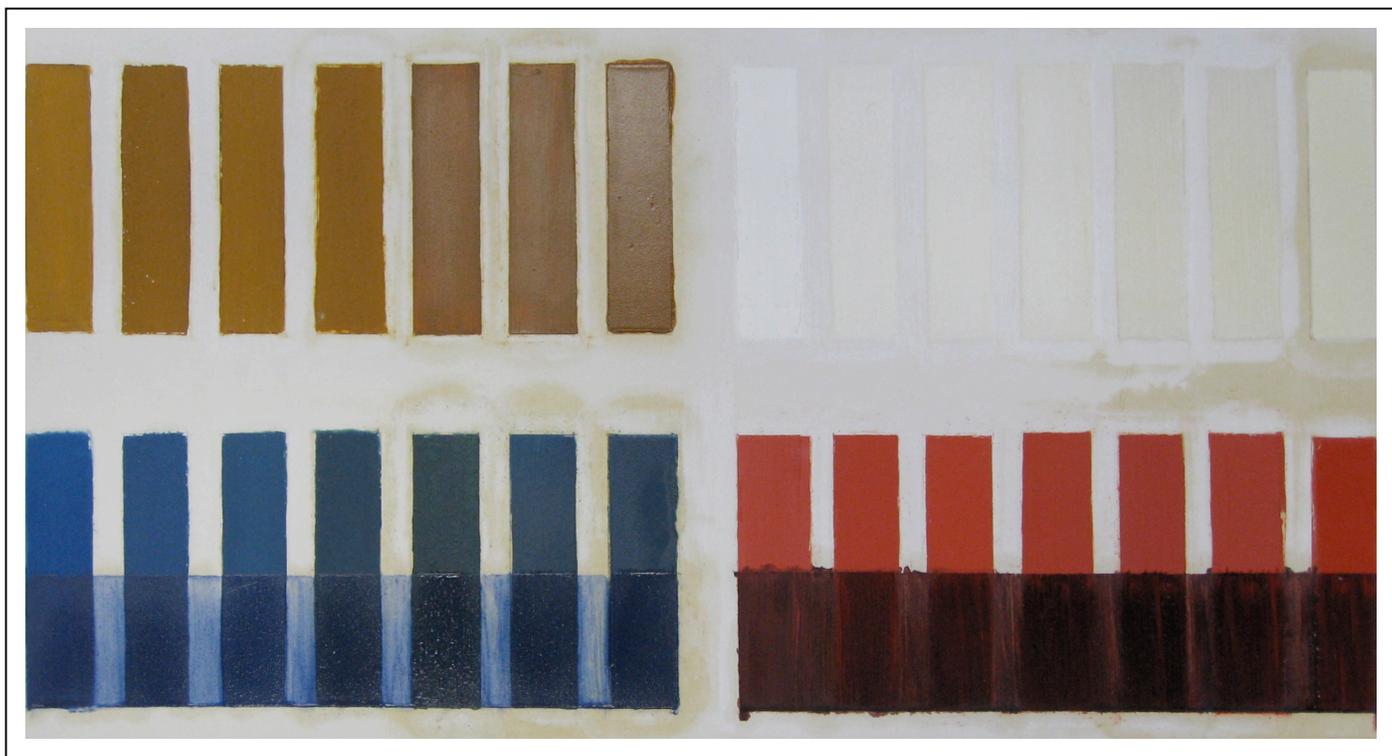


Figure 6.2: Image of the egg-oil paint gradients (schematic shown in Figure 6.1) on the wooden poplar support prepared with traditional gesso. Half of the azurite samples were coated with refined ultramarine bound in oil (lower left) while half of the vermilion samples were coated with brazilwood red lake bound in oil (lower right). Note that these samples were used only for evaluating non-destructive imaging techniques (see Chapter 5, section 5.3.2) while samples prepared on glass substrates were used to evaluate cross-sectional staining, FTIR, GC-MS, and ToF-SIMS.

All four of the color gradients on glass were subjected to accelerated short-term aging at the National Gallery of Art in Washington using an Atlas Ci4000 Weather-ometer, equipped with a Xenon light source (75,000 lux).⁸³⁶ Although long-term artificial aging was

⁸³⁶ I am grateful to conservation scientist Michael Palmer for assisting with the artificial aging process. Samples were aged from July 24, 2009 to August 14, 2009 using the ASTM Gamblin oil paint parameters (45% RH and 25° C for 400 hours).

outside the scope of this experiment, future analytical studies that focus on the characterization of egg-oil paint systems would benefit from samples subjected to long-term aging processes (both artificial and natural). The short-term paint samples on glass were used to evaluate cross-sectional staining techniques as well as Fourier Transform-Infrared Spectroscopy (FTIR), Gas Chromatography-Mass Spectrometry (GC-MS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Paint samples prepared on the wooden poplar support were only used to evaluate non-destructive imaging techniques (see Chapter 5, section 5.3.2).⁸³⁷

6.2 Evaluation of Cross-sectional Microscopy and Staining

Paint samples collected from the gradients summarized in section 6.1 were prepared as cross-sections using the procedure outlined in Appendix E. For the purposes of this study, two stains, Amido Black (II) and Alexa FLUOR 488, were selected. Both are occasionally used to identify and/or characterize proteinaceous materials present in multi-layered paint samples in a number of cultural institutions.⁸³⁸ Amido Black is a non-fluorochrome stain and produces a

⁸³⁷ These tests were carried out by National Gallery imaging scientist Dr. John Delaney in Washington, DC. As non-destructive imaging methods are not yet considered a codified method for the secure identification of egg and/or oil binders, this technique was not extensively explored in this chapter.

⁸³⁸ I am indebted to Richard Wolbers at the University of Delaware and conservation scientists Dr. Barbara Berrie, Dr. Melanie Gifford, and Dr. Michael Palmer at the National Gallery of Art in Washington for their guidance and expertise on staining protocols. It should be noted that at the time this research began in 2008, Amido Black (I, II, and III) was still occasionally being applied to cross-sectional paint samples at various museum laboratories in order to determine the possible presence of animal glue, egg yolk, and other proteins. Alexa FLUOR 488 was first applied to paint cross-sections at the University of Delaware, presumably in the late '90s as Richard Wolbers includes a description of the stain in his

reaction that can be observed using normal visible light (turning a blue-black color) when it comes in contact with proteins (Figure 6.3). Amido Black is a traditional stain that was originally designed for the detection of proteins in electrophoresis. Conservation scientist Elisabeth Martin first adapted the stain to be used on paint cross-sections in 1977 (see Figure 5.19). She summarized the three variations of the stain that can be used to target different classes of proteins:

Amido Black AB1

This staining reagent consists of 1 g of the stain dissolved in 450 mL of glacial acetic acid diluted with 450 mL of .1 M aqueous sodium acetate solution and 100 mL of glycerine. After 5 minutes immersion of this solution the section is washed with 5% acetic acid water. The relatively acid composition of the solution renders it particularly suited to the detection of egg-yolk protein which shows up well regardless of the age of the sample.

Amido Black AB2

1 g of the dyestuff is dissolved in 450 mL of N acetic acid diluted with 450 mL of .1 M aqueous sodium acetate solution and 100 mL of glycerine. Rinsing of the section is carried out with 1% acetic acid water. The reagent is very sensitive and reveals all proteins well, but on the whole it serves less well than AB1 for the detection of egg-yolk protein after ageing. The age of the sample seems to have little influence on the sensitivity and consequently the remains of the protein media in old wall paintings are generally better revealed with AB2 than with reagents utilized previously.

Amido Black AB3

1 g of the dyestuff is dissolved in 900 mL of water with the addition of 100 mL of glycerine. Rinsing of the section is carried out with 1% acetic acid water. It has more or less the same properties as the fuchsine staining reagent previously used, being, like this, in neutral solution. It is used chiefly for revealing gelatine.⁸³⁹

publication from 2000. For more information see Richard Wolbers, *Cleaning Painted Surfaces: Aqueous Methods* (London: Archetype Publications, 2000), 167-83.

⁸³⁹ Elisabeth Martin, "Some Improvements in Techniques of Analysis of Paint Media," *Studies in Conservation* 22 (1977) 63-4.

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Figure 6.3: Chemical structure of Amido Black (Naphthol Blue/Black) staining solution (taken from Sigma Aldrich's website).⁸⁴⁰

Based on Martin's summary above, Amido Black II (AB2) was selected to test its ability to identify egg protein (in the paint layer) and glue protein (in the gesso ground) in the short-term aged paint references (see Appendix E for more information on the staining procedure). In addition, the fluorochrome stain Alexa FLUOR 488 was also evaluated (Figures 6.4 and 6.5). This particular stain was first applied to cross-sectional samples at the University of Delaware (thanks to the efforts of Richard Wolbers); it is a highly sensitive stain and is often used often in the biological field to aid in the identification of proteins. Initial studies using Alexa FLUOR 488 have demonstrated considerable promise when applied to paint cross-sections obtained from works of art so it was decided to include Alexa FLUOR 488 in the cross-sectional staining tests (see Appendix E for more information on the staining procedure).⁸⁴¹ As with the Amido Black II stain, Alexa FLUOR should theoretically be able

⁸⁴⁰ "Amido Black Staining Reagent 2x," accessed March 1, 2016, <http://www.sigmaaldrich.com/catalog/product/sigma/a8181?lang=en®ion=US>

⁸⁴¹ Sharra Grow, "When New and Improved Becomes Outdated and Degraded: The Technical Study and Treatment of a 1964 Pop Art Painted Collage" (paper presented at the Annual

Figure removed due to copyrighting

Figure 6.4 (top) and 6.5 (bottom): Chemical structure of Alexa FLUOR 488 fluorochrome stain solution (taken from ThermoFisher Scientific's website; top) and the excitation (blue) and emission (red) spectra associated with the fluorochrome stain (bottom).⁸⁴²

North American Graduate Program in Conservation Student Conference, Buffalo State College, Buffalo, New York, 2009), accessed December 10, 2015, https://www.ischool.utexas.edu/~anagpic/2009pdf/2009ANAGPIC_Grow.pdf.

⁸⁴² "Alexa FLUOR ® 488 C5 Maleimide," accessed March 1, 2016, <https://www.thermofisher.com/order/catalog/product/A10254>.

to target proteins in egg tempera-containing paint as well as the traditional gesso ground. Both stains were applied to a set of fourteen cross-sectional samples collected from the paint references shown in Figure 6.2 (one set for each stain). In all samples, both stains identified the presence of protein in the glue-containing gesso ground. On the other hand, neither Amido Black II nor Alexa FLUOR 488 was able to identify egg yolk present in the paint layers. This false negative reaction is clearly seen in Figures 6.6 to 6.11 as both stains failed to identify the presence of egg tempera (even without additions of drying oil). The inability of Amido Black and Alexa FLUOR 488 to detect egg yolk proteins is probably due to a number of factors:

- 1) Potential interference from pigments that would prevent the stains from attaching to various binding sites that create the desired color change.
- 2) The pigment to binder ratio may also hinder the necessary reactions from occurring. The proportion of lead white and yellow ochre to egg tempera would be considerably higher as compared with the proportion of calcium sulfate to animal glue in the gesso ground. With a lower amount of calcium sulfate it is possible that there are more binding sites available.
- 3) The small amount of fatty substances that are naturally present in egg yolk may also be inhibiting a positive stain reaction.
- 4) These particular stains may simply be more sensitive to collagen (glue) rather than proteins found in egg yolk.

From these initial experiments, it appears that these two cross-sectional stains may not produce reliable results when attempting to confirm the presence of egg yolk in paint samples, especially as both stains failed to identify egg proteins in paint films that were only aged for a short period of time. While other stains may be able to generate more reliable results, it was



Figure 6.6 (left) and 6.7 (right): Paint cross-section (viewed at 50x magnification) of yellow ochre mixed with egg tempera atop a glue-gypsum ground before (left) and after (right) staining with Amido Black II. Note that only the glue-ground tested positive for the presence of protein.

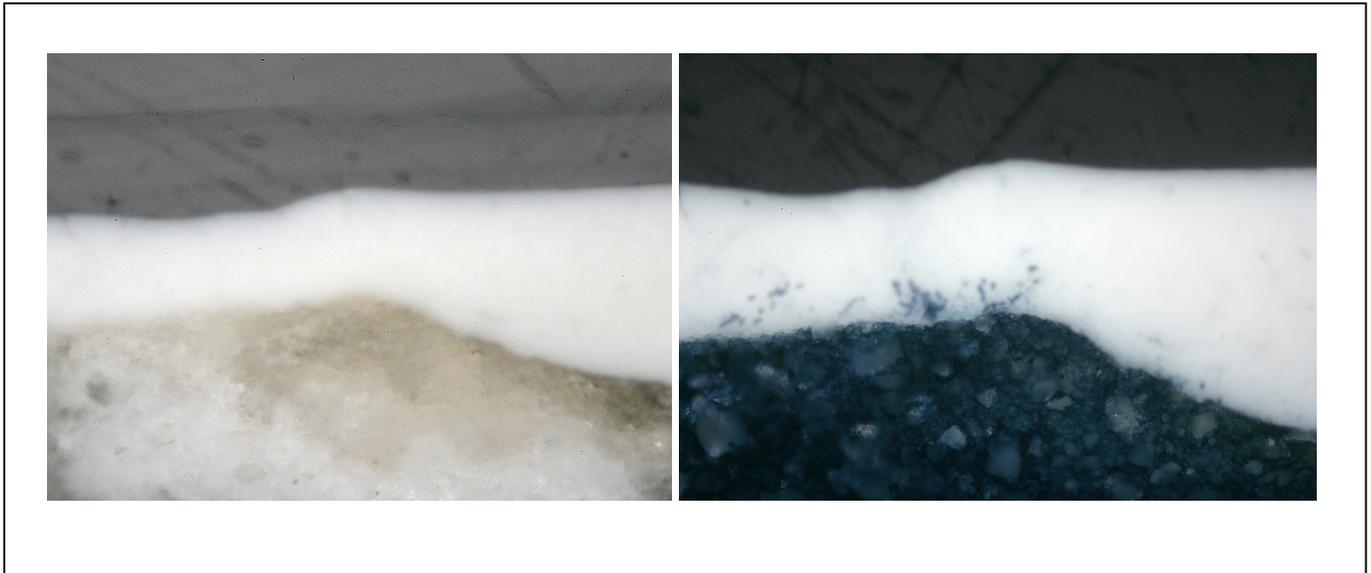


Figure 6.8 (left) and 6.9 (right): Paint cross-section (viewed at 50x magnification) of lead white mixed with egg tempera atop a glue-gypsum ground before (left) and after (right) staining with Amido Black II. Note that only the glue-ground tested positive for the presence of protein.

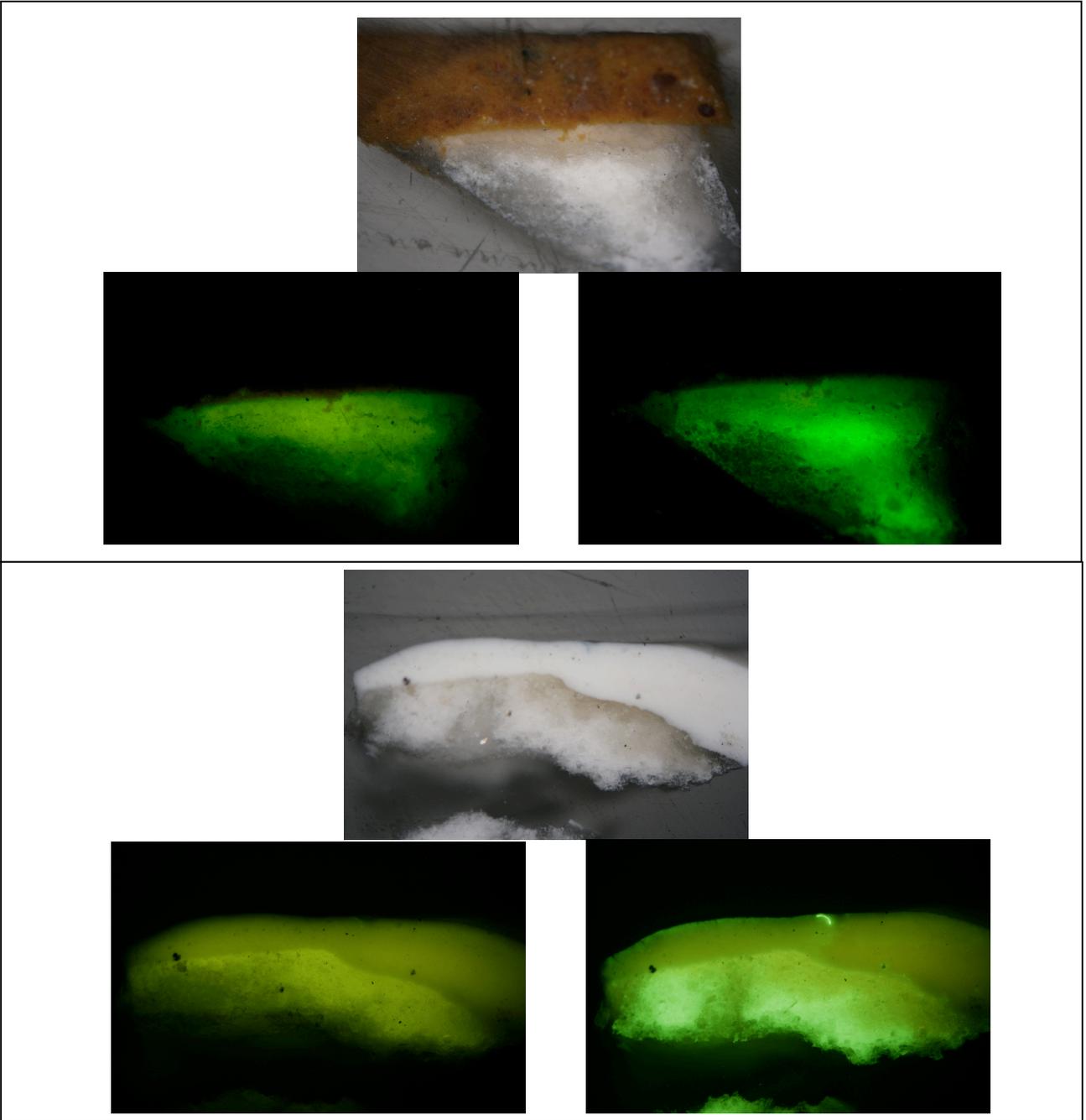


Figure 6.10 and 6.11: Paint cross-sections (viewed at 50x magnification) of yellow ochre (top) and lead white (bottom) mixed with egg tempera atop a glue-gypsum ground as seen in visible light, before (left) and after (right) staining with Alexa FLUOR 488. Note that only the glue-ground tested positive for the presence of protein as indicated by the slight increase in intensity in the green-colored fluorescence seen in the glue ground.

decided not to continue with cross-sectional staining when examining samples obtained from Italian paintings dating from the fourteenth to the sixteenth century.

6.3 Evaluation of Fourier-Transform Infrared Spectroscopy

Fourier-Transform Infrared Spectroscopy (FTIR) was performed on all fourteen paint films (on glass supports) in order to evaluate the efficacy of this technique when attempting to characterize egg and/or oil binders present in paint samples.⁸⁴³ In order to avoid possible interference from proteins in the ground layers (collagen), paint samples were only collected from the side of the glass that did not possess a ground. All samples were compared to reference spectra of aged egg yolk and cold-pressed linseed oil (Figures 6.12 and 6.13). It should be noted that there are presently no reference spectra in the Infrared Users Group database (IRUG) for mixtures representing egg-oil emulsions. Most spectral features represented in the egg and oil references were readily observed in the pigmented paint samples painted with pure egg tempera and pure linseed oil. For example, yellow ochre samples bound in either 100% linseed oil or 100% egg tempera showed positive matches for both media types (Figures 6.14 and 6.15). However, FTIR was only somewhat successful at identifying mixtures of oil and egg when in the presence of the four pigments tested (Figure 6.16 and Appendix F). Characterization of the binder becomes increasingly difficult when egg tempera constitutes 50% or less of the binding medium. In comparing the various spectra associated with each pigment, a distinctive pattern was noted but was limited to peaks that fall within the region of 1750-1500 wavenumbers (Figure 6.16). This problem is further compounded by the fact that there are no references of egg-oil emulsions (pigmented, un-

⁸⁴³ See Appendix F for information relating to the instrumental parameters, make, and model.

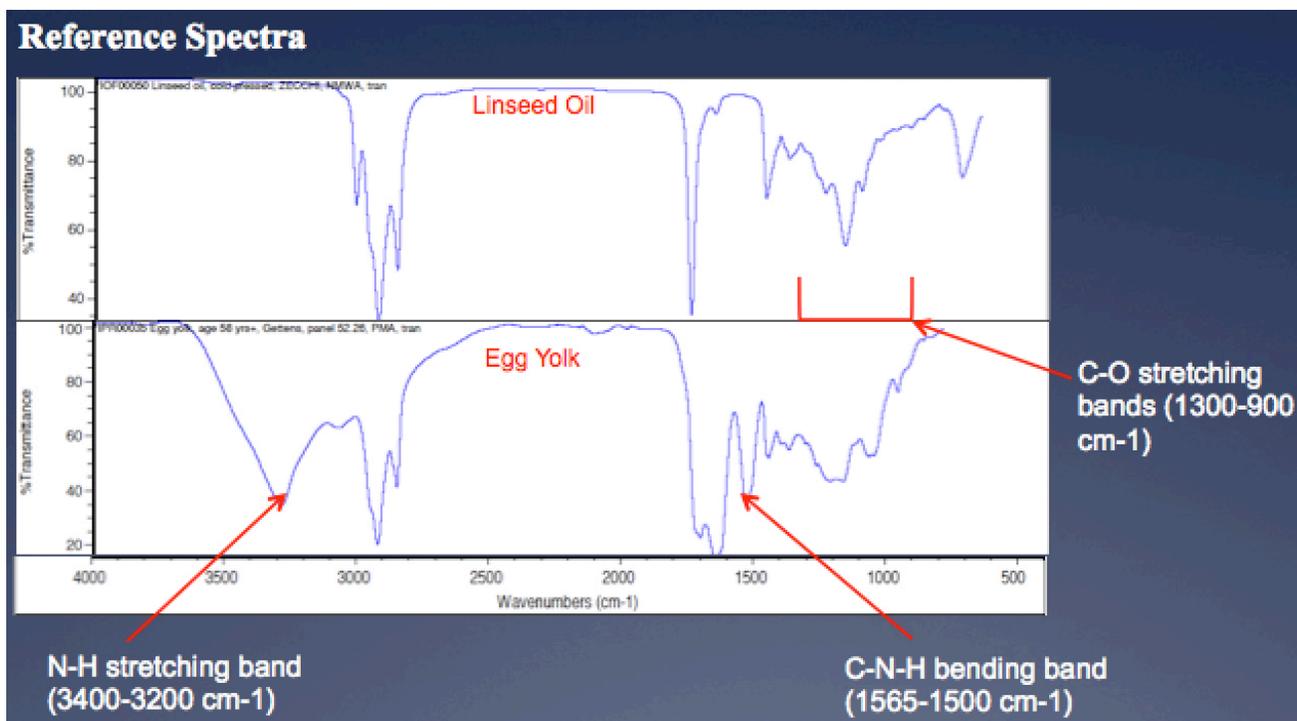
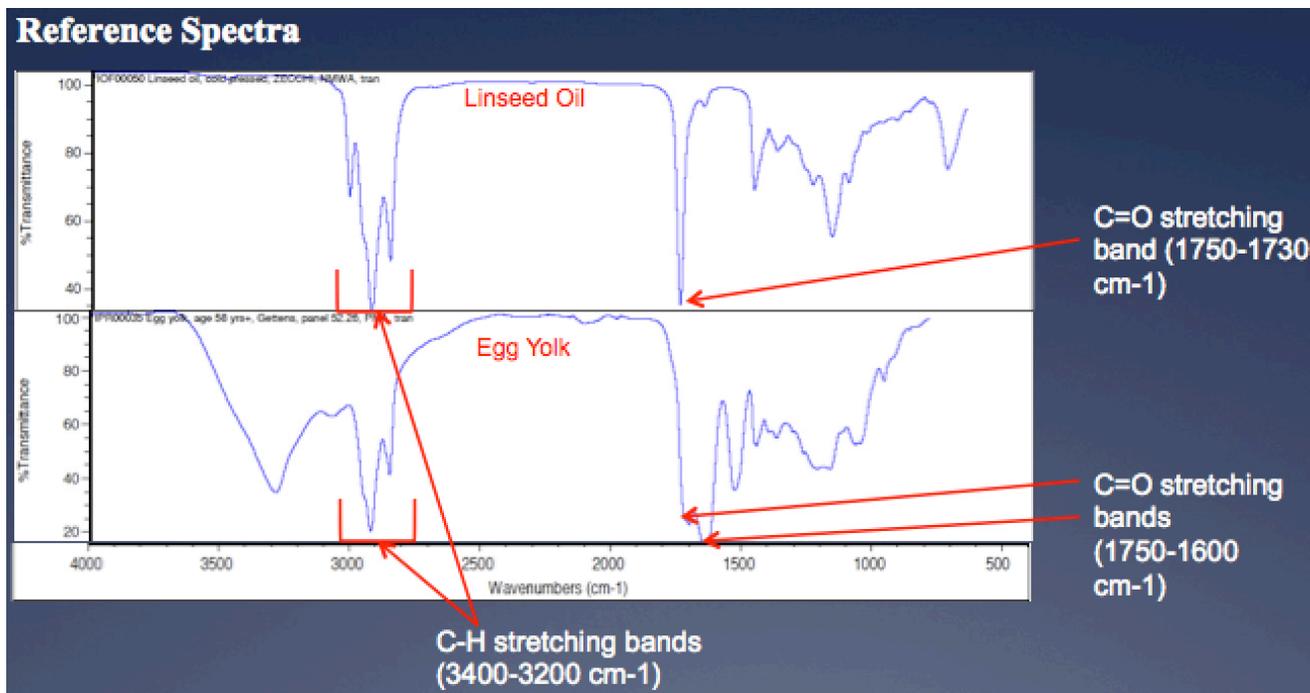


Figure 6.12 (top) and 6.13 (bottom): Comparison of similarities (top) and differences (bottom) between FTIR reference spectra (acquired from the IRUG database) associated with cold-pressed linseed oil (obtained from Zecchi) egg yolk (aged more than 58 years).

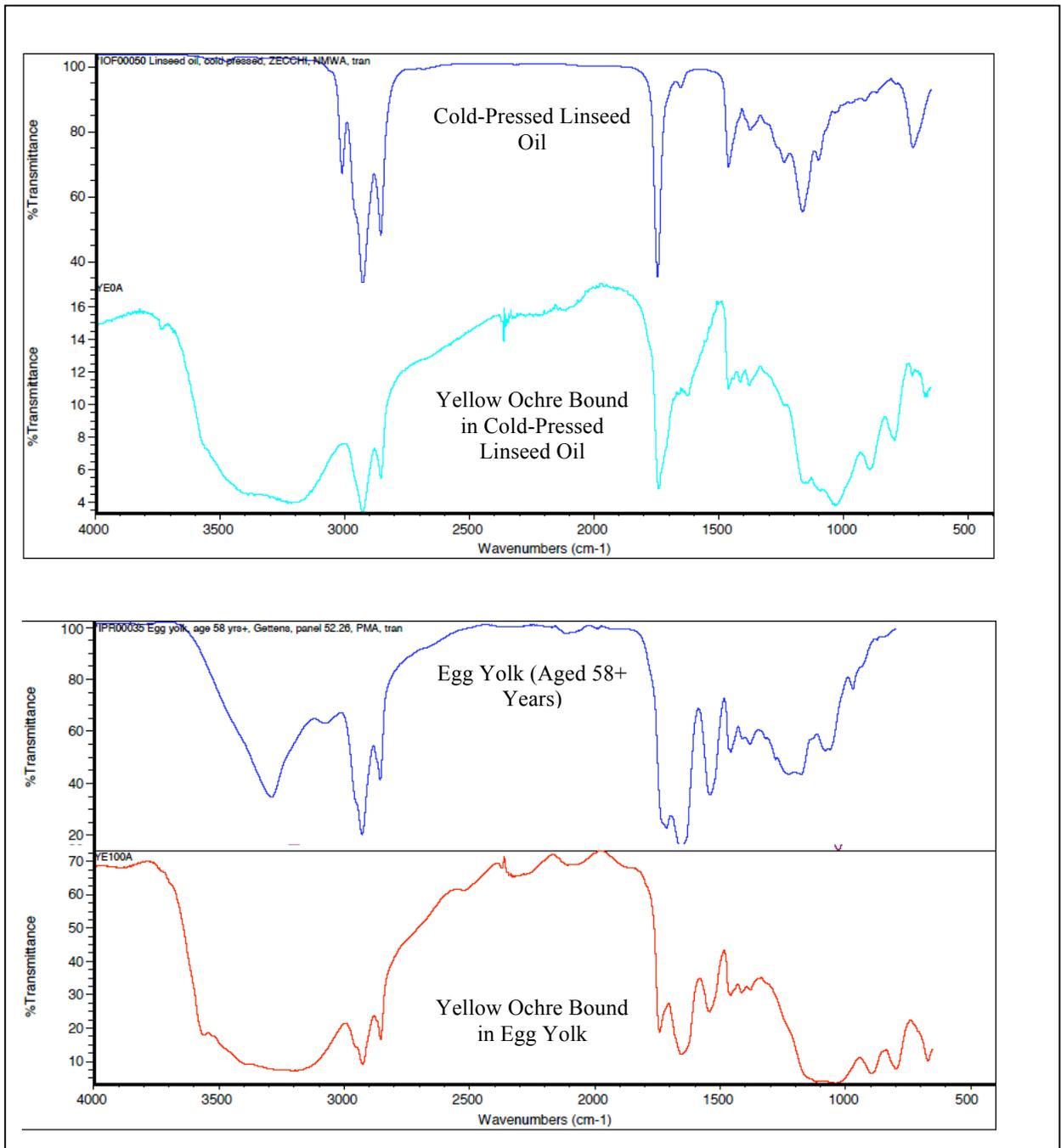


Figure 6.14 (top) and 6.15 (bottom): Reference spectra from the IRUG database (dark blue) compared to FTIR spectra collected from paint samples: yellow ochre bound in egg tempera paint sample (top) and yellow ochre bound in drying oil (bottom). Spectral features from both paint samples corresponded to features visible in the reference spectra.

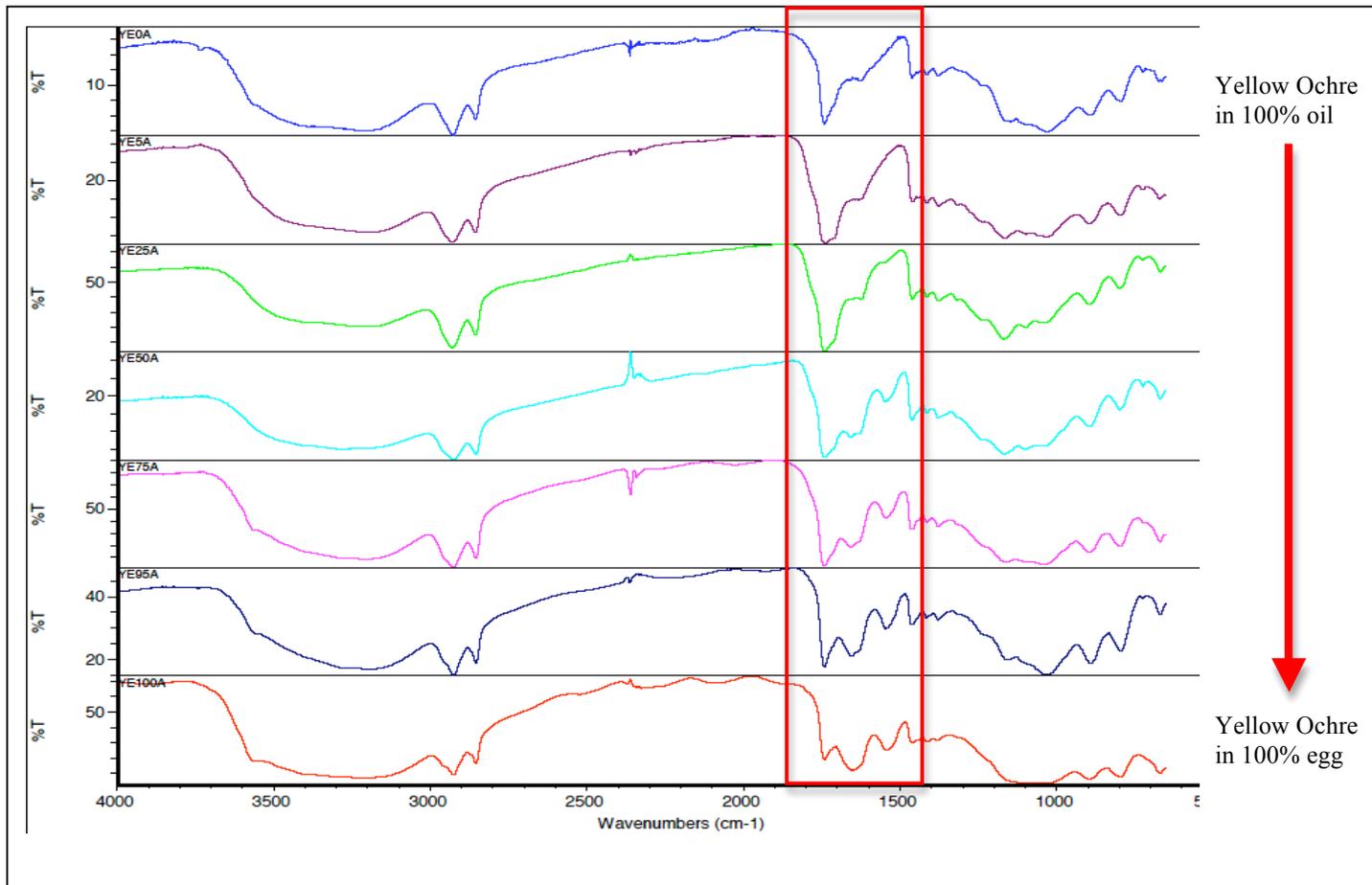


Figure 6.16: FTIR spectra of yellow ochre egg and/or oil-containing paints. Note the distinctive trend in peak patterns observed in the 1750-1500 wavenumber region.

pigmented, fresh, or aged) currently in the IRUG database. In addition, certain pigments were also found to interfere with the data collection, masking peaks in areas of interest that are used to identify the presence of protein and/or drying oils.

Similar results were also obtained when paint cross-sections were analyzed using ATR-FTIR (not pictured).⁸⁴⁴ In some cases, layered systems containing thin oil glazes of

⁸⁴⁴ ATR-FTIR was performed in the laboratory of Professor Karl Booksh (Chemistry Department at the University of Delaware) by Kristin deGhetaldi. Collected spectra were

brazilwood or lapis pigment could not be effectively distinguished from the oil and/or egg-containing lower paint layers. As discussed in the previous chapter, ATR-FTIR systems must be equipped with sophisticated imaging systems when attempting to characterize multi-layered paint systems. Finally, and perhaps most important, FTIR is not able to distinguish one protein source from another (e.g. egg vs. glue). If a painting has been subjected to past restoration campaigns involving glue linings, consolidation, etc., proteinaceous materials identified in paint samples collected from Italian Renaissance paintings using FTIR may be misinterpreted as egg yolk.

6.3.1 Case Studies: Analysis of Italian Paintings using Fourier-Transform Infrared Spectroscopy

The painting shown in Figure 6.17 was treated from 2009-2010 at the National Gallery of Art, affording the conservation staff the opportunity to better examine the materials and techniques used to construct the work.⁸⁴⁵ It should be noted that when performing FTIR analysis of a dispersed sample in transmission mode, multiple spectra can often be collected in order to develop a better understanding of mixtures that may be present (pigments and/or binders). Five samples were collected for FTIR analysis from the following areas: the blue background, the ultramarine robe, a section from a green stem, a red rose, and the neck of the

compared with reference spectra in the IRUG Database. See Appendix F for information relating to the instrumental parameters used and the instrument make/model.

⁸⁴⁵ As the Andrew W. Mellon Fellow in Paintings Conservation between 2008 and 2010, I had the privilege of restoring the painting and was given the opportunity to conduct a technical study of the picture.

Figure removed due to copyrighting

Figure 6.17: Follower of Fra Filippo Lippi and Pesellino, *Madonna and Child* (c. 1420, National Gallery of Art, Washington DC).

Madonna. All samples appeared to be bound in a proteinaceous medium with the exception of the last three.⁸⁴⁶ The FTIR spectrum of the azurite-tempera background was found to correspond quite well with the spectrum collected from the azurite-tempera reference paint sample prepared for this study (Figures 6.1, 6.2, and 6.18). The sample collected from the green stem produced a spectrum which the IRUG database matched with gum derived from

⁸⁴⁶ All FTIR spectra were collected by Kristin deGhetaldi and reviewed with conservation scientist Dr. Suzanne Lomax at the National Gallery of Art in Washington, DC. See Appendix F for information relating to the instrumental parameters used and the instrument make/model.

Figure removed due to copyrighting

Figure 6.18: FTIR spectrum collected from the blue sky (top) in the *Madonna and Child* (Figure 6.17) compared to the spectrum of the azurite bound in egg tempera paint reference (bottom). Based on this comparison and additional reference spectra in the IRUG database, the blue sky was determined to contain azurite bound in tempera.

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Figure 6.19: FTIR spectrum collected from a green stem (middle) in the *Madonna and Child* (Figure 6.17) compared to the IRUG references for malachite (top) and cherry/almond gum (bottom). Additional analysis is required to confirm the presence of gum.

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Figure 6.20: FTIR spectra collected from the flesh of the Madonna's neck (bottom two spectra) in the *Madonna and Child* (Figure 6.17) as compared to the IRUG references for cochineal (top) and egg yolk (second from top). Note that the cochineal pigment generates peaks in the 1750-1500 wavenumber region, the same region that is used to identify the presence of protein (egg yolk) and/or drying oils. Additional analysis is required to confirm that egg yolk is present.

the cherry or plum tree (Figure 6.19).⁸⁴⁷ The red rose and the Madonna's flesh tones both contain red lake pigment(s), colorants that can obscure peaks in the 1750-1500 wavenumber region, making it difficult to identify the binding media (Figure 6.20). It is very likely that this painting is executed entirely in egg tempera with the exception of the green stems, which are presumed to contain an additive that imparts a topographical effect to the paint. From this case study, it appears that the presence of red lake can present problems when attempting to determine the nature of the binding medium using FTIR.

The painting shown in Figure 6.21 was treated from 2010 to 2011 at the National Gallery of Art, affording the conservation staff the opportunity to better examine the materials and techniques used to construct the work.⁸⁴⁸ Four samples were collected for FTIR analysis: one from the red robe, one from the blue background, and two flesh samples (cheek and hands of the sitter).⁸⁴⁹ As with the previous case study, the red lake pigments proved to be problematic when attempting to characterize the nature of the binding medium (Figure 6.22). The blue sky generated a spectrum similar to that shown in Figure 6.18, suggesting the

⁸⁴⁷ I am grateful to conservation scientist Dr. Christopher Maines for performing GC-MS analysis on a sample collected from this area. While he was not able to produce a chromatogram for comparative purposes, it should be noted that additional analytical techniques would need to be performed to confirm the presence of gum.

⁸⁴⁸ The painting was treated by David Bull from 2010-11. I am grateful to Mr. Bull for allowing me to sample the painting during the course of the treatment.

⁸⁴⁹ All FTIR spectra were collected by Kristin deGhetaldi and reviewed with conservation scientist Dr. Suzanne Lomax at the National Gallery of Art in Washington, DC. See Appendix F for information relating to the instrumental parameters used and the instrument make/model.

presence of azurite bound in egg tempera. It is likely that that egg tempera is the primary paint binder in this instance.⁸⁵⁰

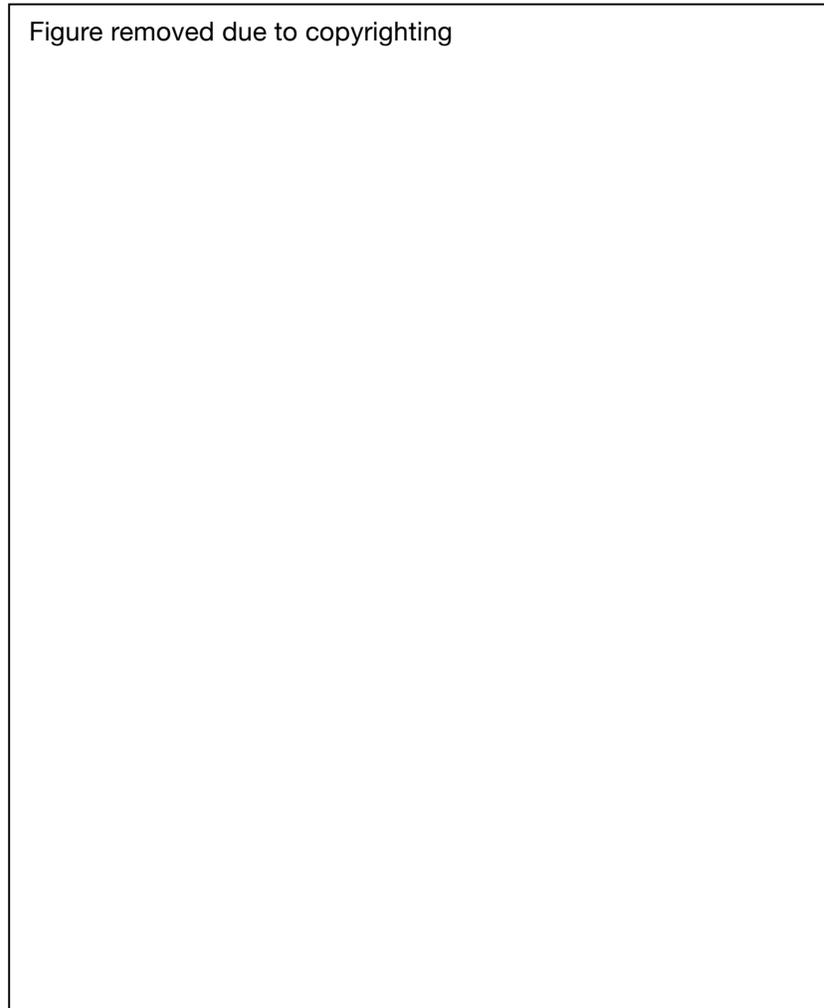


Figure 6.21: Andrea del Castagno, *Portrait of a Man* (c. 1450, National Gallery of Art, Washington DC).

⁸⁵⁰ It should be noted that during the restoration of the picture, the sky was found to be heavily overpainted, something that may complicate the analytical results.

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Figure 6.22: FTIR spectra collected from the flesh of the sitter's cheek (bottom two spectra) in *Portrait of a Man* (Figure 6.21) as compared to the IRUG references for cochineal (top) and egg yolk (second from top). Note that the cochineal pigment generates peaks in the 1750-1500 wavenumber region, the same region that is used to identify the presence of protein (egg yolk) and/or drying oils. Additional analysis is required to confirm that egg yolk is present.

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Figure 6.23: Fra Carnevale, *The Annunciation* (c. 1445/50, National Gallery of Art, Washington DC).

The painting shown in Figure 6.23 was treated from 2010 to 2011 at the National Gallery of Art, affording the conservation staff the opportunity to better examine the materials and techniques used to construct the work.⁸⁵¹ Seven samples were collected from the following locations for FTIR analysis: the pink arch, the blue sky, a white cloud, the green

⁸⁵¹ As the Andrew W. Mellon Fellow in Paintings Conservation between 2008 and 2010, I had the privilege of restoring the painting and was given the opportunity to conduct a technical study of the picture.

garland, two locations in the marbled floor, and flesh from the Madonna's neck.⁸⁵² Nearly all collected spectra suggested the presence of both an oil binder as well as protein (presumably egg yolk), with the exception of the samples from the pink arch, the blue sky, and the green garland (located in the upper left). As with the previous case studies, red lake pigment present in the samples collected from the pink arch and the Madonna's flesh made it difficult to characterize the presence of the binder in both areas.⁸⁵³ The spectrum collected from the blue sky indicated the presence of lapis and chalk (or possibly gypsum); however, both pigments generated peaks that made it difficult to make any definitive conclusions about the binding medium (Figure 6.24). The spectrum obtained from the green garland was somewhat similar to the analytical results of the green stem sample taken from the *Madonna and Child* (Figure 6.17), with the IRUG database again suggesting the presence of malachite mixed with a gum binder (Figure 6.25). Upon further consideration, it seems more likely that the FTIR spectra of the green samples collected from both paintings may contain degradation components (related to the reactive copper green pigment) as opposed to a gum binder. Conservation scientists at the National Gallery London have been able to identify copper oxalates using FTIR and it appears that their published spectrum may account for certain spectral features associated with

⁸⁵² All FTIR spectra were collected by Kristin deGhetaldi and reviewed with conservation scientist Dr. Suzanne Lomax at the National Gallery of Art in Washington, DC. See Appendix F for information relating to the instrumental parameters used and the instrument make/model. Note that the Madonna's robe was also sampled and found to contain both lapis and lead white; however, this area of the painting had been significantly overpainted during a previous restoration campaign and therefore not suitable for characterization of the original binding media.

⁸⁵³ It should be noted that a grey-colored crust (possibly containing oxalates) was observed over the pink paint used to depict the architectural arch once the discolored varnish was removed; however, FTIR was unable to successfully characterize this grey layer.

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Figure 6.24: FTIR spectrum collected from the blue sky (bottom) in *The Annunciation* (Figure 6.23) as compared to the IRUG references for chalk (top), lapis (second from top) and egg yolk (second from bottom). Note that the presence of lapis and chalk generates peaks in the 1750-1500 wavenumber region, the same region that is used to identify the presence of protein (egg yolk) and/or drying oils. Additional analysis is required to confirm that egg yolk is present.

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Figure 6.25: FTIR spectrum collected from the green garland (bottom) in *The Annunciation* (Figure 6.23) as compared to the spectra associated with copper/calcium oxalates (top; Higgitt and White, 2005) and IRUG references for almond gum (second from top) and malachite (second from bottom). Note that the presence of these degradation components can generate peaks in the 1750-1500 wavenumber region, the same region that is used to identify the presence of protein (egg yolk) and/or drying oils. Additional analysis is required to confirm that egg yolk is present.

green samples collected from both paintings (Figure 6.24).⁸⁵⁴ The fact that the IRUG database does not yet contain sufficient spectra representing degradation components (e.g. metal carboxylates, metal palmitates/stearates, etc.) should be considered when attempting to

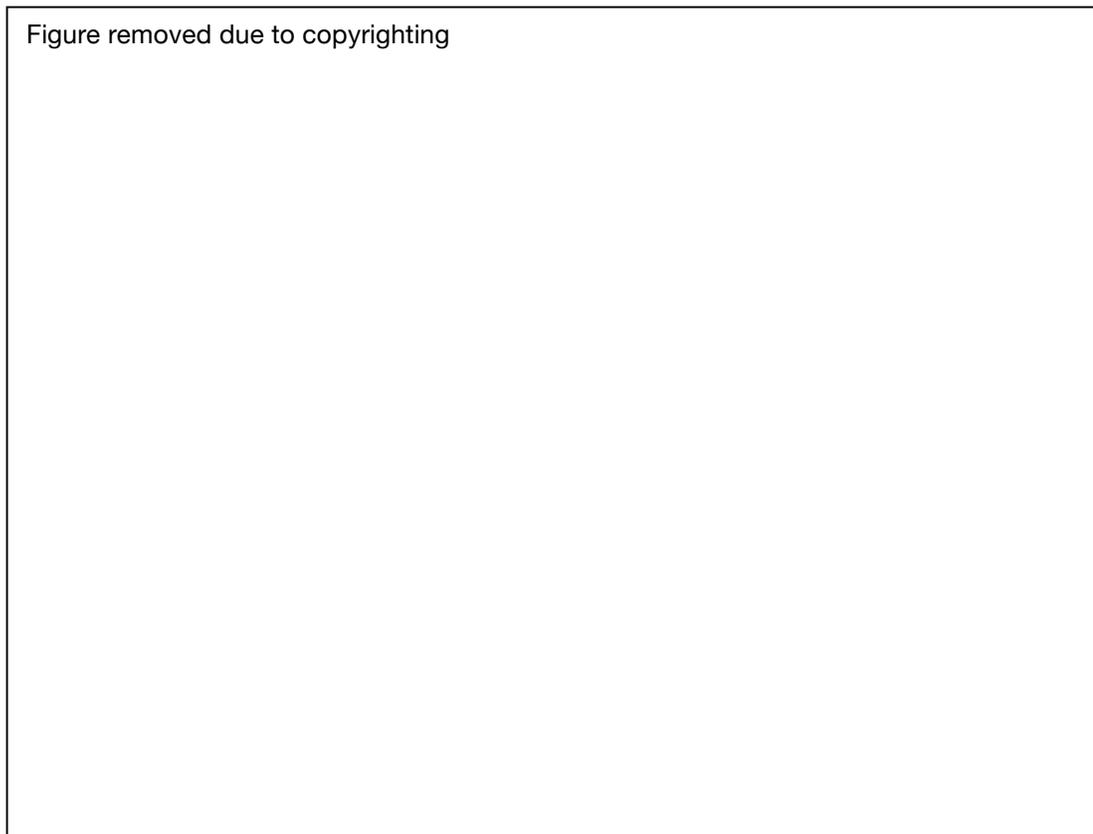


Figure 6.26: FTIR spectra collected from a white cloud and the marbled floor (bottom) in *The Annunciation* (Figure 6.23) as compared to the IRUG reference spectra for lead white (top), egg yolk (second from top), and linseed oil (center). The subtle peaks around 1600-1550 wavenumbers in both paint samples are not sufficient to confirm whether egg and/or oil is present in the binder.

⁸⁵⁴ Catharine Higgitt and Raymond White, “Analyses of Paint Media: New Studies of Paintings of the Fifteenth and Sixteenth Centuries,” *National Gallery Technical Bulletin* 26 (2005): 93-94.

characterize binding media using FTIR, particularly egg and/or oil binders. The FTIR spectra of samples collected from the marbled floor and the white cloud were also difficult to interpret (Figure 6.26): samples collected from the marbled floor produced peaks that suggested the presence of a drying oil, while the spectrum of the white cloud generated two peaks of almost equal height intensity in the region of interest ($1750\text{-}1500\text{ cm}^{-1}$). The presence of lead in both areas generates peaks that complicate interpretation, particularly if degradation components associated with lead are in fact present. It is likely that the painting is painted primarily with egg tempera although a drying oil may have been used to create the rich, transparent colors used to depict the marbled floor.

From these case studies, in addition to the analyses of the paint reference samples, it can be concluded that FTIR is not an ideal technique for confirming the presence of egg and/or oil in Italian Renaissance easel paintings. The potential interference from pigments and degradation components combined with the spectral similarities of both binding media (egg yolk and drying oil) further complicates the interpretation of the analytical results. Finally, FTIR is not able to distinguish one protein source from the next (egg yolk vs. glue) and, unless equipped with sophisticated imaging techniques, cannot characterize organic binding media within discrete paint/ground layers.

6.4 Evaluation of Gas-Chromatography-Mass Spectrometry

For the purposes of this study it was decided to compare at least two of the GC-MS protocols outlined in Chapter 5 (section 5.2.3) that are currently employed in museum laboratories. A larger sized sample is generally required (as compared with FTIR) for GC-MS, particularly when multiple components are extracted from a single sample. The protocol designed by Colombini et al. (Figure 5.63) was deemed to be too extensive for the scope of

this study, therefore protocols designed at the Getty Conservation Institute (Figure 5.60) and the Doerner Institut (Figure 5.61) were chosen for analyzing paint reference samples (summarized in section 6.1) and samples collected from actual artworks.⁸⁵⁵

Protocols developed at both the Getty Conservation Institute and the Doerner Institut were used to perform fatty acid analysis on the yellow ochre and lead white paint reference samples (see Appendix G for analytical procedures). The primary goal of this experiment was to determine whether both protocols would produce similar fatty acid ratios (e.g. palmitic/stearic, azelaic/palmitic) using the steps highlighted in Figures 6.27 and 6.28.⁸⁵⁶ While both protocols were found to generate different results, the Doerner protocol appeared to produce fatty acid ratios that seemed to be more representative of the expected fatty acid ratios corresponding to the *tempera grassa* paints (mixtures of varying proportions of egg and oil); however, additional testing, using both aged and fresh paints, would need to be

⁸⁵⁵ Michael Schilling, “Procedure for Quantitative GC-MS Analysis of Fatty Acids as Methyl Ester Derivatives,” in *MaSC 2007 GC-MS Workshop Handbook*, ed. Kenneth Sutherland (Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies. Users’ Group for Mass Spectrometry and Chromatography, 2007); —, “Procedure for Quantitative GC-MS Analysis of Amino Acids, Fatty Acids, and Glycerol as (t-butyl-dimethylsilyl) Derivatives,” in *MaSC 2007 GC-MS Workshop Handbook*, ed. Kenneth Sutherland (Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies. Users’ Group for Mass Spectrometry and Chromatography, 2007); Ursula Baumer, Johann Koller, Patrick Dietemann and Irene Fiedler, “Doerner Institute Procedure for GC-MS,” in *MaSC 2007 GC-MS Workshop Handbook*, ed. Kenneth Sutherland (Philadelphia Museum of Art/Winterthur Museum/Agilent Technologies. Users’ Group for Mass Spectrometry and Chromatography, 2007). Note that at the time of this study, scientific departments at both the National Gallery of Art in Washington and Winterthur Museum were utilizing a GC-MS protocol that was developed at the Getty Conservation Institute by conservation scientist Michael Schilling. This particular protocol was first developed around 2000 but was later revised and presented at the 2007 MaSC group meeting in Philadelphia.

⁸⁵⁶ *Ibid.*

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Figure 6.27 (top) and 6.28 (bottom): GC-MS protocols developed at the Getty Conservation Institute (top) and the Doerner Institut (bottom). The highlighted sections of each extraction protocol was used to perform fatty acid analysis on the yellow ochre and lead white reference paints.

performed in order to confirm this observation.⁸⁵⁷ As fatty acids were detected in all four stages of the extraction process outlined in the Doerner protocol (Figure 6.28), it is likely that the reference paints were not subjected to artificial aging for a long enough period; short and/or long fatty acid chains were readily extracted in nearly all stages outlined in Table 6.1. The Getty protocol, while less complex, generated a wider range of fatty acid ratios. Certain paint references (namely the 95%/5% oil/egg samples) produced ratios that far exceeded the expected range for linseed oil and/or egg yolk, indicating that these paints may not have been effectively emulsified or that contamination occurred during analysis (Table 6.2). In addition, the Getty protocol was used to evaluate whether the presence of a traditional gesso ground would affect the fatty acid ratio obtained from the overlying paint film.⁸⁵⁸ Slight differences in the fatty acid ratios were observed when comparing the same paint sample with and without a gesso ground which suggests that historically accurate grounds should be incorporated (if possible) in studies that plan on utilizing mock-ups or reconstructions intended for comparative purposes and/or multivariate analysis. Finally, results obtained using both protocols demonstrate that the presence of pigments can also influence fatty acid ratios obtained during media analysis.

⁸⁵⁷ It should be noted that fatty acid ratios obtained using the Doerner protocol were calculated by taking the sum of the peak areas corresponding to a given fatty acid extracted in all eight steps. For example, for P/S ratios, the peak areas associated with palmitic acid and stearic acid in each extraction step were calculated and added to obtain a representative P/S ratio.

⁸⁵⁸ At the time of this study, the Getty protocol was being more widely used in museum laboratories and was therefore chosen as the primary protocol for much of the organic analysis performed on paint reference samples and samples collected from Italian paintings.

Lead White	P/S	A/P	Yellow Ochre	P/S	A/P
100% Egg	2.8388	0.1907	100% Egg	2.8424	0.4415
95% Egg	2.1549	0.2986	95% Egg	2.3977	0.2612
75% Egg	2.2007	0.9915	75% Egg	1.7752	0.2183
50% Egg	1.8309	0.7376	50% Egg	1.9055	0.9564
25% Egg	2.5217	0.6819	25% Egg	2.0124	1.1575
5% Egg	1.7409	0.9725	5% Egg	2.1662	1.8956
0% Egg	1.0424	1.3583	0% Egg	1.5593	1.064
Linseed Oil			Egg Yolk		
(P/S): 1-2 (A/P): 1-1.5			P/S: 2.5-3.5 A/P: .1-.3		

Table 6.1: Palmitic/stearic (P/S) and azelaic/palmitic (A/P) fatty acid ratios obtained from the yellow ochre and lead white paint reference samples using the GC-MS protocol developed at the Doerner Institut (Figure 6.28). Typical ranges associated with pure, un-pigmented linseed oil and egg yolk are also listed.

White Lead (Glass)	P/S	A/P	Yellow Ochre (Glass)	P/S	A/P
100% Egg	1.9058	0.3558	100% Egg	1.8541	0.3622
95% Egg	2.06	0.4632	95% Egg	1.8525	0.3674
75% Egg	1.778	0.9674	75% Egg	1.7791	0.6329
50% Egg	1.784	1.445	50% Egg	1.4701	0.6028
25% Egg	2.095	2.677	25% Egg	1.5774	0.1269
5% Egg*	12.65	0.251	5% Egg	1.4591	1.5072
0% Egg*	6	3.88	0% Egg	1.5622	1.3715
White Lead (Gesso)	P/S	A/P	Yellow Ochre (Gesso)	P/S	A/P
100% Egg	2.4256	0.3089	100% Egg	2.198	0.3036
95% Egg	2.9589	0.3801	95% Egg	2.184	0.3278
75% Egg	2.2966	0.8479	75% Egg	2.174	0.5475
50% Egg	1.644	1.601	50% Egg	1.794	1.1762
25% Egg	1.562	2.193	25% Egg	1.47	1.3262
5% Egg*	1	7.489	5% Egg*	2.565	1.5686
0% Egg	2.021	2.42	0% Egg	1.7518	1.9707
Linseed Oil			Egg Yolk		
(P/S): 1-2 (A/P): 1-1.5			P/S: 2.5-3.5 A/P: .1-.3		

Table 6.2: Palmitic/stearic (P/S) and azelaic/palmitic (A/P) fatty acid ratios obtained from the yellow ochre and lead white paint reference samples using the GC-MS protocol developed at the Getty Conservation Institute (Figure 6.27). The (*) symbol denotes samples that yielded ratios that lie far outside of the expected range. Typical ranges associated with pure, un-pigmented linseed oil and egg yolk are also listed. The figures shown in red were found to lie far outside the expected ranges for linseed oil and/or egg yolk, indicating that the samples may not have been effectively emulsified or that they were contaminated during analysis.

To summarize, the analytical results listed in Table 6.1 and 6.2 suggest that fatty acid ratios can be affected by the following factors:

- a) the particular protocol chosen
- b) the presence of ground layers
- c) the presence of pigments

Therefore, both protocols may only be suitable for qualitative analysis (e.g. determining whether or not drying oil is present) rather than quantitative analysis (e.g. drawing conclusions relating to binding media solely based on fatty acid ratios). While additional dicarboxylic acids (e.g. suberic, sebacic, and heptanedioic acid) were also detected during the analysis of the paint reference samples, it is likely that their relative amounts are also influenced by the factors listed above. For example, low amounts of azelaic acid could simply be a result of contamination, pigment interference, or other external factors. Unless amino acid analysis is performed, fatty acid ratios alone are simply not enough to characterize the nature of the drying oil or to determine whether or not egg proteins are present in a paint sample.

Amino acid analysis was also performed on selected paint reference samples using the Getty protocol (Figure 6.29).⁸⁵⁹ Four samples were analyzed from each of the yellow ochre and lead white gradients (applied over a gesso ground): two samples containing only egg yolk and two more containing 50% egg/ 50% oil (Table 6.3). To summarize, the Schilling protocol was able to successfully detect the presence of amino acids in both of the tempera containing

⁸⁵⁹ Conservation scientist Suzanne Q. Lomax performed the amino acid analysis on some of these samples at the National Gallery of Art in Washington and assisted me in the interpretation of the data. The Doerner protocol was not used for amino acid analysis as it recommends that ion-exchange chromatography be used for the detection of proteins, a technique that was not readily accessible during the time of this study.

Figure removed due to copyrighting

Figure 6.29: GC-MS protocol developed at the Getty Conservation Institute. The highlighted section of the extraction protocol was used to perform amino acid analysis on the yellow ochre and lead white reference paints.

Yellow Ochre 50% Egg (Gesso)		White Lead 50% Egg (Gesso)	
Amino Acid	Count(min)	P Amino Acid	Count(min)
L-Alanine	6.33	L-Alanine	none
Glycine	6.508	Glycine	none
L-Valine	7.03	L-Valine	none
L-Proline	trace	L-Proline	7.234
L-Leucine	7.258	L-Leucine	none
Norleucine (Internal Standard)	7.533	Norleucine (Internal Standard)	7.521
Methionine	8.23	Methionine	none
L-Serine	8.76	L-Serine	8.757
Threonine	8.90	Threonine	none
L-Asparagine	9.485	L-Asparagine	none
L-Aspartic	9.551	L-Aspartic	9.535
Glutamic acid	10.15	Glutamic acid	none

Table 6.3: Results obtained from the amino acid analysis performed on the yellow ochre and lead white paint reference samples containing 50%/50% egg/oil using the protocol outlined in Figure 6.29. The retention times (in minutes) associated with each amino acid is listed as well as the internal standard added to each sample. Note that only three amino acids (in addition to the internal standard) could be detected in the lead white sample, possibly a result of the reactivity of lead carbonate with organic compounds.

samples and the yellow ochre sample containing 50% egg/50% oil; however, only three amino acids were detected in the lead white sample consisting of 50%/50% egg/oil. It is possible that basic lead carbonate is prone to forming complexes with certain amino acids ultimately interfering with the silylation process. Recent studies have found that amino acid analysis can be significantly affected by the presence of certain pigments, especially those containing lead and copper.⁸⁶⁰ Potential pigment interference becomes particularly problematic when dealing with aged paints, as only seven amino acids have been shown to be stable, reliable markers (see Figure 5.5). Additional research is needed to confirm the potential interactions that can occur between certain pigments and proteinaceous materials, as the relative amount and presence of amino acids are often used to determine the nature of binding media used by traditional painters.

6.4.1 Case Studies: Analysis of Italian Paintings using Gas Chromatography-Mass Spectrometry

The paintings shown in Figure 6.30 and 6.31 were treated from 2009-2010 and 2010 to 2011, respectively, at the National Gallery of Art affording the conservation staff the opportunity to better examine the materials and techniques used to construct the work.⁸⁶¹

⁸⁶⁰ Ilara Bonaduce et al. “The development of a gas chromatographic–mass spectrometric analytical procedure for the determination of lipids, proteins and resins in the same paint micro-sample avoiding interferences from inorganic media” in *Journal of Chromatography A* 1216 (2009): 5931–939, doi:10.1016/j.chroma.2009.06.033; Gwenaëlle Gautier, “A Reliable Analytical Procedure for the Characterization and Identification of Proteinaceous Binding Media in Wall Paintings” (PhD diss., University of Pisa, 2006).

⁸⁶¹ As the Andrew W. Mellon Fellow in Paintings Conservation between 2008 and 2010, I had the privilege of restoring the painting shown in Figure 6.30 and was given the opportunity to conduct a technical study of the picture. The painting shown in Figure 6.31 was treated by

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Figure 6.30 (left) and 6.31 (right): Sample locations for GC-MS analysis (Doerner protocol) associated with Follower of Fra Filippo Lippi and Pesellino's *Madonna and Child* (left; Figure 6.17) and Andrea del Castagno's *Portrait of a Man* (right; Figure 6.21).

From the *Madonna and Child*, fatty acid analysis was performed on two samples collected from the red robe as well as a sample from a green stem using the Doerner Protocol.⁸⁶²

David Bull from 2010-11; he graciously allowed me to sample the painting during the course of the treatment.

⁸⁶² Note that only extraction steps 1-4 were performed as outlined in Figure 6.28. I am grateful to conservation scientist Dr. Christopher Maines for performing GC-MS analysis on a

Unfortunately, only negligible amounts of fatty acids were detected, making it impossible to calculate any fatty acid ratios. For Castagno's *Portrait of a Man*, fatty acid analysis was also performed on samples collected from the red robe, the flesh, and the blue sky using the Doerner protocol.⁸⁶³ It should be noted that the sky had been repainted with Prussian blue (presumably bound in oil) during a previous restoration campaign and could not be completely removed during the 2009-10 treatment.⁸⁶⁴ The location for sampling the sky was chosen carefully and performed only after a significant amount of the degraded coatings and restoration glazes had been removed. As with the *Madonna and Child*, only trace amounts of fatty acids were detected in each sample. To ensure that fatty acid ratios could be successfully calculated in subsequent case studies, it was decided to use both the Getty and Doerner protocols for fatty acid analysis.

The painting shown in Figure 6.32 was treated from 2010 to 2011 at the National Gallery of Art, providing the conservation staff to perform a technical study of the work in order to better understand the materials present.⁸⁶⁵ Fatty acid analysis was performed on five samples (Table 6.4) from *The Annunciation*, using both the Doerner and Getty protocols.⁸⁶⁶

sample collected from the green stem. While he was not able to produce a chromatogram for comparative purposes, it should be noted that only trace amounts of fatty acids were detected.

⁸⁶³ Note that only extraction steps 1-4 were performed as outlined in Figure 6.28.

⁸⁶⁴ David Bull, personal communication with the author, 2 March, 2011.

⁸⁶⁵ As the Andrew W. Mellon Fellow in Paintings Conservation between 2008 and 2010, I had the privilege of restoring the painting and was given the opportunity to conduct a technical study of the picture.

⁸⁶⁶ For the Doerner protocol, only extraction steps 1-4 were performed as outlined in Figure 6.28. For the Getty protocol, fatty acid analysis was performed using the procedure outlined in Figure 6.28.

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Figure 6.32: Sample locations for GC-MS analysis associated with Fra Carnevale's *The Annunciation* (Figure 6.23).

As with the previous case studies, the Doerner method only generated negligible amounts of fatty acids; however, the Getty protocol successfully extracted fatty acids from all five samples, generating ratios that were within a reasonable range (see Figure 5.10). Based on the ratios listed in Table 6.4 (left column), it appears that certain sections of the painting were executed using a mixed technique (either using *tempera grassa* or with oil glazes applied over

egg tempera paints). For example, both of the samples collected from the marble floor produced similar P/S ratios (suggesting the presence of linseed oil), while the A/P ratios indicated the presence of egg.

Three samples, two from the marble floor and one from the flesh of the Madonna, were also subjected to amino acid analysis using the Getty protocol (see Figure 6.29).⁸⁶⁷ Using this technique, all three were found to contain protein, most likely from an egg binder; egg proteins are usually identified when the amino acid hydroxyproline is absent (ruling out the presence of animal glue).⁸⁶⁸ It is important to note that both of the extraction procedures (for fatty acids as well as amino acids) outlined in the Getty protocol can be used to generate A/P ratios. In theory, this is one of the main benefits to using this method, particularly when samples are limited; the extraction method for amino acid analysis can be used to determine the possible presence of both egg and oil from a single sample.⁸⁶⁹ It was decided to compare the A/P ratios generated by both extraction procedures (Table 6.4) and significant discrepancies were noted. Both procedures produced different A/P ratios from samples collected from the same area of the picture. While the reason for this discrepancy is currently unknown, this should be considered if fatty acid ratios are used to determine the nature of the binding medium. For example, based on the fatty acid analysis, the flesh sample appeared to only contain egg while the A/P ratio generated from the amino acid analysis suggested the presence of a drying oil as the azelaic acid amount was rather high. It is possible that the artist

⁸⁶⁷ I am grateful to conservation scientist Dr. Suzanne Q. Lomax for performing amino acid analysis at the National Gallery of Art in Washington. The procedure for amino acid analysis is outlined in Figure 6.29.

⁸⁶⁸ Dr. Suzanne Q. Lomax also considers the alanine/glycine ratio as well as the relative amount of glutamic acid to determine whether or not casein is present.

⁸⁶⁹ The A/P ratios generated by the amino procedure outlined in Figure 6.29 produces silylated fatty acids rather than fatty acid methyl esters.

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Table 6.4: Analytical results obtained using the Getty protocols outlined in Figure 6.27 and Figure 6.29 from samples collected from Fra Carnevale's *The Annunciation* (Figure 6.32). Note that the extraction procedures associated with fatty acid analysis (based on methyl ester derivatives) and amino acid analysis (based on silyl derivatives) produced different A/P ratios from the same sampled area. The reason for this discrepancy is currently unknown but should be noted if fatty acid ratios are used to determine the nature of the binding medium.

added oil to his tempera paints (atop an egg-bound *verdaccio* layer) in order to increase the transparency of the flesh tones.⁸⁷⁰ Fra Carnevale was most likely working with Filippo Lippi during the time that this painting was executed and at least two paintings associated with Lippi have also been found to contain oil and egg at the National Gallery in London.⁸⁷¹ On the other hand, it appears that many of these conclusions relating to Lippi and Carnevale's

⁸⁷⁰ Cross-sectional paint samples collected from the flesh were prepared during the treatment of the picture and revealed the presence of a *verdaccio* layer beneath the pink-colored paint used to depict the skin tones.

⁸⁷¹ John S. Mills and Raymond White. "Organic Analysis in the Arts: Some Further Paint Medium Analysis," *National Gallery Technical Bulletin* 2 (1978): 71-6; Raymond White and Jennifer Pilc, "Analyses of Paint Media," *National Gallery Technical Bulletin* 17 (1996): 92.

use of binding media require re-evaluation as most have been based on fatty acid ratios using different extraction procedures.⁸⁷²

The painting shown in Figure 6.33 was treated from 2011 to 2012 at the National Gallery of Art, allowing conservation staff to perform materials analysis and develop a better understanding of the technique used to execute the work.⁸⁷³ Fatty acid analysis was performed on three samples (Figure 6.33) from the *The Madonna and Child*, using both the Doerner and Getty protocols.⁸⁷⁴ As with the previous case studies, the Doerner method did not produce satisfactory results; however, the Getty protocol successfully extracted fatty acids from all three samples, generating ratios that were within a reasonable range (see Figure 5.10). As with the analysis of Fra Carnevale's *The Annunciation* (Figure 6.32), the samples were analyzed using the extraction procedures for both fatty acids and amino acids outlined in the Getty protocol.⁸⁷⁵ Based on the ratios listed in Table 6.5 (left column), it appears that certain sections of the painting were executed using a mixed technique (either using *tempera grassa* or with oil glazes applied over egg tempera paints), particularly in the discolored red robe and the flesh tones.⁸⁷⁶ Cross-sections collected from both regions revealed a rather basic

⁸⁷² Ibid.

⁸⁷³ The treatment of this painting was carried out by David Bull from 2011 to 2012; he graciously allowed me to sample the picture during the course of the treatment.

⁸⁷⁴ For the Doerner protocol, only extraction steps 1-4 were performed as outlined in Figure 6.28. For the Getty protocol, fatty acid analysis was performed using the procedure outlined in Figure 6.27. FTIR could not be performed, as the instrument was not functioning during the period that the painting was being examined.

⁸⁷⁵ Conservation scientist Dr. Suzanne Q. Lomax performed amino acid analysis on these samples at the National Gallery of Art in Washington. The procedure for amino acid analysis is outlined in Figure 6.29.

⁸⁷⁶ The blackened appearance of the robe before the painting was treated is due to the deterioration of the vermilion pigment.

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Figure 6.33: Sample locations for GC-MS analysis associated with Antonella da Messina's *Madonna and Child* (c. 1475, National Gallery of Art, Washington DC).

stratigraphy as no verdaccio layer was present in the flesh and the robe was built up using only a few paint layers.⁸⁷⁷ The unusually high P/S ratio related to the red lake glaze of the brocade is surprising as values greater than four are typically associated with poppyseed

⁸⁷⁷ David Bull graciously allowed me to prepare paint cross-sections of the painting during the course of the treatment

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Table 6.5: Analytical results obtained using the Getty protocols outlined in Figure 6.27 and Figure 6.29 from samples collected from Antonello da Messina's *Madonna and Child* (Figure 6.33). Note that the extraction procedures associated with fatty acid analysis (based on methyl ester derivatives) and amino acid analysis (based on silyl derivatives) produced different A/P ratios from the same sampled area. The reason for this discrepancy is currently unknown but should be noted if fatty acid ratios are used to determine the nature of the binding medium. The blackened appearance of the robe before the painting was treated is due to the deterioration of the vermilion pigment.

oil.⁸⁷⁸ There is no evidence to indicate that poppyseed oil was available or even used by Italian artists during the Quattrocento, raising additional questions relating to the reliance on fatty acid ratios for the characterization of binding media. A cross-section collected from this area revealed multiple layers of paint; it is entirely possible that the fatty acid ratios obtained using the Getty protocol reflect an uneven distribution of fatty acids throughout the various layers (e.g. depletion). It should also be noted that major sections of the picture were overpainted in previous restoration campaigns, something that could also influence fatty acid ratios and therefore the characterization of the binder.

⁸⁷⁸ John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects* (1987; repr., Oxford: Butterworth-Heinemann Ltd., 1996), 14-30, 171-2.

While amino acid analysis of the vermilion robe generated inconclusive results, the two other samples were found to contain egg protein.⁸⁷⁹ As with the analysis of Fra Carnevale's *The Annunciation*, both extraction procedures (fatty acid and amino acid) produced different A/P ratios from samples collected from the same area of the picture (Tables 6.4 and 6.5). For example, samples collected from the flesh and red brocade produced rather high A/P ratios when the amino acid extraction procedure was used. While the analytical results suggest that Antonello da Messina likely used both egg and oil in certain passages, more research is needed to establish whether these ratios can be considered reliable indications of the original binding media no matter what type of extraction procedure is used.⁸⁸⁰

6.5 Evaluation of Imaging Time-of-Flight Secondary Ion Mass Spectrometry

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to analyze cross-sectional samples collected from all four paint gradients described in section 6.1 as well as a select number of Italian easel paintings.⁸⁸¹ This technique provides high-resolution spatial maps of both inorganic and organic components located within a paint cross-section. With recent advancements in surface analysis, ToF-SIMS can now be used to identify specific amino acids present in protein-containing materials as well as fatty acids present in drying

⁸⁷⁹ The absence of hydroxyproline suggested the presence of egg. Dr. Suzanne Q. Lomax also considers the alanine/glycine ratio as well as the relative amount of glutamic acid to determine whether or not casein is present.

⁸⁸⁰ Several other paintings associated with the artist have been found to contain oil and/or egg. See Chapter 4, section 4.1 for more information relating to Antonello da Messina's technique.

⁸⁸¹ See Appendix H for instrumental information and analytical parameters used.

oils. For example, the detection of the ion fragment associated with the amino acid hydroxyproline can be used to characterize proteinaceous materials present in paint and/or ground layers: the absence of the fragment in a paint layer suggests the use of an egg binder in Quattrocento paintings while the presence of the fragment suggests the use of glue (often seen as a consolidant and/or in gesso ground layers). Fatty acids can also be detected and in certain instances used to confirm the presence of a drying oil and/or egg yolk.

As an analytical technique, ToF-SIMS avoids the need for derivatization/silylation reagents as it can be used to extract information from either freshly prepared or extant paint cross-sections (Figure 6.34). Furthermore, the layered systems that are often encountered in historical paint samples remain intact throughout the analytical procedure, allowing for the co-localization of organic and inorganic species in specific layers (e.g., egg-yolk paint atop a glue ground). Because of this ability to localize the analytical signal to approximately 1 μm or less, the mass spectral information can be used to produce mass-resolved and spatially resolved images which can be then be compared with magnified images of the same paint cross-sections.

There are several challenges associated with the preparation of paint cross-section samples for surface-sensitive analyses such as ToF-SIMS. First, the samples tend to be very small, making them difficult to handle and manipulate in orientation. Second, the samples tend to be precious and limited, requiring a sample-preparation method that does not preclude further analyses. Third, particularly for the analysis of paint cross-sections in this study, the method of creating and exposing the cross-section must not introduce artifacts resulting in contamination of the sample surface. Since ToF-SIMS is a surface-sensitive technique, artifacts caused by the effects of sample preparation will be immediately apparent during analysis. Additionally, any oil-based or polymeric residues (resulting from poor handling and/or storage conditions) will be detected in the ToF-SIMS spectra if the samples are

contaminated. To reduce these artifacts, room-temperature microtomy is the preferred method of sample preparation for the relatively hard embedding resins often used in the preparation of paint cross-sections. Preparatory steps involving ion-milling may also hold potential for generating ideal surfaces for analysis of paint samples.

During the microtoming process, the goal was to create a flat surface rather than remove and retain thin sections for subsequent analysis. Proper sample mounting proved to be a critical aspect to achieving this goal. As seen in Figure 6.34A, the embedding resin was trimmed by hand from the paint cross-section (measuring approximately 1 cm) using a Dremel[®] tool, leaving a 4-mm resin cube containing the sample near one face of the cube.⁸⁸² The sample was then mounted on a Cryo Specimen Pin using cyanoacrylate-based glue (Figure 6.34B). The embedding medium was then tapered by hand using a fresh safety razor blade to further reduce the resin area surrounding the cross-section (Figure 6.34C). It was observed during microtomy that thin sections tended to fracture apart when the tip of the specimen was square (i.e. when the microtome knife encountered a constant width of resin as it cut through the sample), creating a rough surface that was not ideal for analysis with ToF-SIMS. It was surmised that mechanical stress during cutting could be lessened if the sample was cut to form a trapezoid-shaped tip, reducing the amount of resin that the microtome knife encountered as it progressed through each cut (Figure 6.34D; the direction of the arrow indicates the direction of microtome blade movement). The exposed surface of the paint cross-section was then considered ready for analysis using ToF-SIMS.

A number of paint reference samples (described in section 6.1) were mounted and prepared for ToF-SIMS analysis for the simultaneous identification of specific markers

⁸⁸² I am grateful to my colleague Zachary Voras, PhD candidate in Chemistry at the University of Delaware, for devising the microtome process outlined in this study.

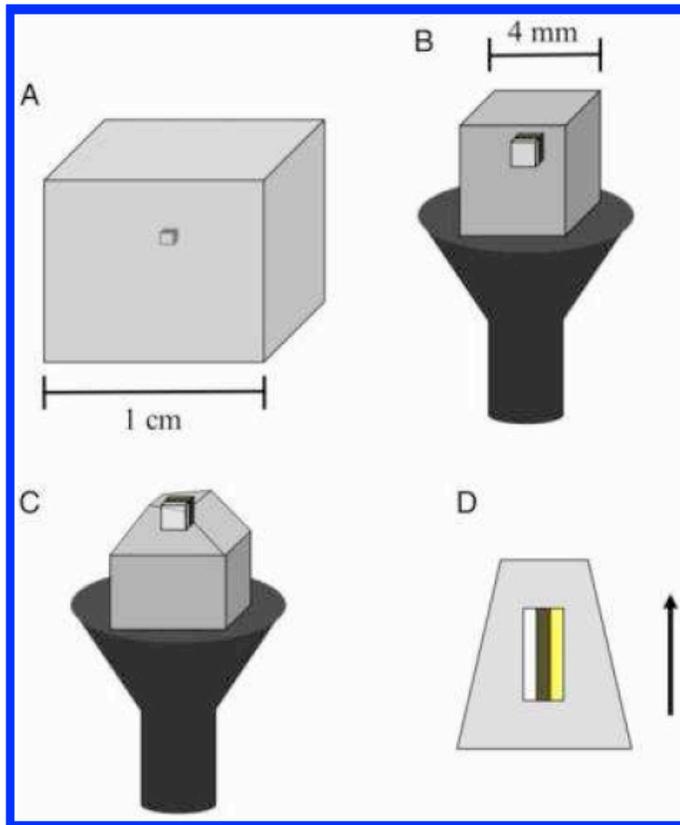


Figure 6.34: Preparation procedure for microtoming paint cross-sections. (A) The sample is trimmed to a 1-cm cube from the original casting (B) Next the cube is trimmed to a small size (~ 4 mm) and attached to a specimen pin (C) The sample is then hand-trimmed in preparation for microtomy (D) The cut direction is indicated by the arrow.⁸⁸³

associated with egg yolk, animal-glue protein, and drying oils (in this case linseed). These paint references allowed for the optimization of the ToF-SIMS spectral and spatial performance while extracting relevant information regarding positive- and negative-ion

⁸⁸³ Zachary Voras, Kristin deGhetaldi, Brian Baadem Eric Gordon, Glenn Gates, and Thomas P. Beebe, "Comparison of oil and egg tempera paint systems using time-of-flight secondary ion mass spectrometry," *Studies in Conservation* (2016), doi:10.1179/2047058414Y.0000000154.

fragments observed in ToF-SIMS. Table 6.6 summarizes the amino-acid fragments that were used for the identification of egg yolk and collagen, as well as the fatty-acid fragments associated with drying oils. Marker fragments were chosen based on previously reported chemical markers identified in drying oils and proteinaceous materials.⁸⁸⁴ Cross-sections

⁸⁸⁴ Matthew S. Wagner et al., “Quantitative time-of-flight secondary ion mass spectrometry for the characterization of multicomponent adsorbed protein films,” *Applied Surface Science*, (203–4): 704–9, doi: 10.1016/S0169-4332(02)00795x; —, and David G. Castner, “Characterization of Adsorbed Protein Films by Time-of-Flight Secondary Ion Mass Spectrometry with Principal Component Analysis,” *Langmuir* 17 (201): 4649–60, doi: 10.1021/la001209t; Nan Xia et al., “Time-of-Flight Secondary Ion Mass Spectrometry Analysis of Conformational Changes in Adsorbed Protein Films,” *Langmuir* 18 (2002): 4090–7, doi: 10.1021/la020022u; Michael R. Schilling, David M. Carson, and Herant Khanjian, “Gas chromatographic determination of the fatty acid and glycerol content of lipids, IV: Evaporation of fatty acids and the formation of ghost images by framed oil paintings,” in *ICOM Committee for Conservation Preprints, 12th Triennial Meeting, Lyon, 29 August – 3 September, 1999*, ed. Janet E. Bridgeland, vol. I (London: James & James, 1998), 242–7; —, Herant P. Khanjian, and Luiz A. C. Souza, “Gas chromatographic analysis of amino acids in ethylchloroformate derivatives, Part I: Composition of proteins associated with art objects and monuments,” *Journal of the American Institute for Conservation* 35 (1996): 45–59, doi: 10.2307/3179937; — and Herant P. Khanjian, “Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part II: Effects of pigments and accelerated aging on the identification of proteinaceous binding media,” *Journal of the American Institute for Conservation* 35 (1996): 123–44, doi: 10.2307/3179992; —, “Gas chromatographic Analysis of Amino Acids as Ethyl Chloroformate Derivatives, Part III: Identification of Proteinaceous Binding Media by Interpretation of Amino Acid Composition Data,” in *ICOM Committee for Conservation Preprints, 11th Triennial Meeting, Edinburgh, Scotland, 1–6 September 1996*, ed. Janet E. Bridgeland (London: James & James, 1996), 211–19; Jana Sanyova et al., “Unexpected materials in a Rembrandt painting characterized by high spatial resolution cluster-TOF-SIMS Imaging,” *Analytical Chemistry* 83 (2011): 753–60, doi: 10.1021/ac1017748; John S. Mills and Raymond White, “The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Paintings by Fatty Acid Analysis,” in *Conservation and Restoration of Pictorial Art*, eds. Norman Brommelle and Perry Smith (London and Boston: Butterworths & Co. Ltd., 1976), 72–7; Vincent Mazel and Pascale Richardin, “ToF SIMS Study of organic Materials in Cultural Heritage,” in Maria Perla Colombini and Francesca Modugno, eds. *Organic Mass Spectrometry in Art and Archaeology in Organic Mass Spectrometry in Art and Archaeology* (New York: Wiley, 2009), 433–457; Katrien Keune et al., “Evaluation of the “added value” of SIMS: A mass spectrometric and spectroscopic study of an unusual Naples yellow oil paint reconstruction,” *International Journal of Mass Spectrometry* 284 (2009): 22–34, .

obtained from reference paint samples were analyzed using ToF-SIMS in order to confirm the presence of the ion fragments summarized in Table 6.6 and to assess whether certain pigments had an effect on the detection of these fragments. Peaks generated by the pigments were found to occasionally interfere and/or overlap with peaks associated with binding media; however, isotopic peak ratios were helpful in confirming the presence of each ion fragment. The characteristic markers for amino acids associated with animal glue were detected in the gesso ground for all samples (see Figures 6.35, 6.36, and 6.37). Likewise, amino acid fragments (with the exception of hydroxyproline) associated with egg yolk were detected in all egg containing paints while characteristic markers for fatty acids were observed in both egg and oil bound paints (see Figures 6.35, 6.36, and 6.37). There was a noticeable decrease in the signals for palmitic and stearic acids moving from the oil-bound paints to the egg-bound paints. It should also be noted that while the ion fragment CN⁻ was used to generate overall maps for proteinaceous materials, caution should be exercised when relying on this marker

[doi:10.1016/j.ijms.2008.10.016](https://doi.org/10.1016/j.ijms.2008.10.016); —, “Comparative study of the effect of traditional pigments on artificially aged oil paint systems using complementary analytical techniques,” in *ICOM Committee for Conservation Preprints, 15th Triennial Meeting, New Delhi, 22-26 September 2008*, ed. Janet E. Bridgland, vol. II (London: James & James, 2008), 833–42; Katrien Keune and Jaap J. Boon, “Imaging Secondary Ion Mass Spectrometry of a Paint Cross Section Taken from an Early Netherlandish Painting by Rogier van der Weyden,” *Analytical Chemistry* 76 (2004): 1374–85, doi: 10.1021/ac035201a; Marie Henry, Christine Dupone-Gillain, and Patrick Bertrand, “Conformation change of albumin adsorbed on polycarbonate membranes as revealed by ToF-SIMS,” *Langmuir* 19 (2003): 6271–6276, doi: 10.1021/la034081z; Ester, B. Ferreira, Rachael Morrison, and Jaap J. Boon, “Imaging Chemical Characterisation of Preparatory Layers in Fifteenth and Sixteenth-century North European Panel Paintings,” in *Preparation for Painting: The Artist’s Choice and its Consequences*, eds. Joyce H. Townsend, Tiarna Doherty, Gunnar Heydenreich and Jacqueline Ridge (London: Archetype Publications, 2008), 50–9; Maria Perla Colombini and Francesca Modugno, “Organic Materials in Art and Archaeology,” in *Organic Mass Spectrometry in Art and Archaeology in Organic Mass Spectrometry in Art and Archaeology*, eds. Maria Perla Colombini and Francesca Modugno (New York: Wiley, 2009) 3–36; Annemie Adriaens and Mark G. Dowsett, “Applications of SIMS to Cultural Heritage Studies,” *Applied Surface Science* 252 (2006): 7096–101, doi:10.1016/j.apsusc.2006.02.193.

Amino and fatty acid species observed (ion polarity)	Empirical formula of indicator ion	<i>m/z</i> of ion calculated (observed ± 0.001)	Expected molar percentages data from Schilling <i>et al.</i> (1998)	
			Egg yolk (mole% ± 9%)	Animal glue (mole% ± 9%)
Glycine, GLY (+)	CH ₄ N ⁺	30.034 (30.034)	15.1%	46.0%
Alanine, ALA (+)	C ₂ H ₆ N ⁺	44.050 (44.050)	23.1%	17.0%
Proline, PRO (+)	C ₄ H ₆ N ⁺	68.050 (68.050)	10.5%	16.1%
Valine, VAL (+)	C ₄ H ₁₀ N ⁺	72.081 (72.084)	16.6%	3.0%
Hydroxyproline, HYP (+)	C ₄ H ₈ NO ⁺	86.061 (86.065)	0.0%	12.1%
Isoleucine, ISO (+)	C ₅ H ₁₂ N ⁺	86.097 (86.100)	12.4%	1.9%
Leucine, LEU (+)	C ₅ H ₁₂ N ⁺	86.097 (86.100)	21.9%	3.7%
Generic protein (-)	CN ⁻	26.003 (26.005)	Not applicable	Not applicable
Palmitic acid, PA (-)	CH ₃ (CH ₂) ₁₄ COO ⁻	255.232 (255.231)	Not applicable	Not applicable
Stearic acid, SA (-)	CH ₃ (CH ₂) ₁₆ COO ⁻	283.264 (283.261)	Not applicable	Not applicable

Percentages are given as mole percent of stable amino acids, determined by the remaining total protein before and after artificial aging at 50°C and 50% relative humidity for 500 hours. Minor differences from a total of 100% result from rounding errors.

Table 6.6: Table of specific positive and negative ion fragments observed during ToF-SIMS analysis, and the expected molar percentages as reported by Schilling, et al. (1998) for aged egg yolk and aged animal glue (rabbit). Percentages are given as mole percent of stable amino acids, determined by the remaining total protein before and after artificial aging at 50°C and 50% relative humidity for 500 hours. Minor differences from a total of 100.0% result from rounding errors.

alone to confirm the presence of egg yolk, glues, and other proteins; this should only be done when additional ion fragments corresponding to amino acids can be identified and when nitrogen is absent (or at least present in trace amounts) from fillers and/or pigments potentially in the cross-section. Finally, the present system used in this study appeared to have difficulty effectively identifying the presence of mercury in the vermilion paints. The reason for this discrepancy is currently unknown; however, it is possible that shifting to a different ion gun or adjusting certain parameters would improve the detection of the ion fragment Hg⁺. Future research should explore the cause and effect of varying ion guns (e.g. bismuth, cesium, gallium, etc.) that have been used in ToF-SIMS imaging studies and how this may impact the fragmentation process and therefore the interpretation of the paint sample.

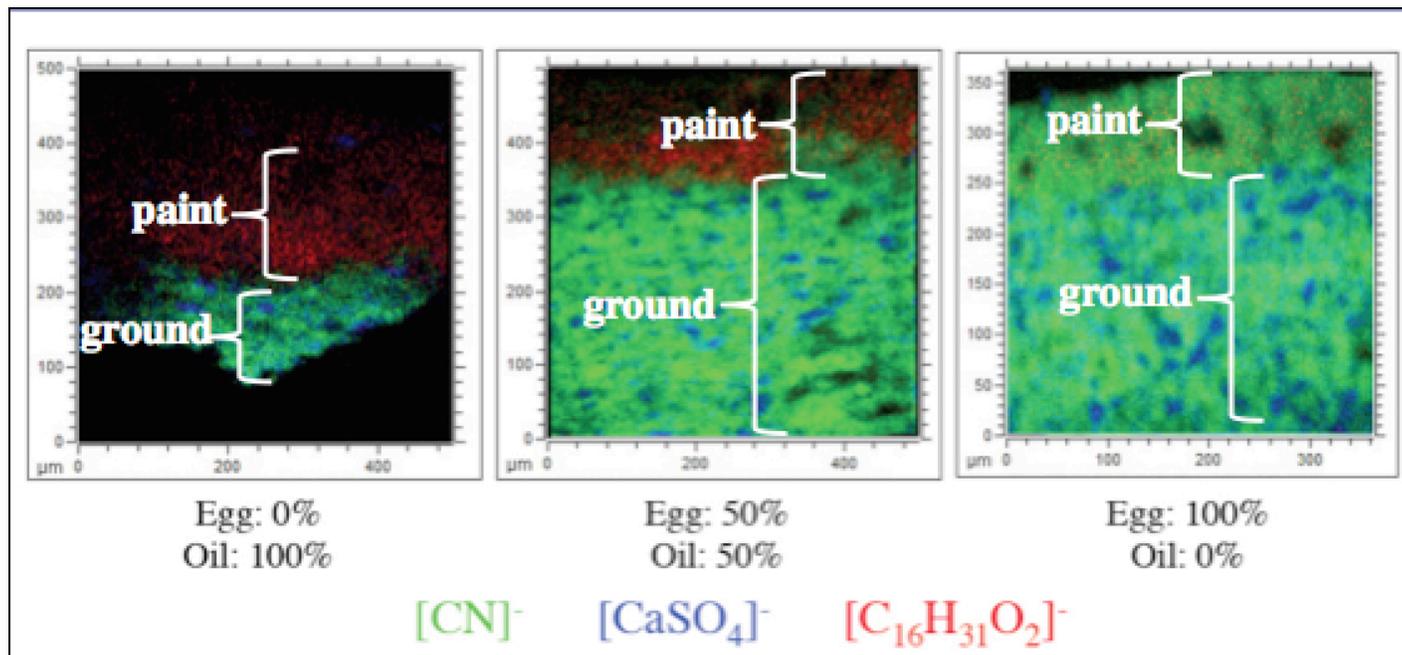


Figure 6.35: ToF-SIMS images obtained from yellow ochre paint references bound in 100% oil (left), 50% egg/50% oil (middle), and 100% egg (right) in negative-ion mode, showing the distribution of protein (CN^- ; shown in green), gypsum in the ground ($CaSO_4^-$; shown in blue), and palmitic acid ($C_{16}H_{31}O_2^-$; shown in red). It should be noted that the signal strength of the CN^- in the egg tempera paint (right) is so strong that it overwhelms the palmitic acid signal when mapped simultaneously (see Figure 6.36).

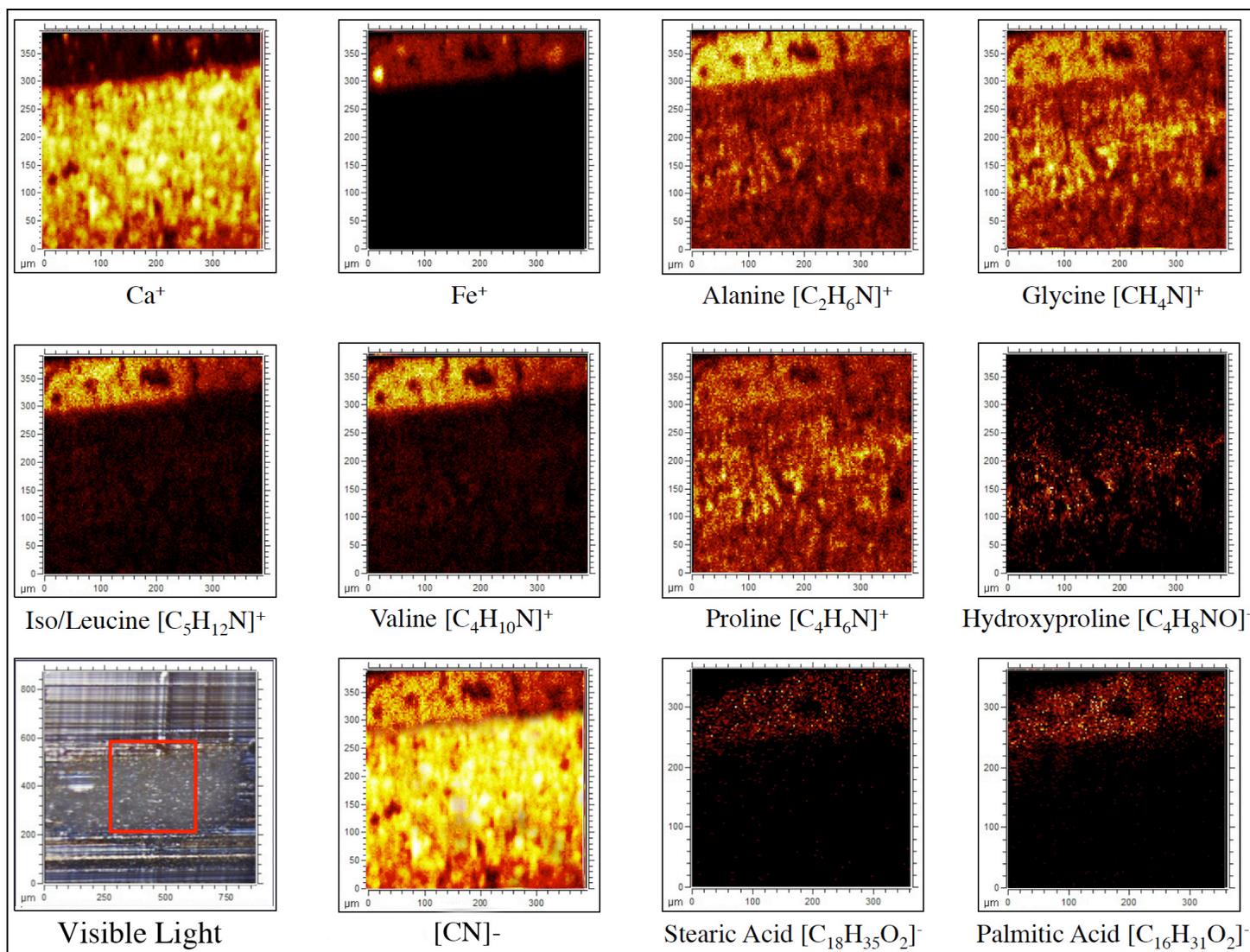


Figure 6.36: ToF-SIMS images obtained from a yellow ochre paint reference bound in 100% egg tempera over a glue-containing ground (visible image shown in bottom left) in both positive- and negative-ion mode. Top row shows the distribution of calcium (Ca^+), iron (Fe^+), alanine ($\text{C}_2\text{H}_6\text{N}^+$), and glycine (CH_4N^+); middle row shows the distribution of isoleucine/leucine ($\text{C}_5\text{H}_{12}\text{N}^+$), valine ($\text{C}_4\text{H}_{10}\text{N}^+$), proline ($\text{C}_4\text{H}_6\text{N}^+$), and hydroxyproline ($\text{C}_4\text{H}_8\text{NO}^+$); bottom row shows the distribution of protein (CN^-), stearic acid ($\text{C}_{18}\text{H}_{35}\text{O}_2^-$), and palmitic acid ($\text{C}_{16}\text{H}_{31}\text{O}_2^-$). The co-localization of amino acid fragments (with the exception of hydroxyproline) and fatty acids suggests the presence of egg yolk while the signal for hydroxyproline can only be seen in the glue-containing gesso ground.

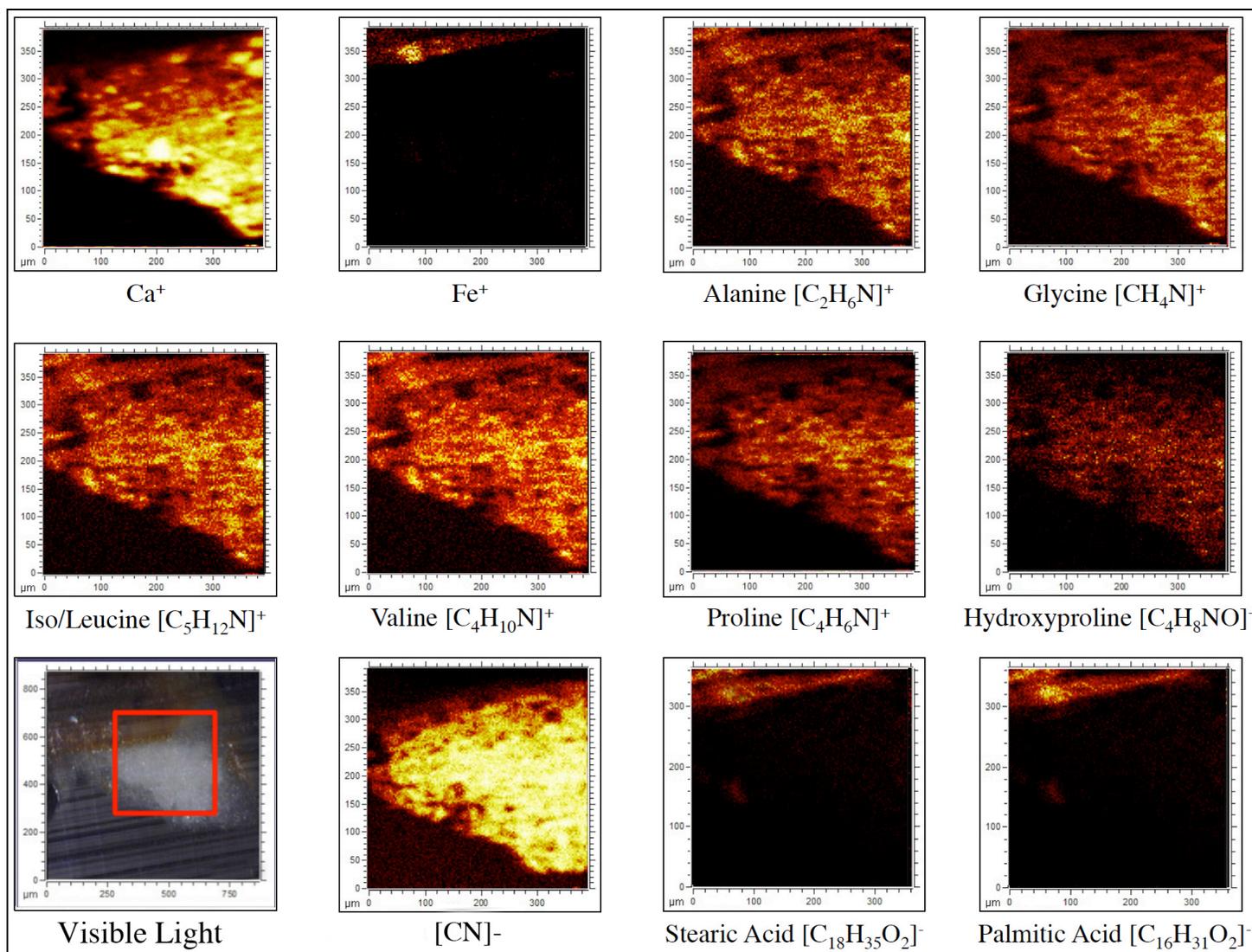


Figure 6.37: ToF-SIMS images obtained from a yellow ochre paint reference bound in 25% egg tempera/75% linseed oil over a glue-containing ground (visible image shown in bottom left) in both positive- and negative-ion mode. Top row shows the distribution of calcium (Ca^+), iron (Fe^+), alanine ($\text{C}_2\text{H}_6\text{N}^+$), and glycine (CH_4N^+); middle row shows the distribution of isoleucine/leucine ($\text{C}_5\text{H}_{12}\text{N}^+$), valine ($\text{C}_4\text{H}_{10}\text{N}^+$), proline ($\text{C}_4\text{H}_6\text{N}^+$), and hydroxyproline ($\text{C}_4\text{H}_8\text{NO}^+$); bottom row shows the distribution of protein (CN^-), stearic acid ($\text{C}_{18}\text{H}_{35}\text{O}_2^-$), and palmitic acid ($\text{C}_{16}\text{H}_{31}\text{O}_2^-$). The co-localization of amino acid fragments (with the exception of hydroxyproline) and fatty acids suggests the presence of egg yolk while the signal for hydroxyproline can only be seen in the glue-containing gesso ground. Note that higher proportion of linseed oil generates stronger signals for stearic and palmitic as compared with the corresponding fragments in the egg yolk paint sample (with no drying oil present) shown in Figure 6.36.

difficulty effectively identifying the presence of mercury in the vermilion paints. The reason for this discrepancy is currently unknown; however, it is possible that shifting to a different ion gun or adjusting certain parameters would improve the detection of the ion fragment Hg^+ . Future research should explore the cause and effect of varying ion guns (e.g. bismuth, cesium, gallium, etc.) that have been used in ToF-SIMS imaging studies and how this may impact the fragmentation process and therefore the interpretation of the paint sample.

6.5.1 Case Studies: Analysis of Italian Paintings using Time-of-Flight Secondary Ion Mass Spectrometry

Imaging of paint cross-sections using Time-of-Flight Secondary Ion Mass Spectrometry was performed on samples taken from a total of three Italian paintings dating from the fourteenth to the early sixteenth centuries.⁸⁸⁵ As many of these cross-sections were prepared at the Walters Art Museum more than 20 years earlier, information relating to the nature of the embedding resin was not always available. For each case study, the primary goals included the following:

- a) to obtain spatially resolved ToF-SIMS information relating to both the inorganic and organic components of the historically accurate samples
- b) to assess whether ToF-SIMS could effectively differentiate between egg yolk (tempera) and animal glue (collagen)

⁸⁸⁵ In fact samples from three additional Italian Renaissance paintings were analyzed from the Walters Art Museum (Fra Carnevale's *The Ideal City* and *The Abduction of Helen and Her Companions attributed to Antonio da Negroponte*) as well as the North Carolina Museum of Art (Francesco Francia's *Madonna and Child with Two Angels*). These case studies are not included in this dissertation.

- c) to evaluate whether ToF-SIMS could identify and distinguish between these materials in layered paint systems
- d) and to assess whether the information listed in a-c could be obtained from old paint cross-sections, thereby avoiding the need to re-sample the artworks.

The *Madonna of the Candelabra* in the collection of the Walters Art Museum dates to about 1513 and has been associated with Raphael's (1483-1520) Roman period (Figure 6.38).⁸⁸⁶ From a stylistic perspective it has been suggested that Raphael's workshop assistants may have played a role in the execution of the painting, and questions remain about the materials



Figure 6.38: Sample location for ToF-SIMS analysis associated with Raphael's *Madonna of the Candelabra* (attr.; c. 1513, Walters Art Museum, Baltimore).

⁸⁸⁶ Tom Henry and Paul Joannides, "The Madonna dei Candelabri," in *Late Raphael*, eds. Tom Henry and Paul Joannides (New York: Thames & Hudson, 2012), 184-7; Frederico Zeri, "Raphael" in *Italian Paintings in the Walters Art Gallery*, vol. I (Baltimore: Walters Art Gallery, 1976), 348-54.

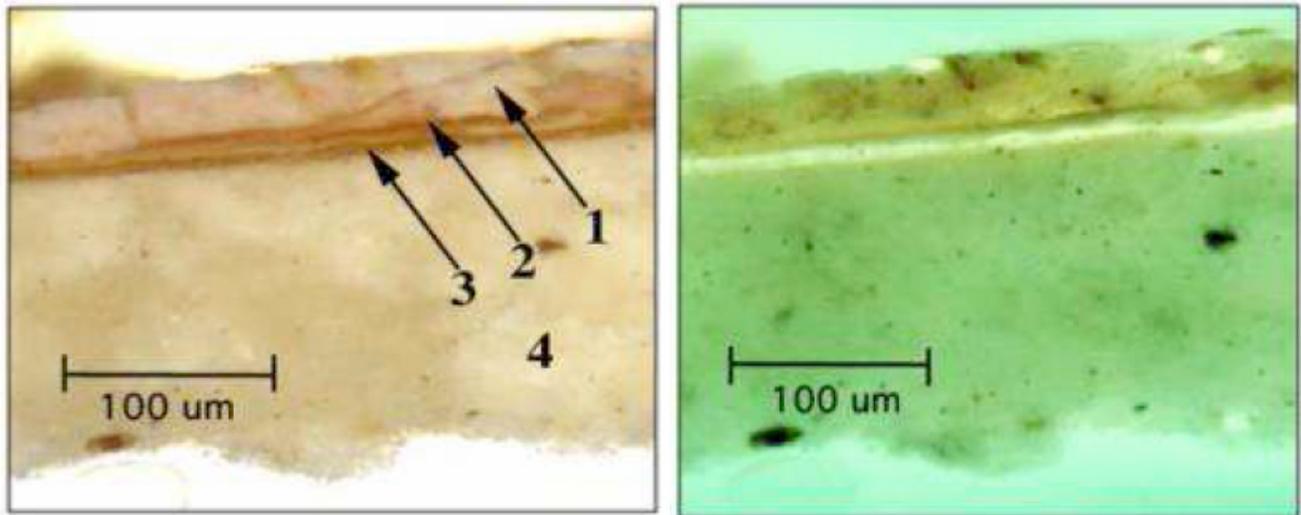


Figure 6.39: Cross-section collected from proper-right arm of the Christ Child in the *Madonna of the Candelabra* attributed to Raphael as seen under high magnification (100x) using visible illumination (left) and ultraviolet illumination (right). A void is present (2, left) between the paint layer (1, left) and the rest of the sample. An auto-fluorescent medium-rich layer (3, left) can be seen directly atop the ground layer (4, left).

and techniques used by the artist or those working within his workshop. Several of Raphael's works have been extensively studied and it appears the artist adopted the use of egg tempera, drying oils, and even tempera grassa (emulsion of egg yolk and drying oil) as binders in his paints.⁸⁸⁷ A cross-sectional sample collected from the proper right arm of the Christ Child shows an extremely fractured paint layer that appears to be cleaving away from the layers

⁸⁸⁷ Jill Dunkerton, "Osservazione sulla tecnica della Madonna londinese di Giovanni Santi," in *Giovanni Santi, Convegno internazionale di studi Urbino*, ed. Ranieri Varese (Milan: Electa, 1999), 57-60; Mills and White, "The Gas Chromatographic Examination of Paint Media: Some Examples of Medium Identification in Paintings by Fatty Acid Analysis," 74; Musei Vaticani, *La Pinacoteca -Vaticana: Catalogo Guida*, eds. Carlo Pietrangeli, Anna Maria De Strobil, and Fabrizio Mancinelli (Rome and citta del Vaticano: Progetti Museali and Musei Vaticani, 1993), 44; Ashok Roy, Marika Spring, and Carol Plazzotta, 'Raphael's Early Work in the National Gallery: Paintings Before Rome,' *The National Gallery Technical Bulletin* 25 (2004): 7-9; Raymond S. White and Jennifer Pilc, "Analyses of Paint Media," *The National Gallery Technical Bulletin* 16 (1995): 86-95.

beneath (Figure 6.39): a gap (location 2) was observed just beneath the paint layer (location 1), as well as a medium-rich auto-fluorescent layer (location 3) immediately atop the ground layer (location 4). As shown in Figure 6.40A, these observations were confirmed in the ToF-SIMS all-masses image (often called the total ion count or TIC image), revealing a lack of signal at the interface between the paint layer and the layer immediately below. Below this void, in Figure 6.40B, ToF-SIMS showed a strong Ca^+ signal at m/z 39.963 corresponding to the medium-rich layer. Lead white was located in the paint layer, as indicated by several characteristic positive lead ions (see Figures 6.40C-E) and their expected isotopic peaks were observed as well.⁸⁸⁸ The presence of a gesso ground layer was confirmed with ToF-SIMS by the presence of calcium ions in positive-ion mode (Ca^+ , m/z 39.963, Figure 6.40B) and associated characteristic fragments in negative-ion mode (CaSO_4^- , m/z 135.914, Figure 6.40B). As SIMS did not detect iron oxides or mercuric sulfide, it is likely that the red colorant in the flesh layer is a red lake, an observation that was later confirmed using scanning electron microscopy (SEM-EDS) that confirmed an absence of iron and mercury; if present, the red lake pigment may be present in concentrations that are too low for either system to detect.⁸⁸⁹

⁸⁸⁸ Additional ion fragments that were detected but not shown in Figure 6.40 include Pb_2^+ (m/z 415.953), $\text{Pb}_3\text{O}_3\text{H}^+$ (m/z 672.923, not shown), Ca_2^+ (m/z 79.923), and CaOH^- (m/z 56.965).

⁸⁸⁹ SEM-EDS was performed at the Scientific Research and Analytical Laboratory at the Winterthur Museum. The cross-section was mounted to an aluminum stub with double-sided carbon tape adhesive. Carbon paint was applied on the side and top surfaces of casting medium, without covering the cross-section itself, to prevent charging. The sample was examined using a Zeiss EVO MA15 scanning electron microscope with LaB6 source at an accelerating voltage of 20kV for the electron beam, stage height of approximately 11mm, and sample tilt of 0°. The EDS data was collected with the Bruker Nano X-flash® detector 6l30 and analyzed with Quantax 200/Esprit 1.9 software. I am grateful for Catherine Matsen for her assistance during the analysis.

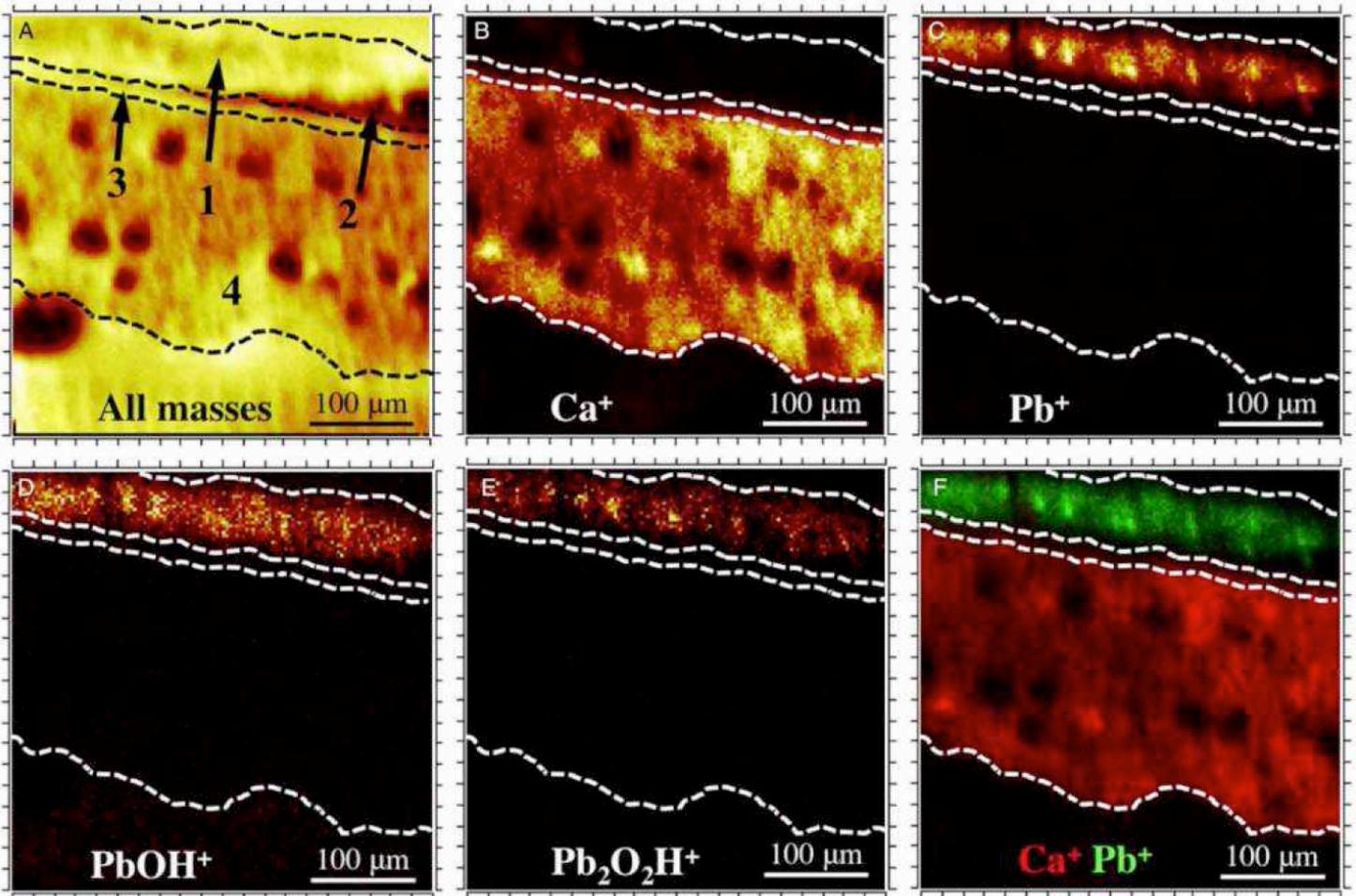


Figure 6.40: ToF-SIMS images obtained from the cross-section in Figure 6.39, in positive-ion mode, showing from left to right, clockwise: (A) all masses (pixel of maximum counts (POMC) has 5,123 counts; total image counts (TIC) is 5.19×10^7); (B) Ca^+ distribution, POMC = 182; TIC = 7.84×10^5 ; (C) Pb^+ distribution, POMC = 100; TIC = 7.80×10^4 ; (D) PbOH^+ distribution, POMC = 19; TIC = 1.72×10^4 ; (E) $\text{Pb}_2\text{O}_2\text{H}^+$ distribution, POMC = 12; TIC = 4.42×10^3 ; (F) Overlay of (B) in red color scale and (C) in a green color scale, with ion counts as above, depicting the ground (bottom of image) and paint (top of image) layers, respectively. Dark voids seen in image (A) indicate voids on the surface of the cross-section. Dashed lines and numbered layers in (A) are drawn from Figure 6.39 to guide the eye.

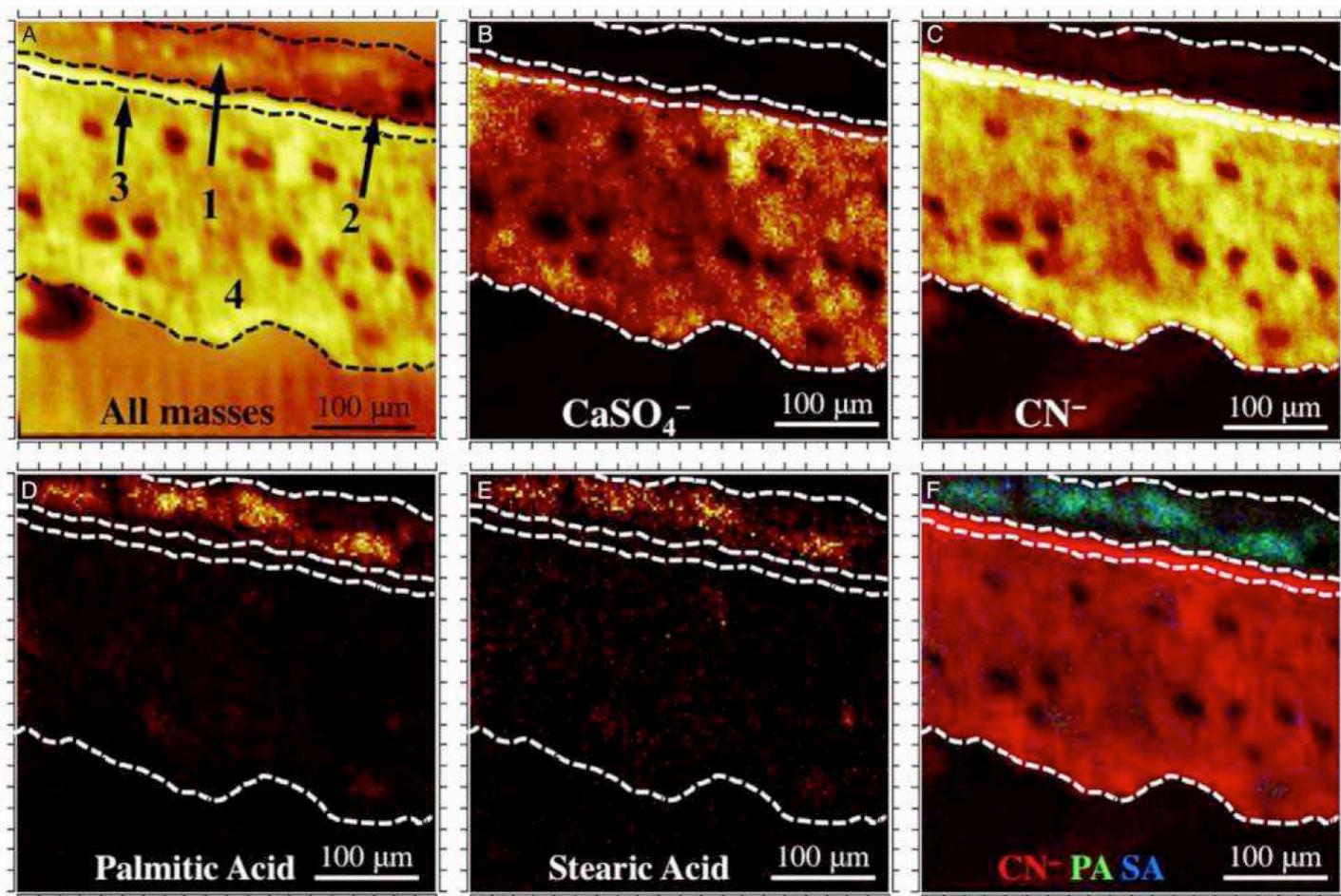


Figure 6.41: ToF-SIMS images obtained from the cross-section in Figure 6.39, in negative-ion mode, showing from left to right, clockwise: (A) all masses, POMC = 11,435; TIC = 1.07×10^8 ; (B) CaSO_4^- distribution, POMC = 96; TIC = 3.22×10^5 ; (C) CN^- distribution, POMC = 721; TIC = 4.48×10^6 ; (D) $\text{C}_{16}\text{H}_{31}\text{O}_2^-$ (palmitic acid, PA) distribution, POMC = 29; TIC = 2.10×10^4 ; (E) $\text{C}_{18}\text{H}_{35}\text{O}_2^-$ (stearic acid, SA) distribution, POMC = 8; TIC = 4.68×10^3 ; (F) Overlay of (C) in red color scale, (D) in green color scale, and (E) in blue color scale depicting the protein-bound ground and oil-bound paint layers. Note in (F) the intense middle layer of CN^- signal between the porous ground and paint layers, absent of CaSO_4^- as shown in (B). Dashed lines and numbered layers in (A) are drawn from Figure 6.39 to guide the eye.

Figure 6.41 depicts the ToF-SIMS images obtained in the same area from the negative-ion ToF-SIMS mode.⁸⁹⁰ The signal for CN^- is a generic marker for proteins, and was observed in abundance in the gesso ground layer (CN^- , m/z 26.003, Figure 6.41C). As depicted in Figures 6.41D-E, negative molecular ions characteristic of the fatty acids palmitic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$) and stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$), observed at m/z 255.232 and 283.264, respectively, corresponded to the thin paint layer atop the ground layer, suggesting the presence of a drying oil. A slight decrease in intensity for these fatty-acid signals was observed along the topmost surface of the paint. While one must be cautious in interpreting signal intensities using ToF-SIMS imaging techniques, the negative-mode intensity overlay in Figure 6.41F may indicate a depletion of these mobile fatty acids in the uppermost layers of the paint surface. While additional research is currently being conducted to further explore the potential causes behind this depletion pattern, certain fatty acids are known to remain mobile over several hundreds of years, migrating to the surface in response to changes in the environment, intrinsic chemical reactions within the paint/ground, and/or previous restoration attempts that have leached fatty acids along the upper portion of the paint layer(s).⁸⁹¹

⁸⁹⁰ While it might be preferential to use a new microarea for analysis in order to lessen the effects of beam-induced sample damage, the small size of the sample only allowed for a single analysis spot. Because of the low beam dosage per analysis (1×10^{12} ions/cm²) the sample was not microtomed between positive-ion and negative-ion analysis so that the sample could be preserved, and so that it could be known with confidence that the analyses corresponded to the exact same surface.

⁸⁹¹ Eugena Ordonez and John Twilley, "Clarifying the haze: Efflorescence on works of art," *Analytical Chemistry* (1997) 69: 416A-422A, doi: 10.1021/ac971692l; Schilling, Carson, and Khanjian, "Gas chromatographic determination of the fatty acid and glycerol content of lipids, IV: Evaporation of fatty acids and the formation of ghost images by framed oil paintings," 242-7; Jaap J. Boon, Frank Hoogland, and Katrien Keune, "Chemical process in aged oil paints affecting metal soap migration and aggregation," in *AIC Specialty Group Postprints, 34th annual meeting, Providence, Rhode Island, 16-19 June, 2006*, ed. Helen Mar Parkin (Providence: American Institute for Conservation, 2007), 18-25; Joyce H. Stoner, "Collaborations with Living Artists: The Wyeths (a.k.a. the Pennsylvania Bruegels)," in

Turning now to a more detailed analysis of the presence of proteins in the sample, the positive-ion mode of ToF-SIMS indicated the presence of several amino acid fragments, as shown in Figure 6.42 including glycine (CH_4N^+ , m/z 30.034), alanine ($\text{C}_2\text{H}_6\text{N}^+$, m/z 44.050), proline ($\text{C}_4\text{H}_6\text{N}^+$, m/z 68.050), valine ($\text{C}_4\text{H}_{10}\text{N}^+$, m/z 72.084), hydroxyproline ($\text{C}_4\text{H}_8\text{NO}^+$, m/z 86.065) and isoleucine/leucine ($\text{C}_5\text{H}_{12}\text{N}^+$, m/z 86.100). These protein marker signals were found throughout the ground layer, and were more intense in the medium-rich layer. Since hydroxyproline (Figure 6.42F) was found in both the medium-rich layer and in the gesso ground layer, it can be concluded that the artist chose to size his gesso-glue ground with an additional, un-pigmented layer of animal glue (collagen) prior to applying his oil paint. Note that the presence of the hydroxyproline marker for collagen does not preclude the possibility that egg-yolk tempera was mixed with the animal glue collagen, although this would seem unlikely based on what is currently known regarding traditional painting practice during this period. Previous studies carried out on Raphael's *Alba Madonna* (Figure 6.43) at the National Gallery of Art in Washington, DC, using different methodologies also revealed the use of an

ICOM Committee for Conservation Preprints, 12th Triennial Meeting, Lyon, 29 August – 3 September, 1999, ed. Janet E. Bridgeland, vol. I (London: James & James, 1998), 412; Carol Mancusi-Ungaro, “Embracing humility in the shadow of the artist,” in *Personal Viewpoints: Thoughts about Painting Conservation – A Seminar Organized by the J. Paul Getty Museum, the Getty Conservation Institute, and the Getty Research Institute at the Getty Center, Los Angeles, June 21-22, 2001*, ed. Mark Leonard (Getty Conservation Institute: Los Angeles, 2003), 83-94; Petria Noble and Jaap J. Boon, “Metal soap degradation of oil paintings: aggregates, increased transparency and efflorescence,” in *AIC Paintings Specialty Group Postprints, 34th Annual Meeting in Providence, Rhode Island, 16–19 June 2006*, ed. Helene Mar Parkin (Washington DC: American Institute for Conservation, 2007), 1-9; Petria Noble and Annelies van Loon, “Evaporation of fatty acids and formation of whitish deposits on the inside of the glass of microclimate frames: a case study in the Mauritshuis” (poster presented at the 38th Annual Meeting of the American Institute for Conservation of Historic and Artistic Works, Milwaukee, 11–14 May, 2010; Scott R. Williams, “Blooms, blushes, transferred images and mouldy surfaces: what are these distracting accretions on art works?” in *Proceedings of the 14th Annual IIC-CG conference, Toronto, Ontario, May 27-30*, ed. Johanna G. Wellheiser (1998, IIC-Canadian Group: Ottawa), 65-84.

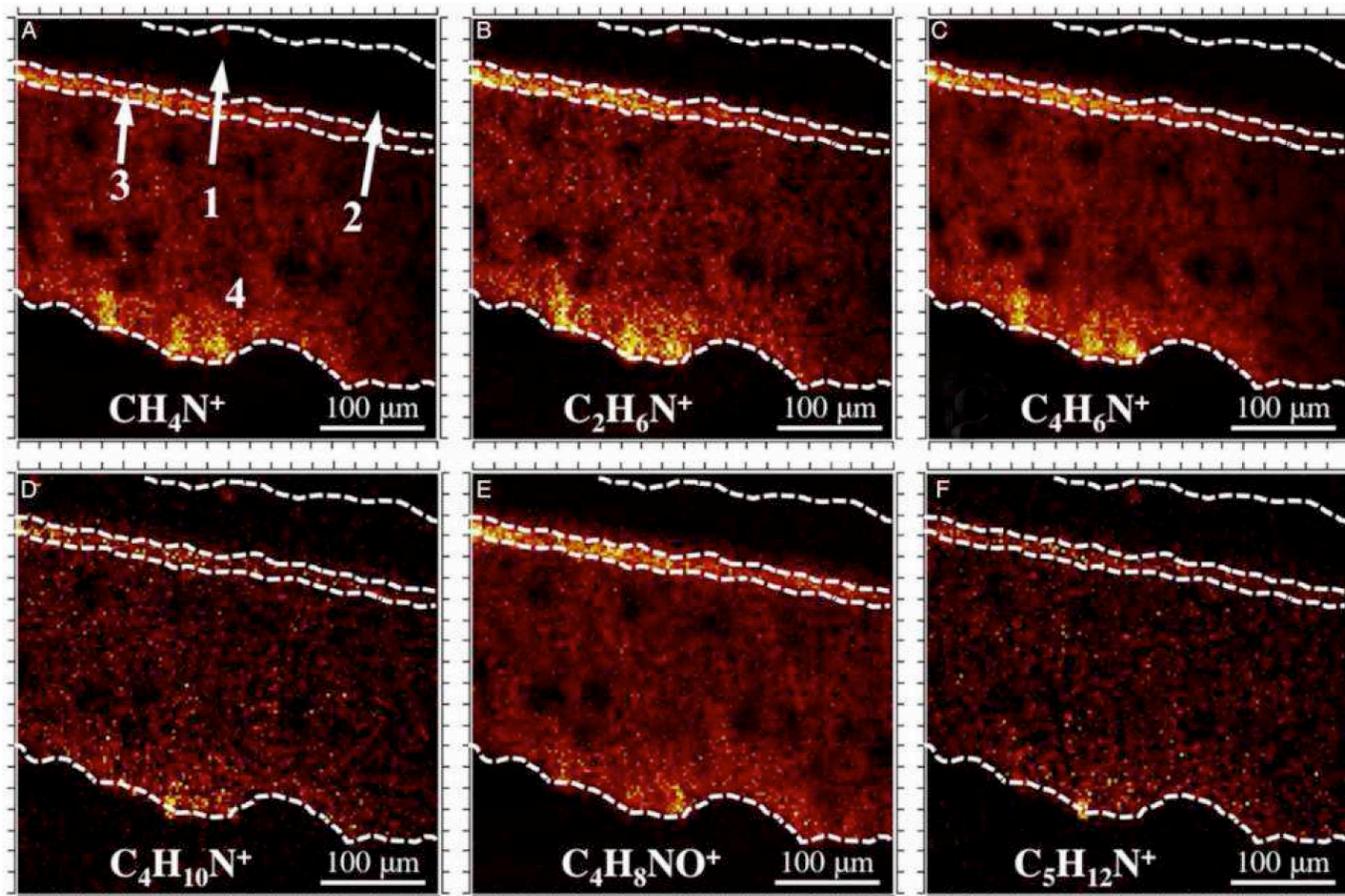


Figure 6.42: ToF-SIMS images of amino acid fragments obtained from the cross-section shown in Figure 6.39 in positive-ion mode from left to right (clockwise) showing (A) CH_4N^+ (glycine) distribution, POMC = 40; TIC = 8.19×10^4 ; (B) $\text{C}_2\text{H}_6\text{N}^+$ (alanine) distribution, POMC = 28; TIC = 6.40×10^4 ; (C) $\text{C}_4\text{H}_6\text{N}^+$ (proline) distribution, POMC = 55; TIC = 1.15×10^5 ; (D) $\text{C}_4\text{H}_{10}\text{N}^+$ (valine) distribution, POMC = 10; TIC = 1.40×10^4 ; (E) $\text{C}_4\text{H}_8\text{NO}^+$ (hydroxyproline) distribution, POMC = 31; TIC = 6.65×10^4 ; (F) $\text{C}_5\text{H}_{12}\text{N}^+$ (isoleucine/leucine) distribution, POMC = 10; TIC = 1.15×10^4 . Note the strong signal for hydroxyproline in (E) along the medium-rich layer immediately on top of the ground layer, indicating the presence of a glue-containing material in this region as well as throughout the gesso ground. Dashed lines and numbered layers in (A) are drawn from Figure 6.39 to guide the eye.

animal-glue size layer atop the gesso ground layer.⁸⁹² In addition, a survey conducted at the Louvre in Paris has shown the presence of both proteins and oils in the *imprimatura* or preparatory layer on a handful of works by Raphael, some of which lacked the presence of pigments and were binder-rich.⁸⁹³ It is our opinion that this demonstrated ability of ToF-SIMS to identify an amino acid that is unique to collagen allows us to make significant conclusions regarding Raphael's technique that may assist art historians, conservators and scientists in answering questions relating to authorship and workshop practice.

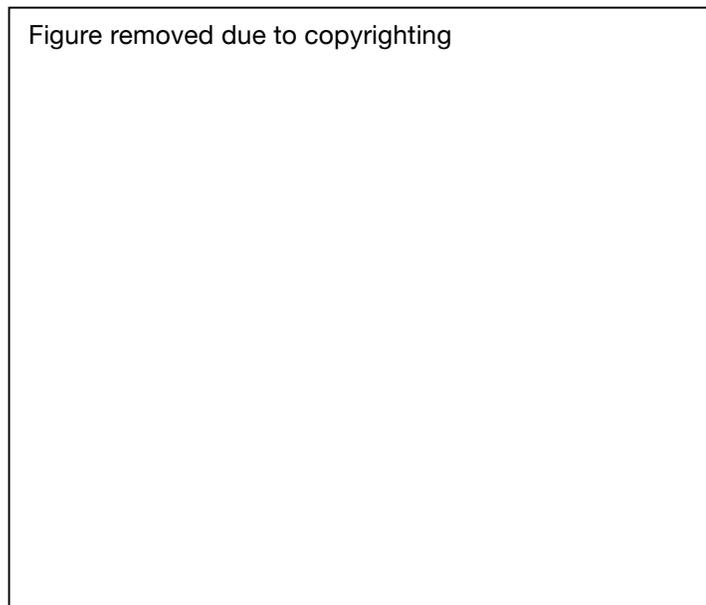


Figure 6.43: Raphael, *Alba Madonna* (1510, National Gallery of Art, Washington, DC).

⁸⁹² Barbara Berrie and Elizabeth Walmsley, "Raphael's 'Alba Madonna,'" in *Raphael's Painting Technique: Working Practices Before Rome*, eds. Marika Spring and Ashok Roy (Florence: Nardini Editore, 2007), 101-8.

⁸⁹³ Bruno Mottin, Elisabeth Ravaud, Gilles Bastian, and Myriam Eveno, "Raphael and his Entourage in Rome: Laboratory Study of the Works in the Musee du Louvre," in *Late Raphael*, eds. Tom Henry and Paul Joannides (New York: Thames & Hudson, 2012), 362-3.

The *Pentecoste* (Figure 6.44) by the Sienese painter Matteo di Giovanni (1430-1495), was likely executed towards the end of the artist's career (c. 1480-89), and questions remained as to whether or not the artist executed this work in egg tempera, drying oils, or *tempera grassa*.⁸⁹⁴ A sample collected from the Madonna's blue robe near the bottom edge of the painting was prepared using the procedures previously described (using a microtome equipped with a diamond knife). Optical examination under high magnification, as seen in Figure 6.45, revealed evidence of an underdrawing (location 3) atop the ground layer (location 4), followed by a thick white layer of paint (location 2) beneath a rather thin degraded paint



Figure 6.44: Sample location for ToF-SIMS analysis associated with Matteo di Giovanni's *Pentecoste* (1490, Walters Art Museum, Baltimore).

⁸⁹⁴ Frederico Zeri, "Matteo di Giovanni," in *Italian Paintings in the Walters Art Gallery*, vol. 1 (Baltimore: Walters Art Gallery, 1976), 127-8.

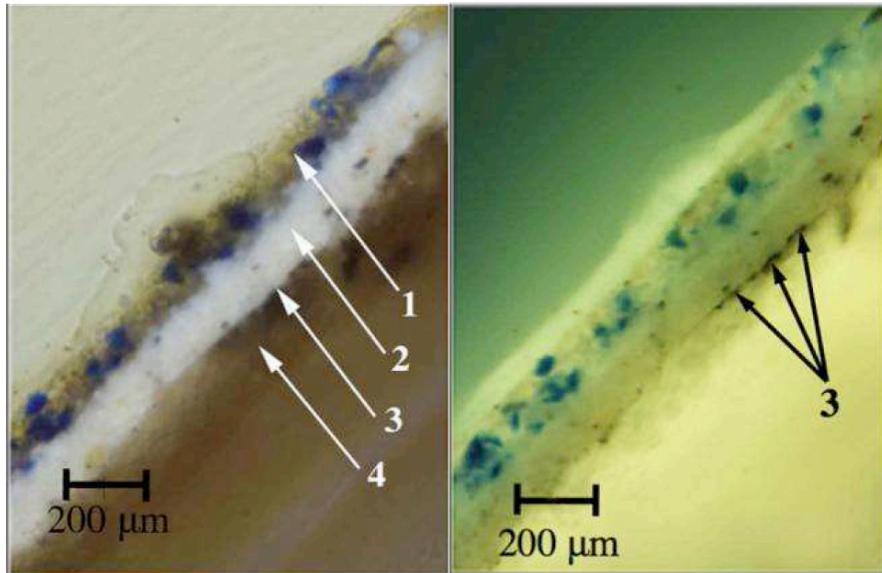


Figure 6.45: Cross-section collected from the Madonna's blue robe in Matteo di Giovanni's *Pentecost* as seen at high magnification (200x) using visible illumination (left) and ultraviolet illumination (right). The degraded paint layer (1) containing particles of lapis is atop a lead white-containing paint layer (2) and a gesso ground layer (4). Evidence of an underdrawing (3) can be seen in the ultraviolet image (bottom) in the form of discrete black particles.

layer (location 1) containing blue lapis particles. Analysis of other paintings by Matteo di Giovanni have also revealed the occasional use of a white *imprimatura*, or preparatory layer, atop a dark, pronounced underdrawing.⁸⁹⁵ Similar to the Raphael cross-section, ToF-SIMS analysis showed ion fragments corresponding with the gesso ground in both positive- and negative-ion mode, while the white paint was found to be rich in lead white, shown in Figures 6.46 and 6.47, respectively. In positive-ion mode, Figure 6.46 shows signals for elemental aluminum and sodium (Figure 6.46F), which were found to co-localize with the blue particles

⁸⁹⁵ Roberto Bellucci and Cecilia Frosinini, "Un 'modello' per la diagnostica integrata," *Kermes* 53 (2004): 29-38; Jill Dunkerton, Carol Christiansen, and Luke Syson, "The Master of the Story of Griselda and Paintings for Sieneese Palaces," *National Gallery Technical Bulletin* 27 (2006): 53-5.

in the optical images (Figure 6.45, left, location 1), confirming the presence of the pigment lapis lazuli. Figure 6.47 shows the mass-resolved ToF-SIMS images for the observed prominent negative ions. A signal for CN^- (m/z 26.003) can be seen throughout the paint and ground layers in Figure 6.47C (a generic marker that can be used to identify protein). Figure 6.48 shows amino acid fragment signals for glycine (CH_4N^+ , m/z 30.034, Figure 6.48A), alanine ($\text{C}_2\text{H}_6\text{N}^+$, m/z 44.050, Figure 6.48B), proline ($\text{C}_4\text{H}_6\text{N}^+$, m/z 68.050, Figure 6.48C), valine ($\text{C}_4\text{H}_{10}\text{N}^+$, m/z 72.084, Figure 6.48D), hydroxyproline ($\text{C}_4\text{H}_8\text{NO}^+$, m/z 86.065, Figure 6.48E), and isoleucine/leucine ($\text{C}_5\text{H}_{12}\text{N}^+$, m/z 86.100, Figure 6.48F). These protein signals were observed both in the ground layer and in the paint layer with the exception of hydroxyproline, which was detected only in the ground layer (Figure 6.48E). This suggests that the artist applied egg-tempera-bound paints atop a glue-containing gesso ground (also confirmed by the presence of fatty acid fragments found in the paint layers). Fatty acid images can be seen in Figure 6.47D (palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{COO}^-$, m/z 255.232) and Figure 6.47E (stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$, m/z 283.264).

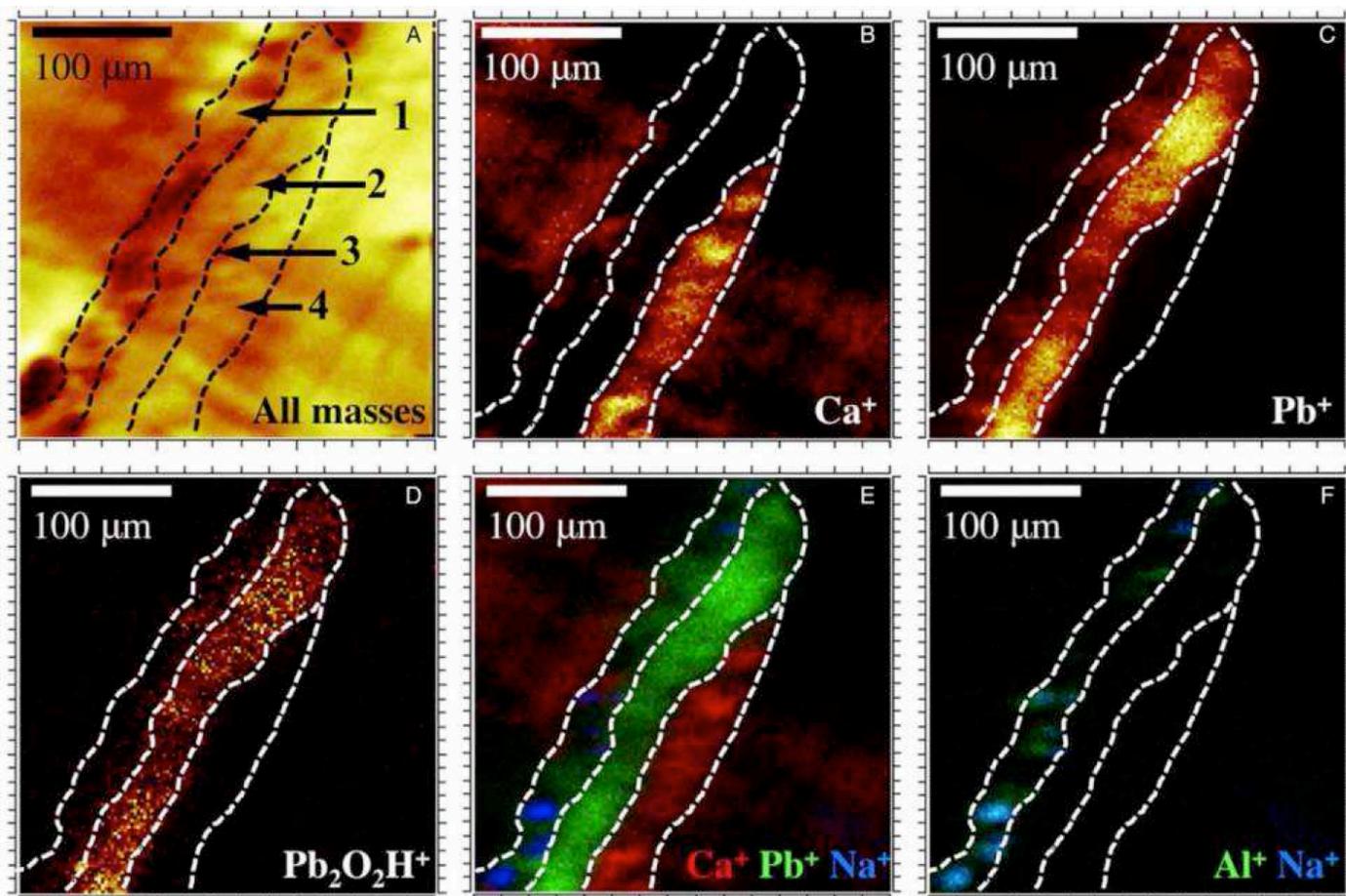


Figure 6.46: ToF-SIMS images obtained from the cross-section in Figure 6.45 in positive-ion mode, showing (A) all masses, POMC = 6,306; TIC = 5.84×10^7 ; (B) Ca^+ distribution, POMC = 156; TIC = 6.60×10^5 ; (C) Pb^+ distribution, POMC = 123; TIC = 1.86×10^5 ; (D) $\text{Pb}_2\text{O}_2\text{H}^+$ distribution, POMC = 9; TIC = 6.82×10^3 ; (E) Overlay of (B) in red color scale, (C) in green color scale, and Na^+ (POMC = 492; TIC = 1.03×10^6) in blue color scale depicting the ground layer (right of image), middle, and upper (left of image) layers; (F) Overlay of Al^+ (POMC = 59; TIC = 2.15×10^4) in green color scale and Na^+ in blue color scale, showing well-aligned, discrete particles, confirming the presence of lapis lazuli in the upper paint layer. Dashed lines and numbered layers in (A) are drawn from Figure 6.45 to guide the eye.

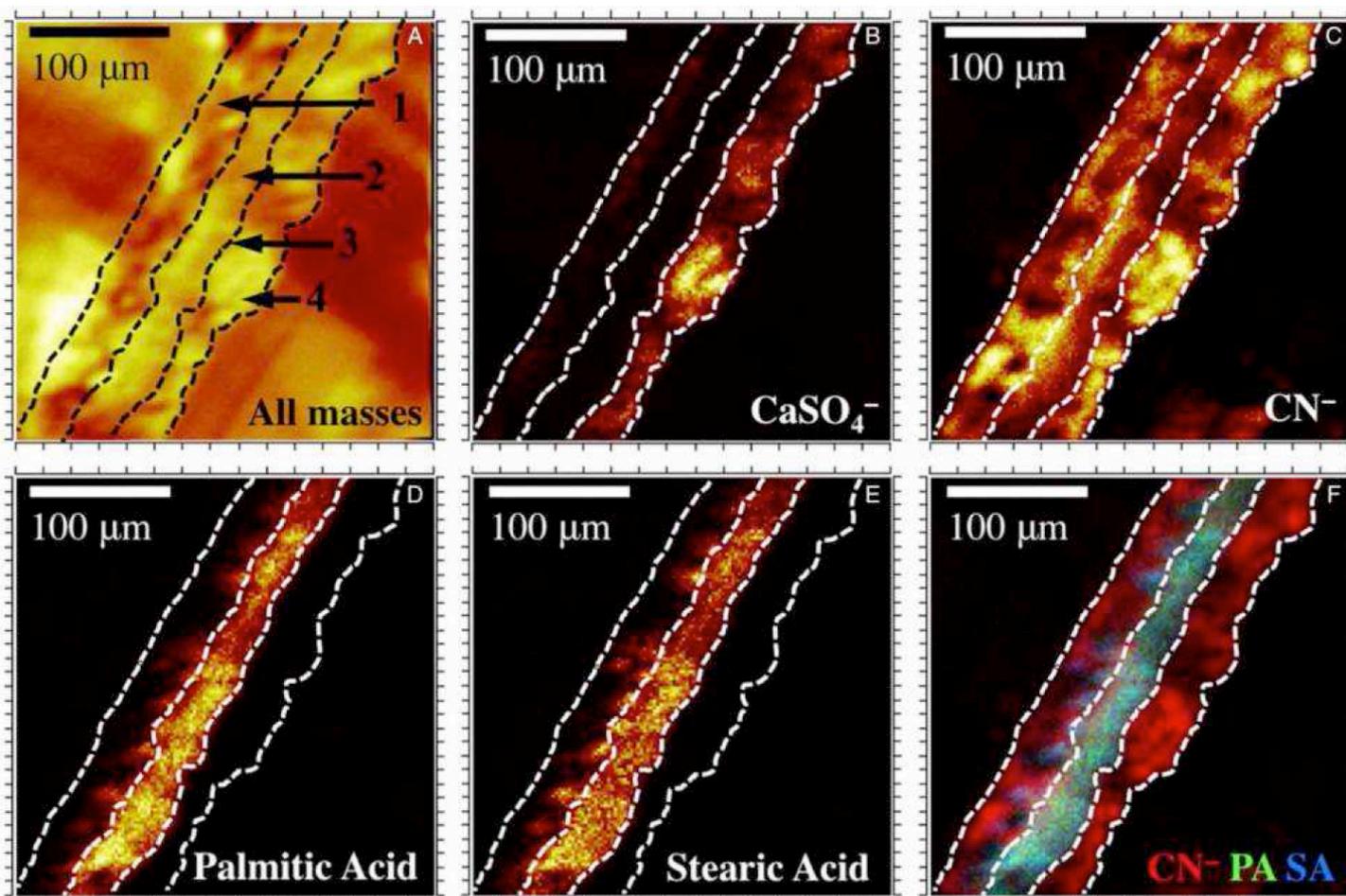


Figure 6.47: ToF-SIMS images obtained from the cross-section in Figure 6.45, in negative-ion mode, showing (A) all masses, POMC = 9,323; TIC = 8.18×10^7 ; (B) CaSO_4^- distribution, POMC = 69; TIC = 6.56×10^4 ; (C) CN^- distribution, POMC = 238; TIC = 9.34×10^5 ; (D) $\text{C}_{16}\text{H}_{31}\text{O}_2^-$ (palmitic acid, PA) distribution, POMC = 78; TIC = 9.49×10^4 ; (E) $\text{C}_{18}\text{H}_{35}\text{O}_2^-$ (stearic acid, SA) distribution, POMC = 38; TIC = 4.49×10^4 ; (F) Overlay of (C) in red color scale, (D) in green color scale, and (E) in blue color scale depicting the protein-bound ground layer (right of image) and protein-bound tempera paint (left of image) layers. Note in (F) the observed decrease in signals for fatty acids approaching the top (left of image) portion of the cross-section. Dashed lines and numbered layers in (A) are drawn from Figure 6.45 to guide the eye.

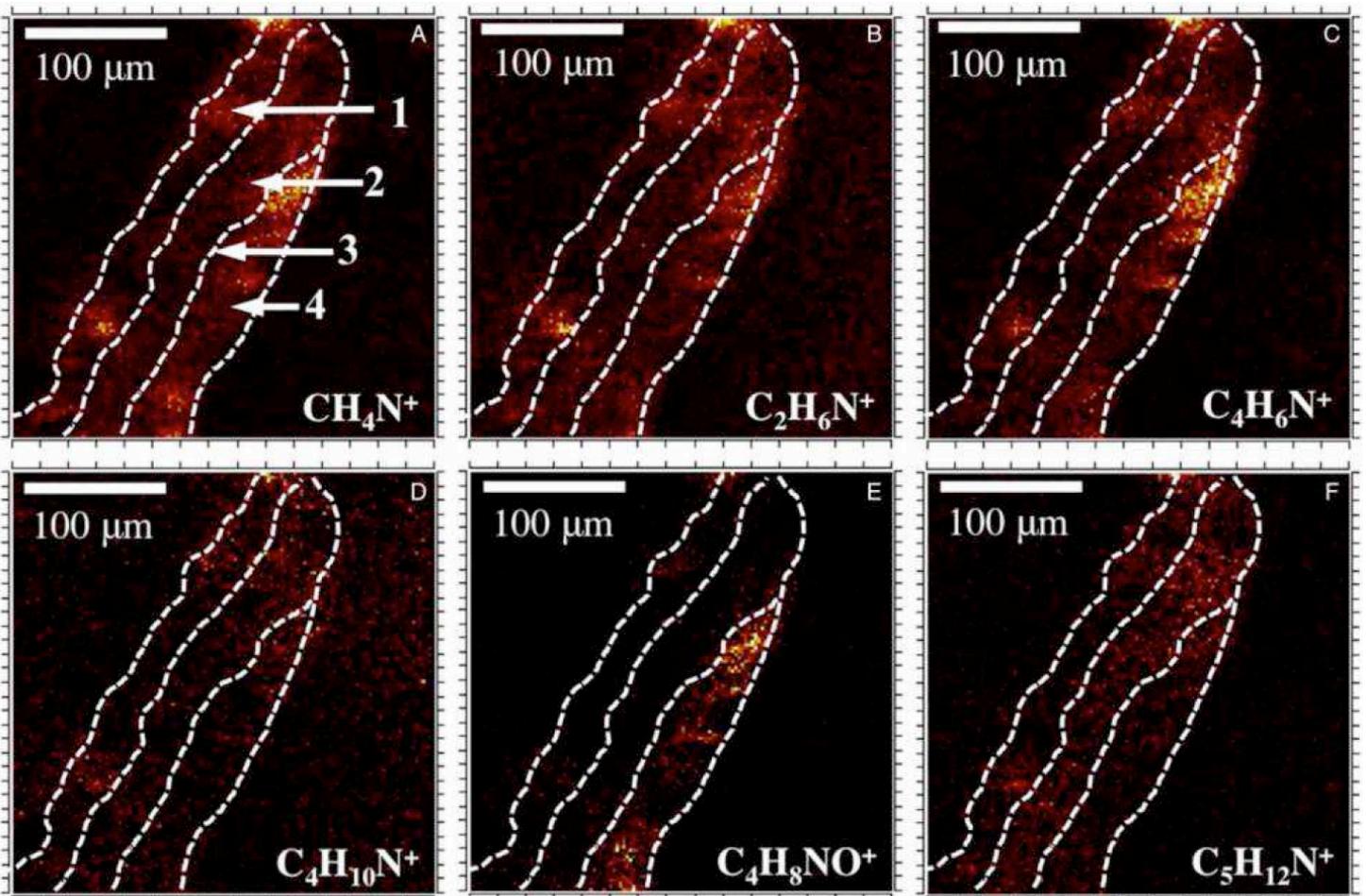


Figure 6.48: ToF-SIMS images of amino acid fragments obtained from the cross-section in Figure 6.45, in positive-ion mode showing (A) CH_4N^+ (glycine) distribution, POMC = 29; TIC = 3.73×10^4 ; (B) $\text{C}_2\text{H}_6\text{N}^+$ (alanine) distribution, POMC = 23; TIC = 3.39×10^4 ; (C) $\text{C}_4\text{H}_6\text{N}^+$ (proline) distribution, POMC = 21; TIC = 2.32×10^4 ; (D) $\text{C}_4\text{H}_{10}\text{N}^+$ (valine) distribution, POMC = 8; TIC = 7.51×10^3 ; (E) $\text{C}_4\text{H}_8\text{NO}^+$ (hydroxyproline) distribution, POMC = 10; TIC = 7.93×10^3 ; (F) $\text{C}_5\text{H}_{12}\text{N}^+$ (isoleucine/leucine) distribution, POMC = 10; TIC = 6.52×10^3 . Note that the signal for hydroxyproline in (E) can only be found in the gesso ground layer and not in the tempera paint layers. Dashed lines and numbered layers in (A) are drawn from Figure 6.45 to guide the eye.

Jill Dunkerton's interpretation of samples collected from Matteo di Giovanni's *Judith* or *Tomyris of Scythia* (Figure 6.49) at the Indiana University Art Museum also suggested the use of egg tempera.⁸⁹⁶ As stated previously, recent research has also shown that Matteo occasionally employed a white *imprimatura* layer consisting of lead white in egg tempera. Similar to the Raphael sample (Figures 6.41D, 6.41E, and 6.41F), a marked intensity gradient of the ToF-SIMS fatty acid marker signals was seen to occur along the top surface of the paint, notably in the degraded top layer containing particles of lapis lazuli, suggesting a depletion of fatty acids in the uppermost layers of the paint surface.

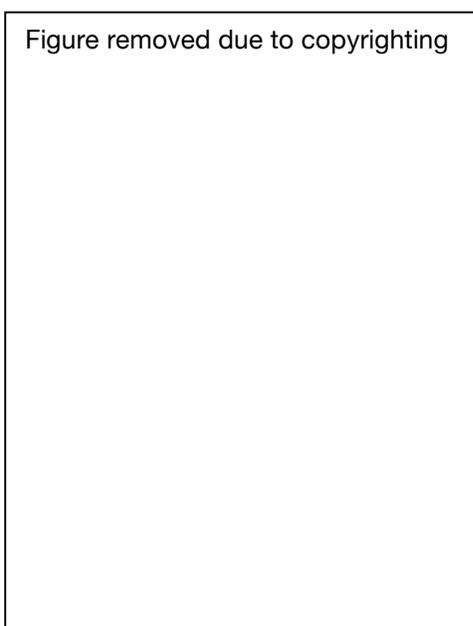


Figure 6.49: Matteo di Giovanni, *Judith with the Head of Holofernes* or *Tomyris of Scythia* (c. 1493-4, Indiana University Art Museum, Bloomington).

⁸⁹⁶ Dunkerton et al., "The Master of the Story of Griselda and Paintings for Sieneese Palaces," 53-5.

The *Entombment* (Figure 6.50) by the Siennese painter Giovanni di Paolo (1403-1482), was painted around 1462 and is one of five predella paintings created for an altarpiece commissioned by the Malavolti family for their family chapel in the church of San Domenico in Siena.⁸⁹⁷ Paintings by Giovanni di Paolo are typically associated with the egg tempera technique, although the artist is also known to cover large sections of his compositions with gold leaf, even under areas that are completely covered with paint. A sample collected from the degraded green paint of one of the figure's robes was prepared using the procedures previously described (using a microtome equipped with a diamond knife). Optical



Figure 6.50: Sample location for ToF-SIMS analysis associated with Giovanni di Paolo's *The Entombment* (1426, Walters Art Museum, Baltimore).

⁸⁹⁷ Frederico Zeri, "Giovanni di Paolo," in *Italian Paintings in the Walters Art Gallery*, vol. 1 (Baltimore: Walters Art Gallery, 1976), 116-21. Note that the central panel of the altarpiece depicts the Virgin and Child and is still located in Italy.

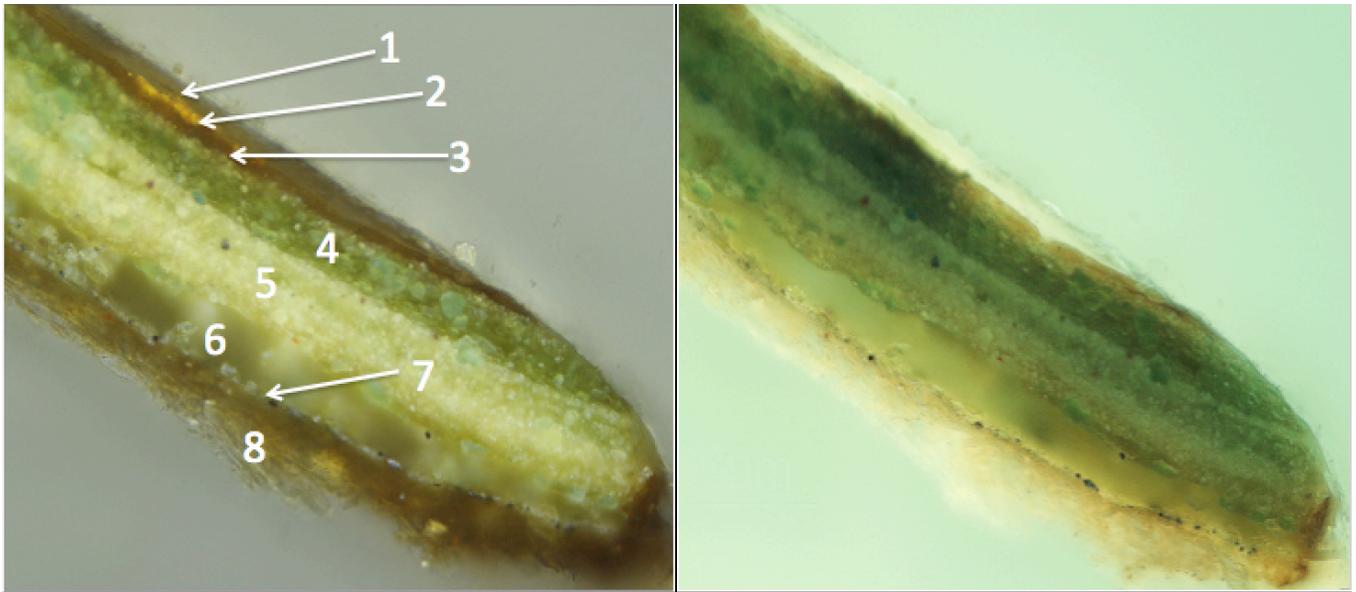


Figure 6.51: Cross-section collected from a figure's green drapery in *The Entombment* by Giovanni di Paolo as seen at high magnification (200x) using visible illumination (left) and ultraviolet illumination (right). A thin layer of degraded varnish (1) can be atop a fragment of gold leaf (2) over what is assumed to be a mordant layer (3). This is followed by a copper-green paint (4) applied over multiple layers of paint containing copper, lead, and tin-containing pigments (5). A void (6) exists between the paint and gesso ground (8). Evidence of an underdrawing (7) can be seen in the form of discrete black particles.

examination under high magnification, as seen in Figure 6.51, revealed evidence of an underdrawing (location 7) atop the ground layer (location 8), followed by a substantial void between the ground and paint layers (location 6). It should be noted that the void corresponds to the pattern of delamination that was observed throughout the green passages by the conservators at the Walters Art Museum during the conservation treatment of the painting (green paint was found to readily flake away from the ground).⁸⁹⁸ Lighter, yellow-green paint (location 5) was found to contain lead white, lead-tin yellow, and traces of copper-green

⁸⁹⁸ I am grateful to paintings conservator Karen French at the Walters Art Museum for sharing her observations with me regarding the condition of *The Entombment*.

pigments using both ToF-SIMS analysis, Raman spectroscopy, and SEM-EDS (see Figures 6.52B, 6.52D, and 6.52F).⁸⁹⁹ Subsequent paint layers were found to be rich in copper-green (location 4), followed by a mordant layer (location 3), a thin fragment of gold leaf (location 2), and a degraded varnish coating (location 1).⁹⁰⁰ Similar to the Raphael and Matteo di Giovanni cross-sections, ToF-SIMS analysis showed ion fragments corresponding with the gesso ground in both positive- and negative-ion mode (see Figure 6.52C, 6.52E and Figure 5.53D); however, as only traces of the ground were present, it was not possible to detect a signal for hydroxyproline ($C_4H_8NO^+$, m/z 86.065). Only faint signals for glycine (CH_4N^+ , m/z 30.034, Figure 6.52E), alanine ($C_2H_6N^+$, m/z 44.050, not shown), and valine ($C_2H_6N^+$, m/z 44.050, not shown) could be detected in the paint and ground layers. This observation may be explained by the presence of the highly reactive copper and/or lead-containing pigments, as lead and/or copper may possibly form complexes with amino acids present in the egg tempera binder. The formation of such complexes may lead to an alteration of the binding medium and

⁸⁹⁹ Raman spectroscopy and SEM-EDS analysis was performed at the Scientific Research and Analytical Laboratory at the Winterthur Museum. Analysis was completed using a Renishaw inVia Raman spectrometer using a 785 nm diode laser, a 50x objective, 1200 l/mm grating, a laser power of 3 mW at the sample, a spectral range of 100 cm^{-1} to 3200 cm^{-1} , and a spectral resolution of 1 cm^{-1} /CCD pixel (functional resolution of 3 cm^{-1}). For SEM-EDS analysis, the cross-section was mounted to an aluminum stub with double-sided carbon tape adhesive. Carbon paint was applied on the side and top surfaces of casting medium, without covering the cross-section itself, to prevent charging. The sample was examined using a Zeiss EVO MA15 scanning electron microscope with LaB6 source at an accelerating voltage of 20kV for the electron beam, stage height of approximately 11mm, and sample tilt of 0°. The EDS data was collected with the Bruker Nano X-flash® detector 6l30 and analyzed with Quantax 200/Esprit 1.9 software. I am grateful for Catherine Matsen for her assistance during the analysis.

⁹⁰⁰ It should be noted that the signal for Au could only be determined using negative mode when performing ToF-SIMS analysis. This should be taken into consideration when analyzing samples collected from works of art that may contain traces of metal leaf (e.g. gold, silver, tin, etc.).

therefore effect the detection of certain ion fragments associated with egg protein, something that has been encountered in other studies relating to verdigris.⁹⁰¹ On the other hand, fatty acid fragments could be successfully detected throughout the paint layers (Figures 6.53A and B) as well as the generic CN- ion fragment (Figure 6.52E) suggesting that egg yolk is likely the primary binding medium. The particular type of copper-green pigment present in this sample may influence the detection of certain ion fragments associated with organic binders; as previously stated, the green painted passages throughout this painting (as well as additional paintings from the same predella series) were found to be in poor condition. Analysis using ToF-SIMS detected a fairly significant amount of chlorine, copper chlorides, and trihydroxychlorines (Figures 6.53C and F). It is possible that this reserve of chlorine is associated with the preparation of the copper-green pigment verdigris. Discussed by Theophilus in the twelfth century, “salt green” refers to one method used to prepare the pigment verdigris by exposing strips of metallic copper to honey, salt, and wine.⁹⁰² Reconstructions of the recipe have yielded a wide range of copper products, including atacamite (trihydroxychloride), copper chlorides, cupric hydroxide, and traces of copper

⁹⁰¹ Narayan Khandekar and Alan Phenix, “Some Observations on the Effects of a Selection of Pigments on a Artificially Aged Egg Tempera Film,” *Australian Institute for the Conservation of Cultural Material Bulletin* 25 (2000): 1-7; David A. Scott, *Copper and Bronze in Art: Corrosion, Colorants, and Conservation* (Getty Trust Publications: Getty Conservation Institute, 2002), 77.

⁹⁰² Nicolas Eastaugh, Valentine Walsh, Tracey Chaplin, and Ruth Siddall, *Pigment Compendium: A Dictionary of Historical Pigments* (Oxford: Elsevier Butterworth—Heinemann, 2007), 390; Scott, *Copper and Bronze in Art: Corrosion, Colorants, and Conservation*, 123-38, 281, 411; Gerhard Banik, “Discoloration of Green Copper Pigments in Manuscripts and Works of Graphic Art,” *Restaurator* 10 (1989): 61-73.

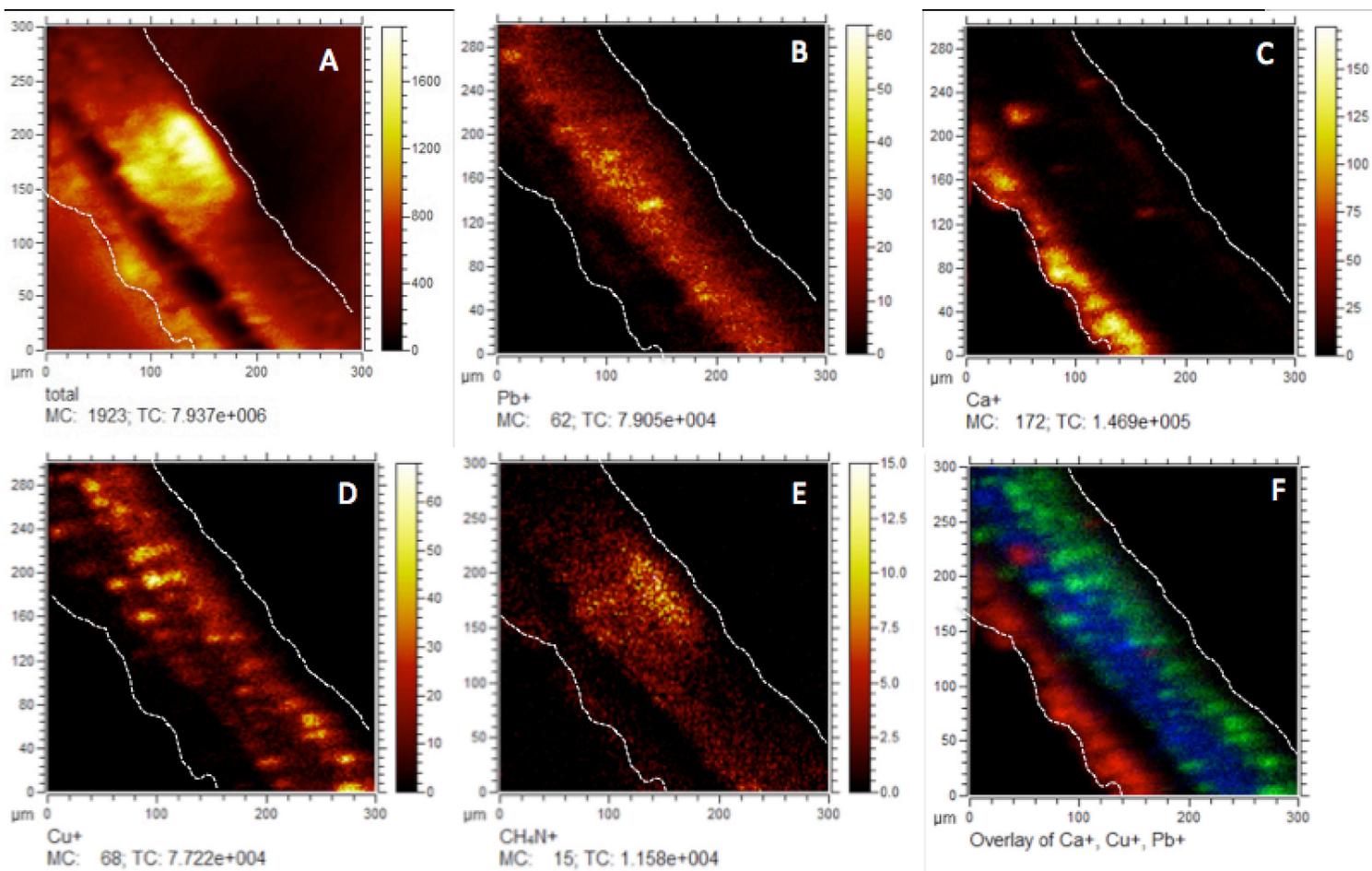


Figure 6.52: ToF-SIMS images obtained from the cross-section in Figure 6.51 in positive-ion mode, showing (A) all masses, POMC = 1,923; TIC = 7.937×10^6 ; (B) Pb^+ distribution, POMC = 62; TIC = 7.905×10^4 ; (C) Ca^+ distribution, POMC = 172; TIC = 1.496×10^5 ; (D) Cu^+ distribution, POMC = 68; TIC = 7.722×10^4 ; (E) CH_4N^+ (glycine) distribution, POMC = 15; TIC = 1.158×10^4 (F) Overlay of (C) in red color scale, (D) in green color scale, and (B) in blue color scale (POMC = 397; TIC = 2.03×10^6) depicting the ground layer (left of image), middle, and upper (left of image) paint layers. Dashed lines are drawn from Figure 6.51 to guide the eye.

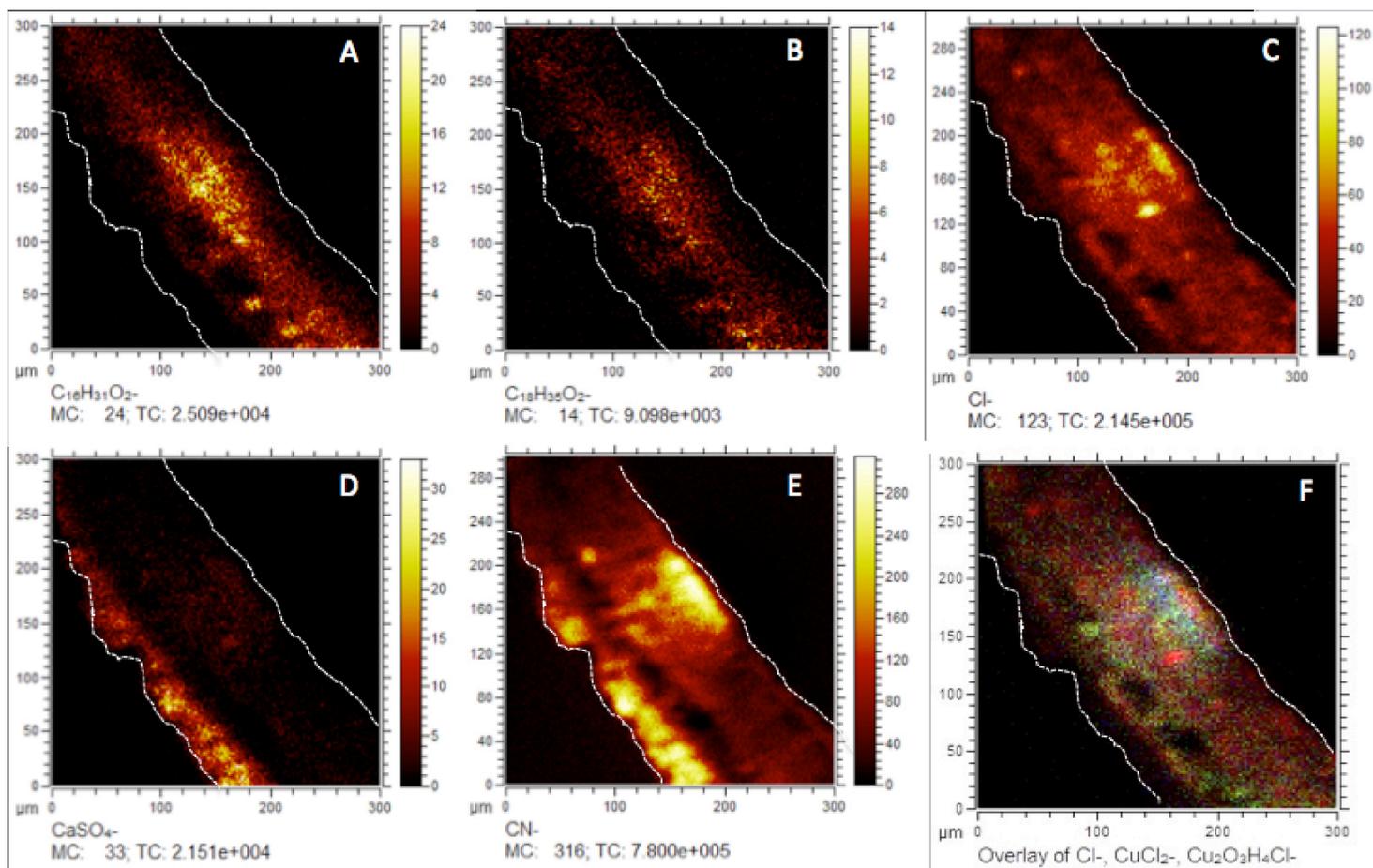


Figure 6.53: ToF-SIMS images obtained from the cross-section in Figure 6.51, in negative-ion mode, showing (A) $C_{16}H_{31}O_2^-$ (palmitic acid, PA) distribution, POMC = 24; TIC = 2.509×10^4 ; (B) $C_{18}H_{35}O_2^-$ (stearic acid, SA) distribution, POMC = 14; TIC = 9.098×10^3 ; (C) Cl^- distribution, POMC = 123; TIC = 2.145×10^5 ; (D) $CaSO_4^-$ distribution, POMC = 33; TIC = 2.151×10^4 ; (E) CN^- distribution, POMC = 316; TIC = 7.800×10^5 ; (F) Overlay of (C) in red color scale, $CuCl_2^-$ distribution in green color scale, and $Cu_2O_3H_4Cl^-$ in blue color scale depicting the presence of various copper chlorides throughout the paint layers. Dashed lines are drawn from Figure 6.51 to guide the eye.

carbonate.⁹⁰³ Given the fact that these predella paintings by Giovanni di Paolo have suffered from extreme delamination in the copper-green passages, it is possible that the residual chlorine leftover from the production of the “salt green” pigment caused a series of reactions to occur within the painting layers. Also known as “bronze disease,” copper chlorides are known to react with moisture and expand to form larger products (such as atacamite), something that would inevitably lead to delamination of the paint film. More research is needed to confirm that “salt green” is in fact present in the sample collected from *The Entombment*; however, the analytical results support the theory that reserves of copper and chlorine may well be linked to instability observed in the green passages.

Based on these preliminary findings it seems that imaging ToF-SIMS is well suited for the simultaneous detection of inorganic and organic materials present in cross-sectional paint samples. It is imperative that the analyst perform initial tests on known reference samples, preferably samples that are prepared using historically accurate materials and/or layering systems (e.g. historically appropriate grounds, etc.). Although this study was not able to analyze aged reference samples, future projects should attempt to include such references in their research for comparative purposes particularly to study the potential migration of mobile fatty acids and metal soap formation. Throughout this study it was found that larger samples tend to generate improved signals as more surface area is exposed on the cross-sectional sample during ToF-SIMS analysis. In addition, ion fragments associated with elemental mercury could not be successfully detected, and metallic gold could be detected only in negative-ion mode. More research is required in order to compare instrumental parameters, namely the ion sources used as cluster guns and the possibility of performing ion milling to

⁹⁰³ Scott, *Copper and Bronze in Art: Corrosion, Colorants, and Conservation*, 123-38, 281, 411; Banik, , “Discoloration of Green Copper Pigments in Manuscripts and Works of Graphic Art,” 61-73

prepare cross-section samples. Finally, it is recommended that all samples which have been subjected to ToF-SIMS analysis be re-microtomed in order to avoid potential complications during subsequent imaging analysis as minimal beam damage to the surface (less than 3 microns) is always a possibility. While ToF-SIMS was found to generate successful results, it is crucial that additional analysis is performed using complementary methods including SEM-EDS, ATR-FTIR, and/or other chromatography methods.

Chapter 7

CONCLUDING OBSERVATIONS AND CONSIDERATIONS FOR FUTURE RESEARCH

Since the development of technical art history, especially in the last quarter of the twentieth century, there has been a continuing interest in the evolution of oil painting in Renaissance Italy. The maturation of conservation as a field is often attributed to its collaboration with science, a relationship that continued to strengthen in response to the art community's fascination with this significant period in Italian art. Since the 1930s, an increasing number of analytical methods have been employed in an effort to better characterize the materials and techniques used by Quattrocento painters. An artist's decision to use an oil binder as opposed to egg tempera is arguably as significant as whether he chooses to use ultramarine over azurite; however, it is the former scenario that remains much more difficult for experts to corroborate. This study has identified a number of misconceptions perpetuated by some of these early scientific studies, research that holds great merit but can no longer be considered as a reliable foundation outlining the adoption of oil painting in Italy; as I have demonstrated in the preceding chapters, the characterization of traditional binding media has proven far more challenging than previous studies have shown.

The gradual shift from egg to oil binders in Quattrocento painting can be directly linked to cultural exchanges between Italy and its Northern neighbors. Oil was the indigenous medium for panel paintings in Northern Europe even before the middle ages, a medium that eventually became synonymous with Flemish paintings among Italian collectors and scholars. In her text *From Flanders to Florence*, Paula Nuttal describes the impact of oil and the gradual influx of northern paintings, stating that “to 15th century Italians [oil paintings] must

have seemed little short of miraculous.”⁹⁰⁴ Exchanges with foreign artists and the importation of Northern works had a profound effect on certain Italian painters, inspiring some to incorporate drying oils into their daily workshop practice. Technical studies on Quattrocento paintings reveal that this transition must be treated as a regional phenomenon: cultural epicenters throughout the North, South, and Central regions of the peninsula operated differently, particularly the guild systems that were often a unique reflection of a city’s political and economic environment. The recovery of the Church following the Papal Schism also played a role in initiating cultural exchanges, prompting a series of international summits and foreign commissions by Italian ecclesiasts. Finally, the fifteenth century witnessed a rise in courtly patronage, as wealthy families throughout Northern Italy commissioned both native and foreign artisans to adorn their palatial establishments with artworks. All of these factors played an integral role in the gradual shift away from traditional tempera painting practice as certain Italian artists, like Antonello da Messina, Giovanni Bellini, and Filippo Lippi, sought to emulate their northern counterparts.

Recent scholarship devoted to the analysis of primary sources, such as artists’ treatises and ancient manuscripts, has also uncovered relevant information relating to early Italian painting technique. While Giorgio Vasari’s account describing the evolution of oil painting in Italy has been repeatedly contested, scholars have been less prone to question the implications that have been traditionally associated with Cennino Cennini’s *Il Libro d’Arte*. Recently re-translated and re-contextualized, much of Cennini’s text appears to have been written in a Paduan dialect with certain sections possibly completed once Cennini had moved from Padua to Florence. Based on these findings, it seems that the text (which does include a handful of

⁹⁰⁴ Paula Nuttal, *From Flanders to Florence* (New Haven & London: Yale University Art Press, 2004), 161.

impractical and impossible recipes) was largely meant to elevate the status of the painting profession, particularly at the Carrara court in Padua where Cennini resided alongside respected philosophers, doctors, and lawyers. This contrasts with earlier notions that the treatise was intended solely as a workshop manual, and therefore more representative of Florentine painting practices. Cennini also wrote that he was able to find oil that was suitable for painting in Florence, indicating that the medium was available for purchase but was still considered somewhat novel. These new findings suggest that Italian painters working in and around the Veneto were introduced to the oil technique well before 1400, possibly earlier than many of their Tuscan counterparts.

In the twenty-first century, technical studies of Quattrocento paintings have improved thanks to advancements in instrumental methodology. However, art historians who specialize in the art of the Italian Renaissance are less likely to be conscious of the ever-changing capacities to characterize traditional binders in easel paintings. While the conservation and scientific communities have made excellent strides in pigment research, there remains much to be explored concerning the organic analysis of artworks such as the identification of animal glues, drying oils, gums, resins, and other materials. In a 2010 interview, David Bomford succinctly summarized this issue:

Pigments have been the most important thing- but that's because pigments are what we can analyze most straightforwardly. Actually, the medium is equally important but much more difficult to analyze. It's only been in relatively recent times that we've had successful and reliable medium analysis. There's still an awful lot about medium analysis we don't understand.⁹⁰⁵

⁹⁰⁵ Terry Drayman-Weisser et al., "The Science in the Art: A Discussion about Collections Research," *Conservation Perspectives: The GCI Newsletter* 25 (Spring 2010): 22-23.

His statement is particularly germane when we consider some of the challenges faced by scientists when attempting to characterize egg and oil paints. As described at length in this dissertation, contamination from restoration materials such as oil-based varnishes, glue-based adhesives, the migration of fatty acids, the presence of reactive pigments, and the formation of degradation products (e.g. metal soaps) are now known to affect the detection of certain chemical markers that are key in helping scientists to identify the binders present in a work of art. We now need to re-evaluate some of the reported findings put forth by early technical studies utilizing gas chromatography-mass spectrometry, particularly as organic analysis requires the destructive sampling of artworks. Given the various complications described above, it may not be possible to successfully identify the original binding media used by Quattrocento painters using chromatography-based analytical methods until further research has been performed and protocols for sample preparation have been standardized.

As scientists continue to tackle these challenges, other techniques have recently demonstrated considerable promise. A more accurate assessment of Quattrocento painting practice can be accomplished if the original stratigraphy of the paint and ground layers is maintained throughout the analytical procedure. Imaging techniques combined with certain methods such as ATR-FTIR and ToF-SIMS allow for the characterization of inorganic and organic materials within discrete layers present in cross-section paint samples. Such methods can aid in differentiating between restoration and original materials without consuming the sample during the process. While ATR-FTIR has proven useful, it is still unable to distinguish between protein sources, something that ToF-SIMS has been able to accomplish. This dissertation has found ToF-SIMS, when combined with other analytical techniques, to be a powerful tool when attempting to characterize samples collected from Italian easel paintings. Not only is the technique able to differentiate between glue and egg protein, but it can be used also to map the location of fatty acid markers. Finally, ToF-SIMS analysis can be used on

cross-sectional samples that have been stored for decades, precluding the need for collecting new samples and allowing samples to be returned to the parent institution once the analysis has been completed. Additional research is needed, however, to compare the efficacy of various ion beams and to explore potential methods for sample preparation that may improve detection of organic and inorganic materials.

No matter what sort of complication can arise during technical analysis, the decision to use an egg vs. an oil binder is inextricably tied to an artist's technique. The manner in which these materials were traditionally used to create certain aesthetic affects is often best learned during the creation of historical reconstructions, using historically accurate pigments and preparation methods to assess the limits and possibilities that are associated with both egg and oil binders. Quick drying egg tempera prevents artists from extensively blending their paints, while drying oils allow for blending to occur over a period of several days. Analysis and examination of thirteenth- and fourteenth-century Italian paintings reveal that oil was occasionally used as a mordant and as the medium for colored glazes applied atop metal leaf. The transparency and saturation imparted by the oil medium would have accentuated the luster of the underlying metal leaf, a technique that may have been learned from other artisans such as those familiar with polychromy. In addition, certain pigments, such as organic colorants, copper-greens, and carbon blacks, can lose their brilliance when applied in egg tempera (Figure 7.1). It is therefore likely that such pigments were among the first materials to have been mixed with an oil medium; Italian painters would have been attracted to the depth and saturation that was not possible to achieve using the traditional tempera technique. Finally, other effects would have lent themselves quite well to the incorporation of oil, particularly the emulation of translucent surfaces such as marble. While additional technical studies are needed to confirm these observations, the first-hand knowledge that can be gained through reconstructing these materials has proved to be invaluable throughout this

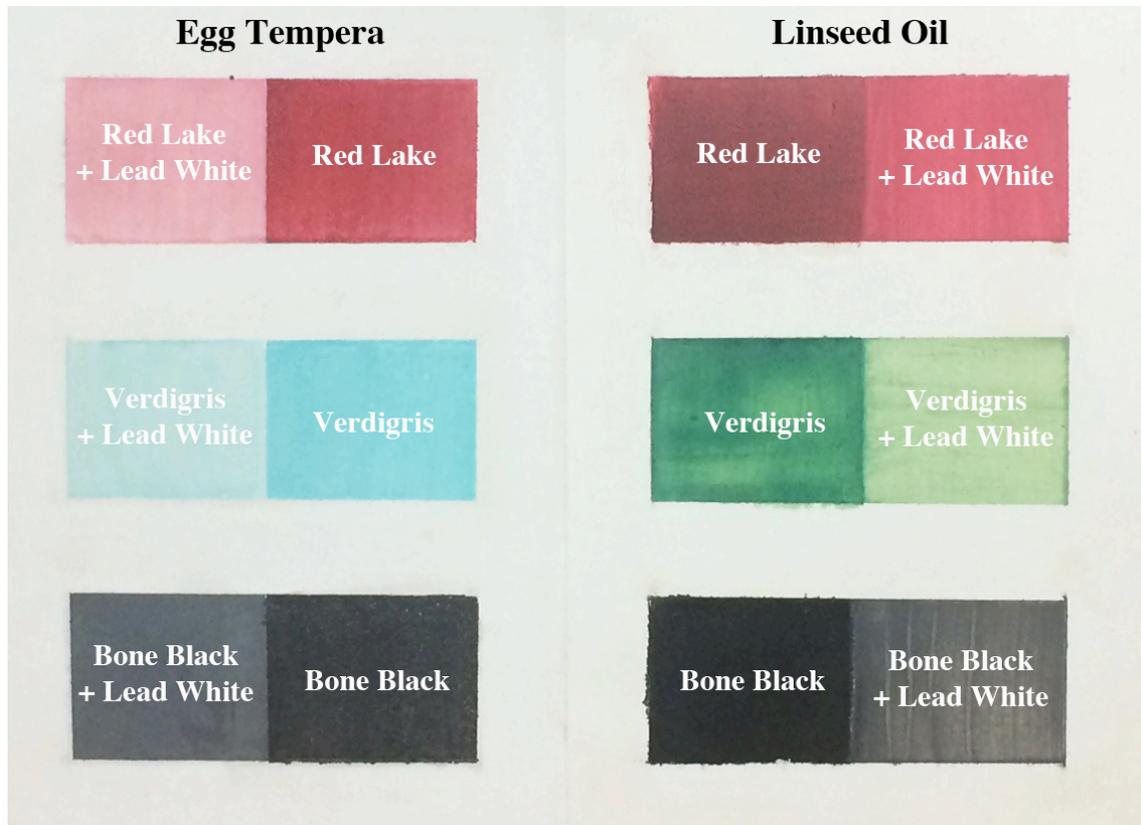


Figure 7.1: Reconstruction (on a wooden panel coated with traditional gesso) demonstrating the aesthetic effects associated with egg (left column) and linseed oil (right column) binders combined with red lake (top), verdigris (middle), and bone black (bottom) with various additions of lead white. Panel prepared by paintings conservator Brian Baade.

dissertation. It is possible that many of these subtle effects can be further used to connect certain Quattrocentro paintings to particular regions and/or workshops, once our analytical methods are able to effectively characterize traditional binding media.

The adoption of oil painting in Renaissance Italy was a gradual process, and one that we are only now beginning to accurately piece together. While technical and scientific studies might suggest that certain analytical techniques have been successfully used to trace the shift from egg to oil, this dissertation has shown that many of these case studies should be revisited in light of recent developments in the scientific field. This oversight can be partially attributed

to the fact that the history associated with the organic analysis of easel paintings remains largely unwritten, a topic extensively explored during the course of this study. For scholars seeking to pursue technical studies relating to Quattrocento painting, this in fact opens up new avenues for collaborative research. If we are to learn more about one of the most important questions that defines this period in art, it will require fresh thinking, an open mind, and an ongoing dialogue between scientists, conservators, and art historians.

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Appendix A

**TABLE SUMMARIZING ANALYTICAL FINDINGS ASSOCIATED WITH
SELECTED WORKS IN THE COLLECTION OF THE NATIONAL GALLERY OF
ART, WASHINGTON DC**

Summary of previous analytical studies of Quattrocento Italian paintings performed at the National Gallery in Washington DC				
<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1988 S.Q.Lomax/ J.S.Tsang	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004).	Antonello da Messina, <i>Portrait of a Young Man</i> , c. 1475/80	Staining (Lissamine/Rhodamine)GC-MS, HPLC (Picotag method)	Staining with Lissamine found the ground to contain protein. HPLC determined that the red paint from the red shirt contained protein.
1988 S.Q.Lomax/ J.S.Tsang (again in 2011-see entry below)		Antonello da Messina, <i>Madonna and Child</i> , c. 1475	Staining (Lissamine/Rhodamine) HPLC (Picotag method)	Staining with Rhodamine revealed the presence of oil in two layers in a sample from the green pillow. Blue from mantle and red from Christ's cloak only tested positive for protein in the ground layer. HPLC revealed that the red sample is proteinaceous.
1990 S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004)/ Conservation Research 1995	Andrea Mantegna, <i>The Infant Savior</i> c. 1460	HPLC (Picotag method)	Samples collected from a red area to the left of the figure and a white area in the same location both revealed the presence of egg.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1990 S.Q.Lomax/ S. Halpine	None	Benozzo Gozzoli, <i>The Descent from the Cross</i> , 1491 (Non-NGA)	GC-MS (esterification of fatty acids with Diazomethane)/ HPLC (Picotag method)	Samples collected did not confirm the presence of a drying oil (GC-MS) but did reveal the presence of egg and some glue, presumably from the ground layers (HPLC).
1990 S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004)/ Conservation Research 1995	Andrea Mantegna, <i>Judith with the Head of Holofernes</i> , c. 1495/500	HPLC (Picotag method)	Samples collected from the blue in the background and an off-white area in the bottom left corner were found to contain egg.
1991 S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004).	Domenico di Bartolo, <i>Madonna and Child Enthroned with Saint Peter and Saint Paul</i> , c. 1430	HPLC (Picotag method)	Samples collected from blue in St. Peter's robe, from the red lake in the St. Paul's robe, and from the grey in the background architecture all revealed the presence of egg (minor traces of glue were determined to be from the ground layer).
1992 S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004).	Domenico Veneziano, <i>Madonna and Child</i> , c. 1445/50	HPLC (Picotag method)	Blue background was found to contain animal glue. All other samples were found to contain egg yolk (two red samples from the flowers in background, flesh sample from Christ's PL thigh, green colored flesh sample from Christ's PL thigh, pale blue sample from Madonna's robe, green sample from background).
1992 S. Halpine	Halpine, S. <i>Studies in Conservation</i> Vol. 37, No. 1 (Feb., 1992), pp 22-38	Cosme Tura, <i>The Annunciation with St. Francis and St. Louis of Toulouse</i> (Four Panels), c.1470/80	HPLC (Picotag method)	St. Francis Panel: Light and dark blue samples from background found to contain animal glue. St. Louis Panel: Dark blue sample from robe found to contain animal glue. Light brown and red samples from robe found to contain egg (some glue present but felt to be contamination from ground). Angel Gabriel Panel: Green sample from wing found to contain both egg and glue.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1993 S.Q.Lomax/ S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004).	Francesco di Giorgio Martini, <i>God the Father Surrounded by Angels and Cherubim</i> , c. 1470	GC-MS (esterification of fatty acids with Diazomethane)/HP LC (Picotag method)	Samples collected from light blue near blue angel, from red bricks, and from green in angel's robe all revealed fatty acid ratios that suggested the presence of a proteinaceous medium. Amino acid analysis performed on an area of original blue paint in the sky and the red brick revealed the presence of egg yolk.
1995 S.Q.Lomax/ S. Halpine	Italian Paintings of the Fifteenth Century, (Washington DC: The National Gallery of Art, 2004).	Filippino Lippi, <i>Portrait of a Youth</i> , c. 1485 (Non-NGA)	GC-MS (esterification of fatty acids with Diazomethane)/HP LC (Picotag method)	Samples collected from the grey architecture and the purple drapery were found to contain a drying oil (GC-MS indicated the presence of linseed). Samples collected from the same areas were found to contain egg when subjected to amino acid analysis.
2000 S.Q.Lomax	None	Cosme Tura, <i>Madonna and Child in a Garden</i> , c.1460/70	GC-MS (Schilling Method)	Blue sample from Virgin's robe was found to contain a drying oil and egg. Red sample from the background the left of the Virgin's head was found to contain a drying oil and egg, with trace amounts of glue (possibly from the ground).
2000 S.Q.Lomax	None	Ercole de'Roberti, <i>Ginevra Bentivoglio</i> , c. 1474/77	GC-MS (Schilling Method)	White highlight from scarf and red sample from the bottom edge revealed the presence of a drying oil and egg.
2005 S.Q.Lomax	National Gallery Technical Bulletin, Vol. 27 (2006)	Master of the Griselda Legend, <i>Joseph of Egypt</i> , c. 1490/95	GC-MS (Schilling Method)	Samples collected from the sky and the grey building both revealed the presence of a drying oil and egg. A sample from the green in the background was only found to contain egg.
2005 S.Q.Lomax	National Gallery Technical Bulletin, Vol. 27 (2006)	Nerrocio de Landi, <i>Claudia Quinta</i> , c. 1490/95	GC-MS (Schilling Method)	Samples collected from the red robe and flesh tones were found to contain both egg and a drying oil. Samples collected from the sky and the green foliage in the background were found to contain egg.
2006 S.Q.Lomax	None	Ferrarese 15 th Century, <i>Madonna and Child with Angels</i> , 1455-70	FTIR and GC-MS (Schilling Method)	Flesh sample from the neck of angel found to contain egg. Sample from a zinc-containing area on Virgin's neck (restoration layer present) contained both egg and a drying oil.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Interesting Observations</i>
2007 S.Q.Lomax	None	Carlo Crivelli, <i>Madonna and Child Enthroned with Donor</i> , 1470	FTIR and GC-MS (Schilling Method)	FTIR found that a sample from the marbling contained protein, while the spectrum of the red paint was overwhelmed by gypsum. GC-MS found that sample collected from the same area contain egg, glue, and a drying oil (the glue is most likely from the ground).
2008 S.Q.Lomax/ Kathryn Morales (previous analysis performed by S.Q.Lomax in 1989 and 2003 and S. Halpine/ S.Q.Lomax in 1991)	None	Benozzo Gozzoli, <i>The Raising of Lazarus</i> , mid 1490s	1989: GC-MS (esterification of fatty acids using borono trifluoride and methanol); 1991: GC-MS (esterification of fatty acids with Diazomethane)/ HPLC (Picotag method) 2003: FTIR/GC-MS (Schilling Method) 2008: Staining (Amido Black)/GC-MS (Schilling Method)	1989: One samples removed near the edge of the painting revealed the presence of a drying oil (GC-MS). 1991: Two samples collected from the white highlights in the rock ledge and one sample from a robe containing red vermilion revealed the presence of animal glue which was assumed to be from the ground layer (HPLC). Samples collected from the same areas also revealed the presence of a drying oil (GC-MS). 2003: Analysis with FTIR was inconclusive. Samples collected from the white robe of Lazarus, the green foliage, and a robe containing blue all revealed the presence of a drying oil in addition to trace amounts of glue, presumed to be from the ground (GC-MS). 2008: Staining proved to be inconclusive. Analysis of brown surface coating was found to contain a drying oil and diterpenes.
2008 S.Q.Lomax/ M. Palmer	National Gallery Technical Bulletin, Vol. 30 (2011)	Nerrocio de Landi, <i>Madonna and Child with St. Anthony Abbot and St. Sigismund</i> , c. 1490/1495	Staining (Sudan Black/Amido Black)/ GC-MS (Schilling Method)	All cross-sections that were subjected to staining tested positive for the presence of oil save for the thin blue underlayer of the Virgin's robe which tested positive for protein. Samples collected from the blue Virgin's robe, the flesh tones from the neck of the Virgin, the flesh tones from the hand of St. Sigismund, and the green from the floor tile all revealed the presence of egg with traces of a drying oil. A sample from the red robe of St. Sigismund was found to contain mostly drying oil with trace amounts of protein (possibly from egg or from the ground).

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Interesting Observations</i>
2009 K. deGhetaldi/ S.Q.Lomax/ C. Maines	None	Follower of Filippo Lippi and Pesellino, <i>Madonna and Child</i> , c. 1470	FTIR/GC-MS (Doerner Method)	FTIR only revealed the presence of a proteinaceous binder in samples collected from the sky and the blue mantle. It is unclear whether the peaks seen in the IR spectra for the flesh are due to the presence of red lakes or protein. While GC-MS revealed the presence of a carbohydrate in the green stems (most likely a gum) GC-MS performed on a sample from the flesh was inconclusive (Doerner Method used for this sample).
2010 K. deGhetaldi/ S.Q.Lomax	None	Andrea del Castagno, <i>Portrait of a Man</i> , c. 1450	FTIR/GC-MS (Doerner Method)	FTIR only revealed the presence of a proteinaceous binder in a sample collected from the sky. It is unclear whether the peaks seen in the IR spectra for the flesh and the red coat are due to the presence of red lakes or protein. GC-MS performed on a sample from the flesh was inconclusive (Doerner Method used for this sample).
2010 K. deGhetaldi/ S.Q.Lomax	None	Fra Carnevale, <i>The Annunciation</i> , c. 1445/50	FTIR/GC-MS (Schilling Method)	FTIR produced mixed results for samples collected from the blue sky, the green garland, the flesh tones, the marbled floor, and the pink gate, yielded spectra that occasionally pointed towards the possible mixture of a drying oil and a proteinaceous binder. GC-MS found that two samples collected from the marble and one from the flesh of the Madonna's neck contained both egg and a drying oil. A sample from the white cloud and another from the red lake of Gabriel's robe also suggested the presence of a drying oil (amino acid was not performed).
2011 K. deGhetaldi/ S.Q.Lomax	None	Antonello da Messina, <i>Madonna and Child</i> , c. 1475	GC-MS (Schilling Method)	GC-MS revealed the presence of egg and a drying oil for a sample collected from the flesh of the Madonna's neck and the red lake brocade. A sample from the blackened vermilion of Christ's robe also revealed the presence of a drying oil (amino acid analysis yielded results that were inconclusive).

Appendix B

TABLE SUMMARIZING ANALYTICAL FINDINGS ASSOCIATED WITH SELECTED WORKS IN THE COLLECTION OF THE NATIONAL GALLERY, LONDON

Summary of previous analytical studies of Quattrocento Italian paintings performed at the National Gallery in London				
<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1978	National Gallery Technical Bulletin, Vol. 2	Fra Filippo Lippi, <i>S. Bernard's Vision of the Virgin</i> , 1447?	Staining confirmed presence of protein; GC detected oil.	Egg with some oil was found in the grey of the Saint's robe and the dark background along the right hand edge. It should be noted that the painting has a long history of treatment and evidence of oil may be from an earlier coating/overpainting.
1978	National Gallery Technical Bulletin, Vol. 2	Carlo Crivelli, <i>The Vision of the Blessed Gabriele</i> , 1489/90	Staining confirmed presence of protein and oil.	Egg and oil was found in the lead white/azurite sky, beige of path (lead white with scattered black/red particles), and the green/blue along the top edge. The green foliage was found to be underpainted in black (egg) followed by an egg-oil layer consisting of verdigris and lead white. The flesh of the saint's foot may also contain egg mixed with a bit of oil.
1978	National Gallery Technical Bulletin, Vol. 2	Filippino Lippi, <i>Moses Brings Forth Water out of the Rock and Worship of the Egyptian Bull God</i> c.1500	Staining and GC were performed.	In <i>Moses Brings Forth Water out of the Rock</i> , egg with some oil was found in the red smock on the third figure from the left. In the <i>Worship of the Egyptian Bull God</i> , egg with a trace of oil was found in the white dress in the sixth figure from the right.
1989	National Gallery Technical Bulletin, Vol. 13	Pesellino, <i>The Trinity with Saints</i> , 1457	Analyzed with GC.	Egg and oil were found in the green of the trees along the left hand edge, the sky, as well as in the warm white of the bishop's smock and bright red robe of the rightmost saint. The predella paintings belonging to this picture were mostly done with pure tempera and are thought be by workshop hands.
1993	National Gallery Technical Bulletin, Vol. 14	Jacopo di Cione and Workshop, <i>Coronation of the Virgin</i> , 1370-1	Probably analyzed with FTIR and GC-MS.	Egg and a little oil were found in a sample of brown glaze-like paint as well as the ultramarine sample taken above the red book.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1993	National Gallery Technical Bulletin, Vol. 14	Cosimo Tura, <i>St. Jerome</i> , c. 1475	Probably analyzed with FTIR and GC-MS.	Egg and some oil were found in samples taken from the pale green grass (walnut) and the blue sky.
1993	National Gallery Technical Bulletin, Vol. 14	Carlo Crivelli, <i>The Annunciation with St. Emidius</i> , 1486	Probably analyzed with FTIR and GC-MS.	Egg and some oil (walnut) were found in a sample taken from the white of the window frame.
1995	National Gallery Technical Bulletin, Vol. 16	Domenico Ghirlandaio, <i>The Virgin and Child</i> , c. 1480	Analyzed with FTIR and GC-MS.	Egg and oil (walnut) was found in the rich red paint from the rub near the bottom of the picture. Egg alone was found in the flesh of Christ's right hand, in the yellow underpaint of the Virgin's robe and in the yellow cushion. Oil (walnut) was found in the Virgin's blue robe and in the dark green paint in the raised diamond pattern on the rug.
1995	National Gallery Technical Bulletin, Vol. 16	Botticelli, <i>Four Scenes from the Early Life of St. Zenobius</i> and <i>Three Miracles of St. Zenobius</i> , c. 1505	Analyzed with FTIR and GC-MS.	In <i>Four Scenes from the Early Life of St. Zenobius</i> , egg and a little oil (walnut) were found in the green carpet of the foreground. Egg and some oil were also found in the pink glaze of the man's cloak and the orange-red glaze from the man's garment in <i>Three Miracles of St. Zenobius</i> . Both paintings also listed in NGTB Vol 17.
1995	National Gallery Technical Bulletin, Vol. 16	Raphael, <i>The Procession to Calvary</i> , c. 1504	Analyzed with FTIR and GC-MS.	Egg and a little oil (walnut) found in the green dress along the left hand edge. Egg alone was found in the darker blue paint of the distant hill and the deep red-brown fold of the drapery (fifth from left).
1995	National Gallery Technical Bulletin, Vol. 16	Gerolamo da Vincenzo, <i>The Death and Assumption of the Virgin</i> , 1488	Analyzed with FTIR, cross-sectional staining, and GC-MS.	Egg alone found in grey layer over blue sky (left of aureole). Egg plus trace of oil (?) found in another sample in similar location. Oil alone (walnut) found in the grey moulding at the base of the Virgin's feet.
1995	National Gallery Technical Bulletin, Vol. 16	Davide Ghirlandaio, <i>The Virgin and Child</i> , 1480s	Analyzed with FTIR (?) and GC-MS.	Egg found in underpaint of red glaze in carpet, in flesh of St. John's left arm, and the left shoulder of the Virgin's blue robe. Oil found in upper red glazes of carpet and the green trees above the rock.
1995	National Gallery Technical Bulletin, Vol. 16	Francesco Morone, <i>The Virgin and Child</i> , c. 1500	Analyzed with FTIR and GC-MS.	Oil (walnut) found in green foliage in background (right edge). Egg found in red curtain.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
1995	National Gallery Technical Bulletin, Vol. 16	Michelangelo, <i>Madonna nad Child with Saint John and Angels (Manchester Madonna)</i> , c. 1497; <i>The Entombment</i> , 1500/1	Analyzed with FTIR and GC-MS.	1) Egg and oil found in red lake of Madonna's dress and in brownish green-grass in foreground. Egg alone found in grayish blue sample from sky and in the black hatching (undermodelling) of Madonna's cloak. Background lipids (?) found in glaze on exposed gesso in unfinished figure. 2) Egg alone found in white imprimatura of Saint John's midriff. Oil found in discolored brown paint of St. Joseph's cloak, the flesh of Christ's arm, the flesh of St. John's right leg and in the pale blue sky along top edge.
1996	National Gallery Technical Bulletin, Vol. 17	Masolino, <i>Saints Liberius (?) and Matthias and Saints Jerome and John the Baptist</i> , c. 1427	Analyzed with FTIR at the National Gallery and GC at the Philadelphia Museum of Art	Egg with some oil found in the flesh of St. Matthias. Egg with a trace of oil found in the red cloak of St. John. Other areas contained oil such as St. Liberius' pinkish-cream cassock and St. Matthias' olive-green robe (the hands and feet in Saints Peter and Paul at the PMA have egg alone while other areas contain tempera grassa).
1996	National Gallery Technical Bulletin, Vol. 17	Giovanni Antonio Boltraffio, <i>The Virgin and Child</i> , c. 1493-99	Analyzed with FTIR and GC-MS.	Egg tempera found in dark underpainting (with a trace of oil) while upper paint layers contained mostly walnut oil (flesh of Christ).
1996	National Gallery Technical Bulletin, Vol. 17	Filippino Lippi, <i>The Virgin and Child with Saint John</i> , 1480	Analyzed with FTIR (?) and GC-MS.	Egg found in lining of Virgin's mantle (malachite over lead white). Also found a copper green glaze containing linseed oil. Pink of St. John's drapery bound in walnut oil.
1996	National Gallery Technical Bulletin, Vol. 17	Francesco Pesellino, <i>The Trinity with Saints</i> and <i>Predella of the Trinity with Saints Altarpiece</i> , 1455-60	Analyzed with GC-MS.	1) Egg and oil was found in the green trees of the horizon and in the yellow of inside of cloak of left-hand saint. Confirmed an earlier study (NGTB Vol 13). 2) Egg alone was found in the white rocks, upper right hand corner.
2000	National Gallery Technical Bulletin, Vol. 21	Carlo Crivelli, <i>The Dead Christ Supported by Two Angels</i> , c. 1470-5	Analyzed with GC-MS.	Egg and traces of oil (walnut) were found in both the dark green in the marbling as well as the crown of thorns. In both cases the paint had darkened and turned brown.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
2001	National Gallery Technical Bulletin, Vol. 22	Paolo Uccello, <i>Battle of San Romano</i> , c. 1440	Analyzed with FTIR and GC-MS.	Egg and oil (walnut) were found in a sample of green from the foliage.
2005	National Gallery Technical Bulletin, Vol. 26	Botticelli, <i>The Three Miracles of St. Zenobius</i> , 1500	Analyzed with FTIR and GC.	Egg and traces of oil (probably walnut) were found in both the pinkish glaze in the outer robe as well as the translucent orange-brown over the yellow draperies.
2005	National Gallery Technical Bulletin, Vol. 26	Botticelli, <i>The Virgin adoring the Sleeping Christ Child (Wemyss Madonna)</i> , c. 1480-5	Analyzed with FTIR and GC-MS.	Egg tempera was found in both the under and upper layers of the green lining of the Virgin's robe. Both samples contained traces of oil and pine resin although a note in the publication states that this is most likely contamination from a restoration layer. Other areas of the painting tested positive for either egg or oil.
2005	National Gallery Technical Bulletin, Vol. 26	Master of the Story of Griselda, <i>The Story of the Patient Griselda, Part I-III</i> , c. 1493-1500	Probably analyzed with FTIR and GC-MS.	While very few areas on the panel tested positive for mixtures of egg and oil various colors in all of the pictures tested positive for either egg or oil. In cases where a trace of oil was found mixed with egg tempera this was mostly attributed to contamination. For example in Part I, egg with a trace of oil (linseed) was found in the dark green-brown of the hillside. A note in the publication explains that this could simply be from oiling out.
2005	National Gallery Technical Bulletin, Vol. 26	Giannicola di Paolo, <i>The Annunciation (Main Panel)</i> , late 15 th C	Probably analyzed with FTIR and GC-MS.	Egg and oil were found in the cream-white color found in the background of the additions that are thought to have been added on later. Most of the painting was found to have been in executed in egg tempera although previously it was thought to have been in oil.
2006	National Gallery Technical Bulletin, Vol.27	Master of the Story of Griselda, <i>Claudia Quinta</i> , c. 1493-4	Probably analyzed with FTIR and GC-MS.	Egg and oil were found in red samples taken from the dress. Traces of oil combined with egg were also found in the flesh tints although the publication states that this could very well be from an oil-varnish that had been applied earlier.
2007	National Gallery Technical Bulletin, Vol.28	Bernardo Daddi, <i>Coronation of the Virgin</i> , c. 1430	Analyzed using FTIR and GC-MS.	Oil containing glaze found over silver leaf. Primary binding media of paint found to be egg tempera.
2010	National Gallery Technical Bulletin, Vol.31	Sassaetta, <i>The Funeral of St. Francis and Verification of the Stigmata</i> , 1437-44	Analyzed using FTIR/cross-sectional microscopy	Evidence of oil found in yellow translucent glaze atop marbled area.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
2011	National Gallery Technical Bulletin, Vol.32	Giovanni Antonio Boltraffio, <i>The Virgin and Child</i> , c. 1493-99	Analyzed using ATR-FTIR and GC-MS	Earlier study performed in 1996 (NGTB Vol 17; using FTIR and GC-MS) reported that the dark underpaint beneath the green hanging contained egg tempera but 2011 study found only evidence of an oil binder.
2011	National Gallery Technical Bulletin, Vol.32	Giovanni Antonio Boltraffio, <i>Portrait of a Man</i> , c. 1500	Analyzed using GC-MS	Found to contain heat-bodied oil (likely walnut) in two samples from the greenish-blue background.
2011	National Gallery Technical Bulletin, Vol.32	Leonardo da Vinci, <i>Virgin of the Rocks</i> , 1491/2 and 1506-8	Analyzed using FTIR and GC-MS	Analysis performed in 1995/6 (National Gallery Technical Bulletin 17) using GC-MS identified walnut oil in five samples collected from the London <i>The Virgin of the Rocks</i> : 1) a sample from the right side in the brownish-black paint of the rocks 2) a red-brown <i>imprimatura</i> from sample 1 3) blue-black of angel's robe 4) a sample from a green leaf along the lower edge 5) a sample from the pale blue-green sky between the two rocks towards the top. The 2011 analysis yielded the following results: 1) partially heat-bodied walnut oil was present in the azurite-underlayer and ultramarine upperlayer of the sky 2) ultramarine paint on the right side of the picture was found to contain heat-bodied linseed oil 3) the grey underpainting of the Virgin's tunic and the red-lake containing underpainting beneath the angel's blue robe contained heat-bodied linseed oil 4) non-heat-bodied walnut oil was found in the uppermost <i>imprimatura</i> layer 5) the dark brown, thinly applied paint of the rocks in the foreground contained heat-bodied walnut oil 5) a similar sample collected from the left side of the picture contained heat-bodied linseed oil 6) a flesh sample from the foot of St. John the Baptist was found to contain walnut oil 7) the ultramarine paint from the Virgin's mantle was found to contain predominately oil. The latter sample is described by the authors as being particularly difficult to analyze; FTIR suggested the presence of protein while the GC-MS results yielded surprisingly low amounts of azelaic acid for a normal drying oil (no protein analysis was performed with GC-MS in this instance). These results are partially attributed to the presence of calcium oxalates which the authors state can complicate the characterization of binding media. Furthermore, the sample collected from the flesh of St. John was also complicated by the presence of lead soaps (identified using FTIR), organo-metallic complexes that can alter the ratio of fatty acids.

<i>Date of Analysis</i>	<i>Relevant Publications</i>	<i>Artwork</i>	<i>Analytical Techniques</i>	<i>Results and Observations</i>
2011	National Gallery Technical Bulletin, Vol.32	Marco d'Oggiono, <i>Portrait of a Man Aged 20</i> , 1494	Analyzed using GC	Analysis performed in 1985 (National Gallery Technical Bulletin 9) using GC identified walnut oil in the greenish-blue mantle and the blue doublet.
2011	National Gallery Technical Bulletin, Vol.32	Marco d'Oggiono, <i>Virgin and Child</i> , c. 1520	Analyzed using GC-MS	Walnut oil was found in samples collected from the sky, the foliage, and Christ's flesh.

Appendix C

**TABLE SUMMARIZING ANALYTICAL FINDINGS ASSOCIATED WITH
SELECTED WORKS BY GIOVANNI BELLINI (AND WORKSHOP)**

<i>Painting</i>	<i>Date of Painting/ Institution</i>	<i>Results of Medium Analysis</i>	<i>Publication</i>
<i>Virgin and Child</i>	c. 1459-60/Philadelphia Museum of Art	Egg-Oil mixtures and/or in discrete layers (Microspectrofluorometric on paint cross-sections)	Cinzia Maria Mancuso and Antonietta Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," in <i>Giovanni Bellini and the Art of Devotion</i> (Indianapolis: Indianapolis Museum of Art, 2004), 129-142
<i>The Transfiguration of Christ</i> (one sample collected from the sky)	c. 1455-60/Museo Correr, Venice	Linseed oil (GC/cross-sections)	R&C Scientifica, "Sezioni stratigrafiche e riconoscimento dei pigmenti a dei leganti," in <i>Carpaccio, Bellini, Tura, Antonello: e altri restauri quattrocenteschi della Pinacoteca del Museo Correr</i> , ed. Attila Dorigato (Milan: Electa, 1993), 218-9
<i>Pieta</i>	c. 1460/Museo Civico, Correr	Drying Oil (GC-MS/cross-sections)	R&C Scientifica, "Sezioni stratigrafiche e riconoscimento dei pigmenti a dei leganti," in <i>Carpaccio, Bellini, Tura, Antonello: e altri restauri quattrocenteschi della Pinacoteca del Museo Correr</i> , ed. Attila Dorigato (Milan: Electa, 1993), 218-9
<i>Saint Jerome</i>	c. 1460/Birmingham, Barber Institute	Egg (GC-Fatty acid ratios indicated egg)	Allan Braham, Martin Wyld, and Joyce Plesters, "Bellini's 'The Blood of the Redeemer,'" <i>National Gallery Technical Bulletin 2</i> (1978): 24
<i>Madonna with Child Blessing</i>	c. 1460-5/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>The Blood of the Redeemer</i> (Blue Sky and White Tile)	c. 1460-5/National Gallery London	Egg (GC-Fatty acid ratios indicated egg)	Allan Braham, Martin Wyld, and Joyce Plesters, "Bellini's 'The Blood of the Redeemer,'" <i>National Gallery Technical Bulletin 2</i> (1978): 24; John Mills and Raymond White, "Analysis of Paint Media," <i>National Gallery Technical Bulletin 2</i> (1978): 74-5

<i>Pesaro Altarpiece</i> (two samples from the <i>Coronation of the Virgin</i> and one from <i>St. Terence</i> ; presence of a medium-rich brown layer on top of the ground and underdrawing, possibly glue (?))	c. 1462-5/Musei Civici, Pesaro	Drying oil with no evidence of proteins, cholesterol, or lecithin (GC-MS/TLC/chemical tests)	Gianluca Poldi and Giovanni C. F. Villa, 'A new examination of Giovanni Bellini's 'Pesaro Altarpiece': Recent findings and comparisons with other works by Bellini' in <i>Studying Old Master Paintings: Technology and Practice</i> , ed. Marika Spring (London: Archetype Publications Ltd., 2011); Marisa Laurenzi Tabasso, "Le indagini scientifiche," in <i>La pala ricostituita. L'Incoronazione della Vergine e la cimasa vaticana di Giovanni Bellini. Indagini e restauri</i> , ed. Maria R. Valazzi (Venezia: Cataloghi Marsilio, 1988), 127-43
<i>St. Sebastian Altarpiece</i> (workshop)	1464-70/Galleria dell'Accademia, Venice	Egg and linseed oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>St. Ferrer Altarpiece</i>	1464-8/Basilica dei Santi Giovanni e Paolo, Venice	Egg-Oil mixtures and/or in discrete layers (GC, cross-sectional staining)	Roberto Stevanato, Manuela Rovea, Stefano Volpin, and S. Calogero, "Analisi di Pigmenti e Leganti in Alcuni Dipinti del Bellini," in <i>Atti del Convegno Nazionale su Chimica e Beni Culturali</i> (Acireale: Chimica e Beni Culturali, 1993), 22; Simone Caglio, Gianluca Poldi and Giovanni C.F. Villa, "Analisi Scientifiche," in <i>Bellini a Venezia. Sette opere indagate nel loro contesto</i> , eds. Gianluca Poldi and Giovanni C. F. Villa (Milano: Silvana Editoriale S.p.A., 2008), 55, 61.
<i>Agony in the Garden</i> (blue paint of trees)	c. 1465/National Gallery London	Egg (GC-Fatty acid ratios suggested egg)	John Mills and Raymond White, "Analyses of Paint Media," <i>National Gallery Technical Bulletin 1</i> (1977), 58; Allan Braham, Martin Wyld, and Joyce Plesters, "Bellini's 'The Blood of the Redeemer,'" <i>National Gallery Technical Bulletin 2</i> (1978): 24
<i>St. Justine</i>	c. 1470/Bagatti Valsecchi, Milan	Egg (GC-MS)	Giovanni Agosti in <i>Restituzioni 2006: Tesori d'arte Restaurati</i> , 3 rd ed., eds. Carlo Bertelli, Giorgio Bonsanti, and Salvatore Settis (Vincenza: Banca Intessa, 2006), 176-182
<i>Resurrection</i>	c. 1470-75/Gemalddegaleria, Staatliche Museen zu Berlin	Drying Oil (GC-MS/cross-sections)	Mauro Lucco and Giovanni C.F. Villa, eds., <i>Giovanni Bellini</i> (Rome: Scuderie del Quirinale, 2008), 208; Francesco Sansovino, <i>Venetia citta nobilissima et singolare, descritta in XIII. libri</i> (1581; repr., Venice: Filippi, 1998), 86; Gianluca Poldi, "Note quasi Sparse sul Colore e la Tecnica di Giambellino: Nuovi Studi Analitici" in <i>Indagando Bellini</i> , eds. Gianluca Poldi and Giovanni C. F. Villa (Milan: Skira, 2009), 202
<i>St Francis in the Desert</i>	1475-80/Frick	Drying Oil (GC-MS/FTIR)	Charlotte Hale, "Appendix A: The Technical Examination of 'St. Francis in the Desert,'" in <i>In A New Light: Giovanni Bellini's St. Francis in the Desert</i> , eds. Susannah Rutherglen and Charlotte Hale (New York: The Frick Collection, 2015), 59-64

<i>Madonna Enthroned Adoring the Sleeping Child</i>	1475/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>San Giobbe Altarpiece</i>	c. 1487/Galleria dell'Accademia, Venice	Egg and Walnut Oil (GC)	Stefano Volpin and Roberto Stevanato, "Studio dei leganti pittorici della Pala di S. Giobbe di Giovanni Bellini," <i>Quaderni Della Soprintendenza ai Beni Artistici e Storici di Venezia</i> 19 (1994): 39-43
<i>Madonna of the Small Trees</i> (samples collected from the sky and from an area of brown paint)	c. 1487/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80.
<i>Barbarigo Altarpiece</i>	1488/San Pietro Martire	Possibility a mixed technique with egg and oil (Solubility tests and staining)	Gianluca Poldi and Giovanni C.F.Villa, "Analisi Scientifiche," in <i>Bellini a Venezia. Sette opere indagate nel loro contesto</i> , eds. Gianluca Poldi and Giovanni C. F.Villa (Milano: Silvana Editoriale S.p.A., 2008), 116,121; Lorenzo Lazzarini, "La pala Barbarigo di Giovanni Bellini: L'analisi di laboratorio," <i>Quaderni della Soprintendenza dei Beni Artistici e Storici di Venezia</i> , 3 (1983): 23-7.
<i>Madonna and Child with Two Saints</i>	1490/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>Adoration of the Kings</i> (attributed)	c. 1490/National Gallery London	Partially heat-bodied drying oil (GC-MS)	Catherine Higgitt, Marika Spring, David Saunders, "Pigment-medium Interactions in Oil Paint Films containing Red Lead or Lead-Tin Yellow," <i>National Gallery Technical Bulletin</i> 24 (2003): 75-95.
<i>Madonna and Child with Saints Paul and George</i>	1490-1500/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>Madonna and Child with St. John the Baptist</i> (Bellini and Workshop)	1490-1500/Indianapolis Museum of Art	Egg-Oil mixtures and/or in discrete layers (Microspectrofluorometric on paint cross-sections)	Cinzia Maria Mancuso and Antonietta Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," in <i>Giovanni Bellini and the Art of Devotion</i> (Indianapolis: Indianapolis Museum of Art, 2004), 129-142
<i>Madonna and Child with the Baptist and the Holy</i> (<i>Conversation Giovannelli</i>)	1500-04/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80

<i>The Madonna of the Meadow</i> (unpigmented priming on ground and blue underpaint)	c. 1500/ National Gallery London	Egg present with possible traces of drying oil (GC-Fatty acid ratios suggested egg)	John Mills and Raymond White, "Analyses of Paint Media," <i>National Gallery Technical Bulletin</i> 1 (1977), 58; Allan Braham, Martin Wyld, and Joyce Plesters, "Bellini's 'The Blood of the Redeemer,'" <i>National Gallery Technical Bulletin</i> 2 (1978): 24
<i>St. Peter the Martyr</i> (workshop, attributed also to Cima da Conegliano)	1504/Pinacoteca Provinciale di Bari, Milan	Linseed Oil (GC-MS; Py-GC-MS; Note that amino acids were found and attributed to the presence of animal glue from restoration and/or garlic)	Alessandro Monno, Rocco Laviano, Inez van der Werf, Damiana Calvano, Luigia Sabbatini, and Ilaria Bonaduce, "Indagini diagnostiche del 'San Pietro martire' di Giovanni Bellini," in <i>Giovanni Bellini San Pietro martire: Storia, Arte, Restauro</i> , ed. Clara Gelao (Venezia: Marsilio Editori S.p.A., 2008), 49-52
<i>Baptism of Christ</i> (five samples contained a medium-rich oil containing layer with lead white over the ground; also drying oil and occasionally terpenes found in pictorial layers; also found calcium carbonate in paint layers)	1500-2/Santa Corona Church, Vincenza	Drying Oil (ATR-FTIR of cross-sections)	Simone Caglio, Fabio Frezzato, and Gianluca Poldi, "Pigmenti, leganti, strati: osservazioni analitiche sulla tecnica pittorica del Battesimo di Cristo di Giovanni Bellini a Vicenza," in <i>Bellini a Vicenza</i> , eds. Maria E. Avagnina and Giovanni C.F. Villa (Vincenza: Byblos, Cittadella, 2007), 83-5
<i>Pieta (Dona dalle Rose)</i>	c. 1505/Galleria dell'Accademia, Venice	Egg and Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80; Vasco Fassina, Mauro Matteini, and Arcangelo Moles, "Studio dei leganti pittorici in sette dipinti a Venezia" in <i>Tiziano</i> (Venice and Washington: Palazzo Ducale and National Gallery of Art, 1990), 389.
<i>The Sermon of Saint Marc in Alessandria, Egypt</i>	1504-7/Pinacoteca di Brera, Milan	Oil with traces of Egg (Cross-section staining, Micro-spectrofluorometric on paint cross-sections)	Antonietta Gallone and Olga Piccolo, "La 'Predica di San Marco ad Alessandria d'Egitto' di Gentile e Giovanni Bellini: Nuovi contributi dalle indagini tecniche," <i>Arte Lombarda</i> 146, 147, 148 (2006): 83
<i>An Episode from the life of Publius Cornelius Scipio</i>	After 1506/National Gallery, Washington DC	Unknown	Jill Dunkerton, "Bellini's Technique" in <i>The Cambridge Companion to Giovanni Bellini</i> , ed. Peter Humphrey (Cambridge: Cambridge University Press, 2004), 220
<i>Madonna and Child with Saints Peter and Mark and and Three Venetian Procurators</i>	1510/The Walters Art Museum, Baltimore	Egg and Drying Oil (Cross-sectional staining; Note that oil was only detected in the green background sample)	Elizabeth Packard, "A Bellini Painting from the Procuratia di Ultra, Venice. An Exploration of its History and Technique," <i>Journal of the Walters Art Gallery</i> 33-34 (1970-71), 82; Elizabeth Packard and Meryl Johnson, "Methods used for the Identification of Binding Media in Italian Paintings of the Fifteenth and Sixteenth Centuries," <i>Studies in Conservation</i> 16 (1971), 145-64

<i>Virgin in Glory with Eight Saints</i>	1510-15/San Pietro Martire, Murano	Linseed Oil (GC-MS)	Stefano Volpin, Antonella Casoli, and Linda Alberici, "I materiali nella pittura di Giovanni Bellini: Tredici opere analizzate," in <i>Il colore ritrovato: Bellini a Venezia</i> , eds. Rona Goffen and Giovanna Nepi (Rome: Electa, 2000), 175-80
<i>Madonna and Child</i> (Bellini and Workshop)	1500-15/Indianapolis Museum of Art	Egg-Oil mixtures and/or in discrete layers (Microspectrofluorometric on paint cross-sections)	Cinzia Maria Mancuso and Antonietta Gallone, "Giovanni Bellini and His Workshop: A Technical Study of Materials," in <i>Giovanni Bellini and the Art of Devotion</i> (Indianapolis: Indianapolis Museum of Art, 2004), 129-142

Appendix D

PIGMENTS AND MATERIALS USED FOR PAINT REFERENCE SAMPLES

List of Pigments and Materials

Egg Yolk – Used only USDA Organic Brown eggs from free-range hens.

Swedish Cold-Pressed Linseed oil – While not completely representative of oils used during the fourteenth, fifteenth, and sixteenth centuries, this process subjects the flax seeds to the least amount of heat prior to extracting the oil. It is difficult to note how much pre-processing (heat, bleaching using sunlight) was applied during the preparation of drying oils (walnut or linseed) in Renaissance Italy.

Water – Distilled water.

Calcium Sulphate – Terra Alba-Natural Selenite (Kremer) – Available to Italian artists since antiquity.

Parchment scraps (Talas)- Scraps obtained from the hides of calf, sheep, and goat. These scraps were boiled down in order to extract the animal skin glue (collagen) for preparing the gesso ground.

Wood (Local Source) – Tulip Poplar (planed smooth and sized with animal glue).

Glass (Local Source) – Surface slightly abraded to impart tooth for better adhesion.

Vermilion (Rublev/Nat. Pigments) – This particular grade of vermilion would have been readily available during the fourteenth, fifteenth, and sixteenth centuries. Vermilion (mercuric sulfide) is made from ore deposits in the Huan province of China and prepared according to an Chinese ancient process known as the "dry process."

Lead White (Rublev/Nat. Pigments) – The lead white used in this experiment was prepared using the historical “Dutch Stack Method,” a process that involves taking a coiled strip of lead metal, placing it inside a ceramic vessel and suspending it over a pool of vinegar (avoiding direct contact). The vessel is then placed in a small enclosure and then immersed for a time in manure (for heat and carbon dioxide). The metallic lead (Pb(s)) is converted into lead acetate and the carbon dioxide continues to convert the lead acetate into a mixture of lead carbonate and lead hydroxide (the mixture is about 70/30).

Natural Sienna Monte Amiata (Kremer) – Yellow Ochre from the hills of Northern Italy. Available to Italian artists since antiquity.

Fine Grade Azurite (Rublev/Nat. Pigments) – Available to Italian artists since antiquity.

Lapis Lazuli (Rublev/Nat. Pigments) – Non-refined lapis from high quality stones with few impurities. Lapis or ultramarine would have been imported from Afghanistan to Italy during the fourteenth, fifteenth, and sixteenth centuries.

Brazilwood (Kremer) – Native throughout Europe (wood from the Pernambuco tree) and available to artists in the the fourteenth, fifteenth, and sixteenth centuries. Approximately 1 kg of brazilwood (in the form of small sized shavings) was barely covered with distilled water. About 200g of potassium carbonate was added to the mixture and heated until enough color was extracted (taking care to avoid boiling). The liquid contents were strained using a coarse strainer and the wood shavings were removed. The solution was further filtered using a more finer strainer. The solution was then placed in a large container and mixed with 500 g of predissolved aluminum potassium sulphate in distilled water. The mixture was vigorously stirred until the solution began to foam and allowed to set for approximately 8 hours. Half of the liquid was then siphoned off the top and the vessel was refilled with water. The solution was allowed to set for another eight hours repeating the siphoning process until the water is clear. The pigment was collected by filtering off the water, setting the colorant aside to dry.

Procedures for Preparation of Substrates

Preparation of Panel

- 1) To make the animal glue: 4 oz. of parchment scraps (Talas) were added to 32 oz of water. This mixture was allowed to simmer (mostly covered using a double-boiler) on medium-high heat for about 2.5 hours. The scraps were then strained, pressing the excess glue out of the remaining parchment. This glue was used to size all surfaces of the panel support (even along the edges).
- 2) To make gesso: 425 mL of animal glue (see step 1) was mixed with 552.5 mL of calcium sulphate (gypsum). The gypsum was added in increments, adding spoonfuls of gypsum to the heated glue (avoiding boiling). Stirring was avoided completely to prevent the formation of bubbles or pinholes in the gesso during the drying process.
- 3) Once all of the gypsum was added to to the glue, the mixture was gently stirred. The gesso was then strained further in order to remove a few clumps that had formed during the stirring process (using a double layer of cheese-cloth and a funnel). Approximately 5-6 coats of the gesso were applied to the recto surface while the verso

was given one coat. The top section of the double boiler was kept on the hotplate while the gypsum was being added.

Preparation of Gesso for Glass substrates

- 1) To make the animal glue: 4 oz. of parchment scraps (Talas) were added to 32 oz of water. This mixture was allowed to simmer (mostly covered using a double-boiler) on medium-high heat for about 2.5 hours. The scraps were then strained, pressing the excess glue out of the remaining parchment. The glue was left to simmer until about half of the liquid glue remained (approx. 16 oz or 500 mL).
- 2) To make gesso: 425 mL of animal glue (see step 1) was mixed with 552.5 mL of calcium sulphate (gypsum). The gypsum was added in increments, adding spoonfuls of gypsum to the heated glue (avoiding boiling). Stirring was avoided completely to prevent the formation of bubbles or pinholes in the gesso during the drying process.
- 3) Once all of the gypsum was added to the glue, the mixture was gently stirred. The gesso was then strained further in order to remove a few clumps that had formed during the stirring process (using a double layer of cheese-cloth and a funnel). Approximately 5-6 coats of the gesso were applied to the recto surface while the verso was given one coat. The top section of the double boiler was kept on the hotplate while the gypsum was being added.

Procedures for Preparation of Paint Outs

Water Pigment Pastes

- 1) Weighed empty vial
- 2) Weighed out dry pigment and record amount. Mixed into water-pigment paste.
- 3) Placed pigment paste into vial. Filled vial with water.
- 4) Next day decanted water and weighed full vial. This amount was recorded.

Preparation of Media and Related Observations

Medium 1 (100% Tempera) – Removed contents from egg yolk sac and measured volume in graduated 2 oz container. Approx. 10 mL. Added approx 5 mL of water (2:1).

Medium 2 (95 % egg/ 5 % oil) – Weighed empty graduated 2 oz container (78.01 g). Added egg yolk to graduated 2 oz container and then weighed contents (92.01 g). Added Swedish cold-pressed linseed oil dropwise into container (approx. .75 g actual...should be closer to .86 g but this was after only one drop) and weighed contents (92.76 g). This mixture dried quickly much like straight egg tempera but simply adding one drop of oil changed the behavior of the medium during the mixing period. Areas where the paint was thickest on the glass plate remained higher for a slightly longer period of time, retaining its body more so than if the medium were

straight egg. During application the paint also seemed slightly smoother. Needed to add water during mixing and applying paint.

Medium 3 (75 % egg/ 25 % oil) - Weighed empty graduated 2 oz container (78.05 g). Added egg yolk into graduated 2 oz container and then weighed contents (88.08 g). Added Swedish cold-pressed linseed oil and weighed container (91.41 g). Was slightly more buttery during mixing and smoother during application. Dried slightly faster than B or A but quite similar to B. Shaking required to re-emulsify (yolk settled to bottom). Needed to add water during mixing and applying paint.

Medium 4 (50 % egg/50 % oil) - Weighed empty graduated 2 oz container (77.56 g). Added egg yolk into graduated 2 oz container and then weighed contents (88.56 g). Added Swedish cold-pressed linseed oil and weighed container (99.56 g). Was slower to dry than all previous. Was considerably more buttery in appearance on the glass plate and slightly more workable during applying. Shaking required to re-emulsify (yolk settled to bottom). Depending on which pigment, needed to add water during mixing and/or applying paint...but not always.

Medium 5 (25 % egg/75 % oil) - Weighed empty graduated 2 oz container (78.18 g). Added egg yolk into graduated 2 oz container and then weighed contents (83.16 g). Added Swedish cold-pressed linseed oil and weighed container (98.16 g). Slow to dry but egg seemed to speed up drying process. Shaking required to re-emulsify (yolk settled to bottom). Did not add water.

Medium 6 (5 % egg/95 % oil) – Weighed empty graduated 2 oz container (79.85 g). Added about 50 mL of Swedish cold-pressed linseed oil into graduated 2 oz container and then weighed contents (129.85 g). Added 5% by weight of egg yolk dropwise (133.91 g). Extremely slow to dry. Had to shake vigorously every time before added to pigments as bits of egg yolk separated out and remained on the bottom of jar. Even after a short period of shaking fragments of the yolk could be seen floating in the oil. Had to use a bamboo stick to agitate yolk contents at bottom, stir, and then shake for approx. 2-3 min.

Medium 7 (100 % oil) – Used Swedish cold-pressed linseed oil. Was extremely slow to dry. Took several weeks.

Note: Between each mixing period all instruments were washed with detergent and then wiped clean with acetone.

Appendix E

PROCEDURES USED FOR MICROSCOPIC EXAMINATION AND CROSS-SECTIONAL STAINING

Procedure for Cross-Sectional Examination

Polarizing Confocal Microscope

All cross-sections collected from the paint gradients shown in Figures 6.1 and 6.1 were imbedded in Extec® Polyester Resin and analyzed under reflected light using a Leica DMRX polarizing microscope equipped with PL Fluotar objectives and a 100W Hg fluorescent light source. All images were collected at the National Gallery of Art in Washington DC (Department of Scientific Research) using a Canon EOS-1 Ds Mark II Digital camera in conjunction with EOS Canon Utility and Capture Software. The filter cubes used to examine the cross-sections in this study include the following:

Cube used for Ultraviolet illumination:

D cube - excitation range: uv & blue BP 355-425 (Exciting filter) / RKP455 (Beam-splitting mirror) / LP 460 Suppression filter

Cube used in conjunction with Alexa Fluor 488:

I 2/3 cube / excitation range: blue BP 450-490 (Exciting filter) / RKP510 (Beam-splitting mirror) / LP 515 Suppression Filter

Preparation of Cross-sectional Stains

AlexaFluor 488 succinamide (ThermoFisher) – Prepared by Professor Richard Wolbers at the University of Delaware

0005% in water buffered with borate .05M

1. Apply to surface of sample (direct reaction)
2. Rinse directly with water and blot excess stain
3. Allow to dry
4. Immediately apply coverglass and aromatic-free mineral spirits

Amido Black II (Sigma Aldrich) - Prepared by Kristin deGhetaldi under the supervision of scientists Michael Palmer at the National Gallery of Art in Washington:

.125g AB2

56.25 mL 1 M acetic acid (3.23 mL plus water)

56.25 mL .1M aq Sodium Acetate (.46g plus water)

12.5 mL glycerine

1. Combine all materials listed above.
2. Stain is typically left on sample for approximately 5 minutes
3. Excess solution is removed (blotted)
4. Surface of the sample is rinsed with 1% (v/v) acetic acid

Additional Notes on Staining Procedures

Many common natural binding materials used in art either fluoresce or develop fluorescent properties with age. When certain proteins, gums, natural resins, and drying oil can become increasingly more aged/oxidized they also become more visible when subjected to near UV light. Quenching and photobleaching are two mechanisms should always be considered when trying to observe emission spectra of auto-fluorescing materials or dyes. *Quenching* can occur when electron deficient materials are present as they can a) form complexes with fluorescent materials preventing excitation or b) steal electrons once they have been excited. *Photobleaching* (or fading) causes fluorochromes to permanently lose their fluorescent properties; this is usually due to prolonged interactions with oxygen and light. It should be noted that each fluorochrome has a given number of excitation/emission cycles before it begins to undergo permanent chemical changes.

Appendix F

FOURIER-TRANSFORM INSTRUMENTATION/PARAMETERS AND ANALYSIS OF PAINT REFERENCE SAMPLES

ATR-FTIR instrumentation and related procedure for sample preparation:

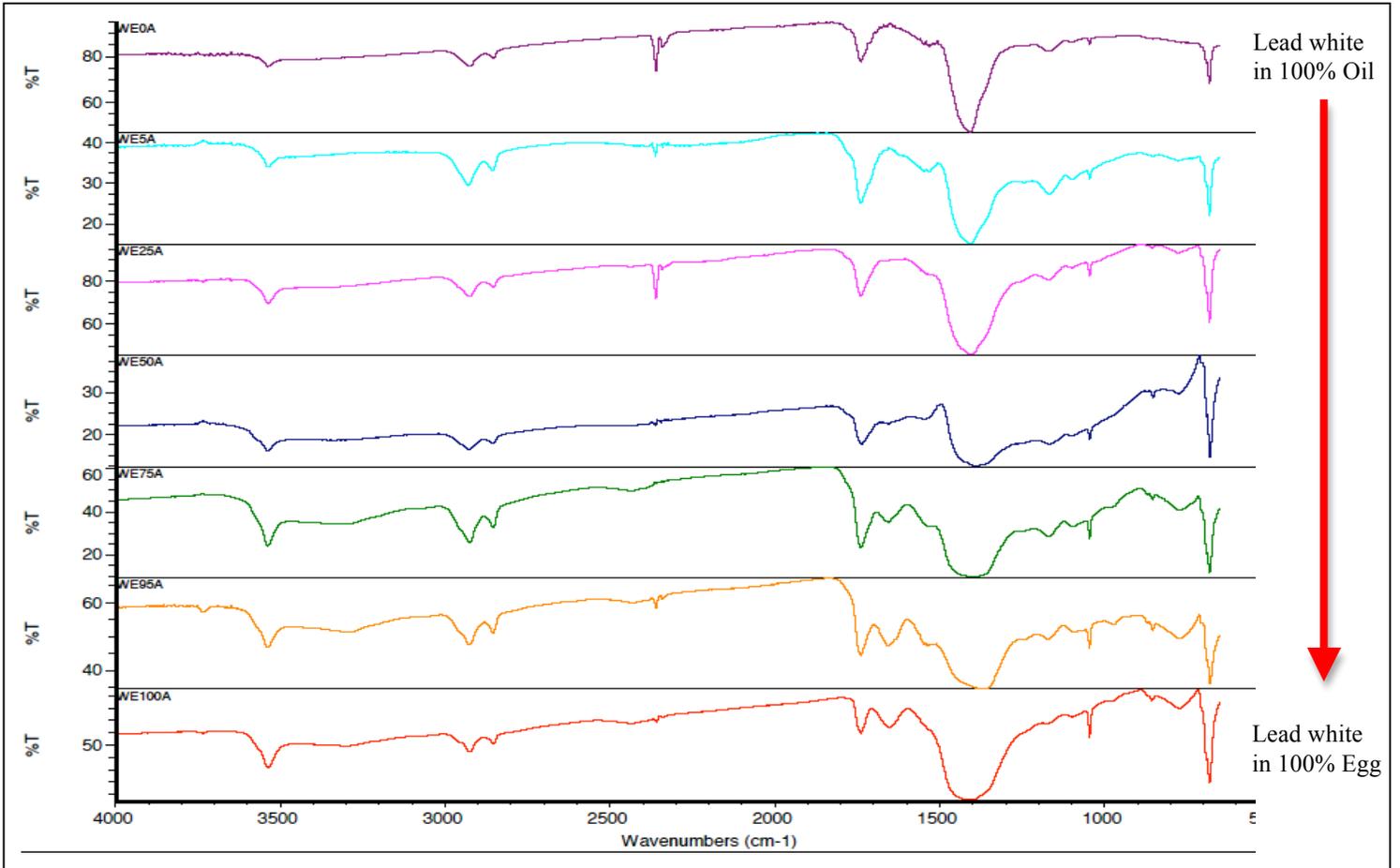
A Bruker Hyperion IR microscope equipped with an affiliated vertex was used for all spectroscopic studies. The instrument is equipped with a Whatman purge gas generator to remove water vapor and CO₂, a N₂(l)-cooled MCT detector, and a horizontal ATR-FTIR accessory from Spectra-Tech. The vertex is capable of multi-angle SPR measurements from 0.8 to 10 microns, although the resolution of the collected spectra were around 100 x 100 microns. Spectra were collected directly from the surface of cross-sections using a 45° ZnSe crystal. Sixteen scans were collected at 4 cm⁻¹ resolution and all spectra were captured using the OPUS software. All ATR-FTIR spectra were collected at the FTIR Laboratory run by Dr. Karl Booksh in the Chemistry Department at the University of Delaware.

Procedure for FTIR data collection

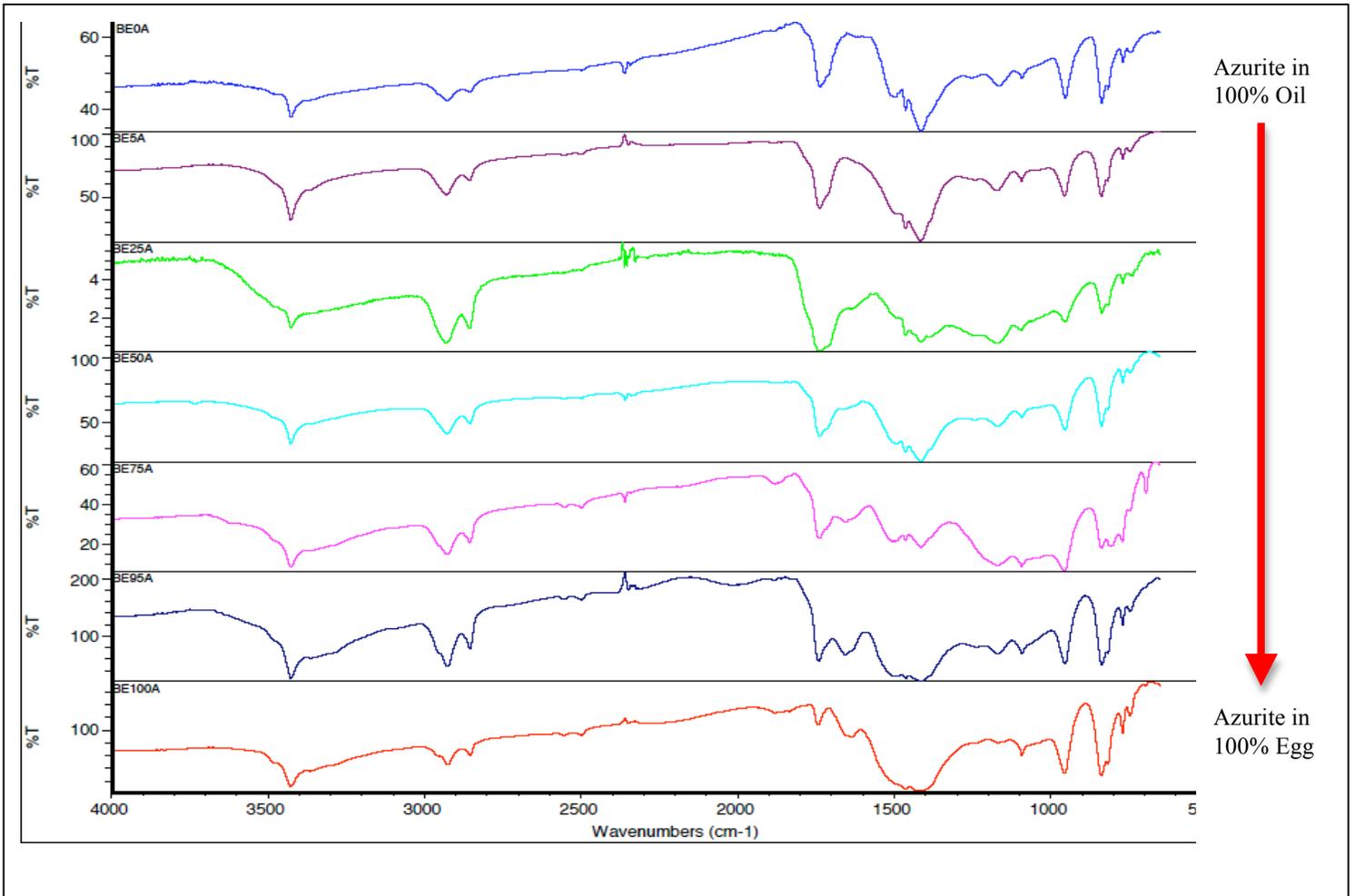
A Nicolet Nexus 670 Optical Bench equipped with a Continuum Microscope was used to collect all spectra. Two hundred scans are generally collected at 4 cm⁻¹ resolution. The samples are compressed between two windows of a Diamond Cell (Spectra Tech). All FTIR spectra were collected at the National Gallery of Art, Washington, DC in the Department of Scientific Research.

FTIR Spectra obtained from Paint Reconstructions

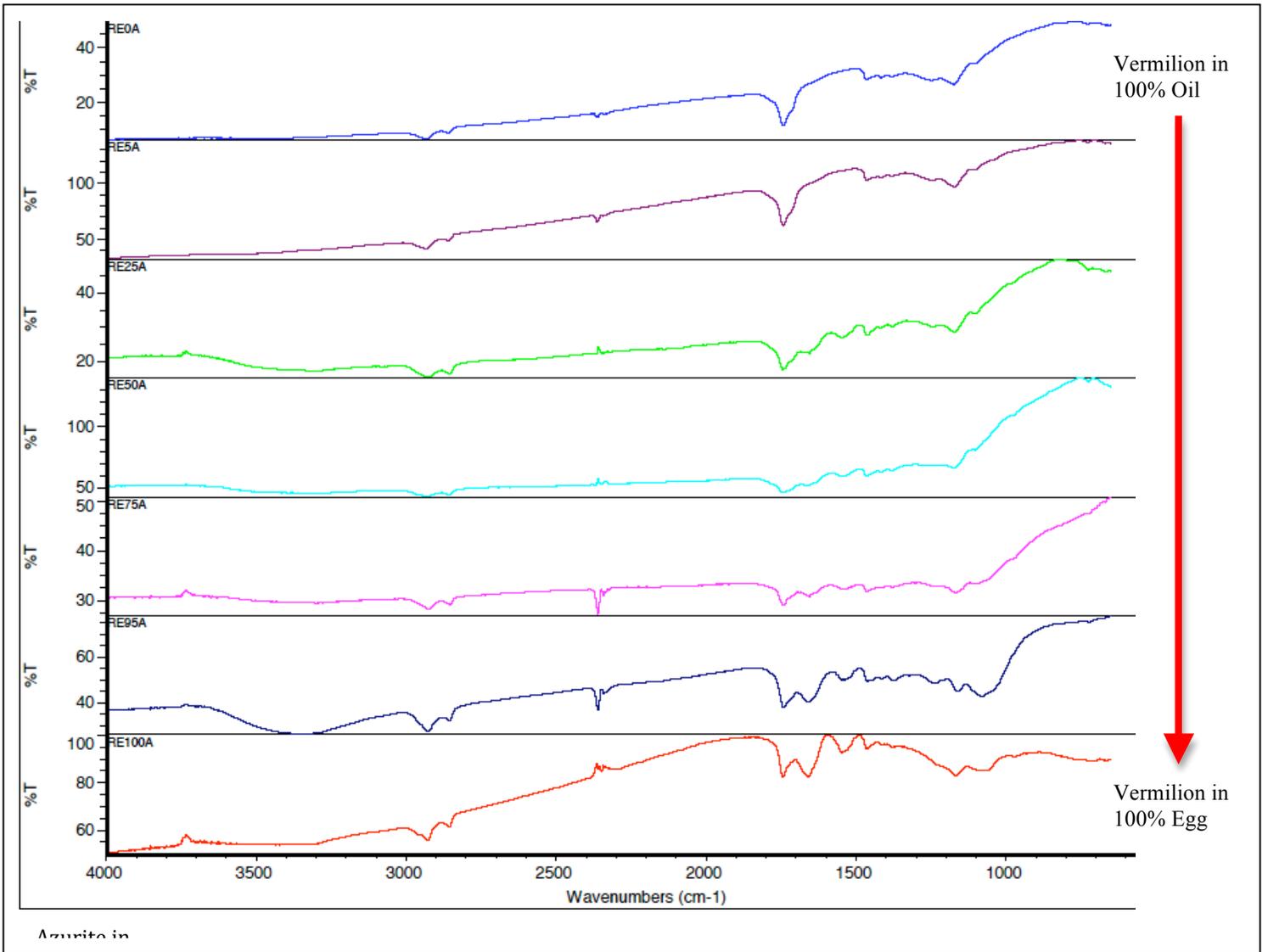
LEAD WHITE COLOR GRADIENT



AZURITE COLOR GRADIENT



VERMILION COLOR GRADIENT



Appendix G

GAS CHROMATOGRAPHY-MASS SPECTROMETRY INSTRUMENTATION AND ANALYTICAL PARAMETERS

All samples were placed in glass inserts inside a 1 mL reaction vial and analyzed using a Varian CP3800 gas chromatograph (equipped with an autosampler and a Saturn 2200 mass spectrometer). Varian software was used to interpret all chromatograms. All samples were analyzed at the National Gallery of Art, Washington DC in the Department of Scientific Research under the supervision of conservation scientists Dr. Christopher Maines and Dr. Suzanne Q. Lomax.

Fatty Acid Analysis – Protocol Developed at the Getty Conservation Institute

The samples were hydrolyzed and methylated to examine the fatty acid profile, using 10 μ L of m-(trifluoromethyl)phenyltrimethylammonium hydroxide (TMTFTH, TCI America, 0.5M in MeOH). This quaternary ammonium salt converts labile fatty and terpenoid acids to their methyl esters. It also converts glycerides to methyl acids of the component acids. The vials were allowed to sit overnight, and were then examined by gas chromatography. The 30 meter DB5 column (film thickness .25 micron, column diameter .25mm) was temperature programmed from 50°C (0.5 minutes) to 100°C at 25°C/minute, and then 6°C/minute to 280°C. The column was held at 280°C for 10 minutes. The injector temperature was maintained at 300°C and the flow was 1.1 mL/min.

Fatty Acid Analysis –Protocol Developed at the Doerner Institut

Extracts 1-3 are first injected into the GC in unaltered form and only subsequently derivatized. It should be noted that only steps 1-4 of the Doerner protocol were performed. All samples are heated for about 30-60 minutes prior to injection and derivatized overnight. Derivatization (methylation) is done in methanol solution, using trimethylsulfonium hydroxide (TMSH) or oxalic acid as catalysts. Extract 4 is allowed to sit for 3-5 days before being injected into the GC. The free and glyceride-bound fatty acids are converted (transformed) to the fatty acid methyl esters (FAMES, column 6) and then once more injected into the GC-MS. It should be noted that the two derivatization methods are only suitable for injection in the split or splitless mode. The vials were allowed to sit overnight, and were then examined by gas chromatography. The 30 meter DB-5 column (film thickness .25 micron, column diameter .25mm) was temperature programmed from 55°C (2 minutes) to 300°C at

14°C/minute, and then 8°C/minute to 360°C. The injector temperature was maintained at 250°C and the flow was 32 mL/min.

Amino Acid Analysis – Protocol Developed at the Getty Conservation Institute

All samples were placed in glass inserts inside 1 mL reaction vials. Sufficient nucleucine solution is added to yield a final concentration of approximately 50 ppm in the final injection volume. Fifty µL of 6.0N hydrochloric acid is added to the insert and the vial is capped with a septum and evacuated using a vacuum pump. The sample was heated at 105°C for 24 hours on a heating block, removed from heat and allowed to stand until cool. The vial is then centrifuged, and evaporated to dryness using a nitrogen stream while warming to 60°C. One µL of silylating reagent was added per 2µg of sample. The silylating reagent is prepared by mixing 300 µL of MTBSTFA/TBDMCS with 700 µL of a solution made from 40 mg of pyridine hydrochloride per mL of pyridine. The vial is capped with a septum cap, heated to 60°C for 30 minutes and then to 105°C for 5 hours. After cooling to room temperature, the sample was transferred to an autosampler vial and examined by gas chromatography/mass spectrometry. GC-MS conditions: 30 M x .32 mm x .25 µm DB-1 column (from J&W Scientific); helium carrier set to 1.7 mL/min; splitless injection; GC oven temperature program: 80°C for 1 min; 20 C/m to 280°C; isothermal for 3 min. injector temperature 260°C.

Appendix H

TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY INSTRUMENTATION AND ANALYTICAL PARAMETERS

ToF-SIMS analysis on all samples was performed by Zachary Voras at the Surface Analysis Facility in the Chemistry Department at the University of Delaware under the supervision of Dr. Thomas Beebe, Jr.

Optical Imaging of Reference and Historical samples

Reference and historical samples were analyzed under high magnification using a Nikon Eclipse 80i Binocular Microscope (4x, 10x, and 20x objectives) with a Nikon X-cite[®] 120 Mercury Lamp for reflected ultraviolet light. Under ultraviolet light, the samples were viewed using a BV-2A cube (excitation wavelengths between 400-420 nm/470 nm barrier filter). Digital images were obtained using the Digital Eclipse DXM 1200f Nikon Camera in conjunction with the Automatic Camera Tamer (ACT-1) control software for PC systems.

Microtomy

A series of cross-section cuts was then made on a microtome (Leica Jung Biocut, model 2035), first by a stainless-steel trimming knife (no part number) obtained from Delaware Diamond Knives, removing approximately 10 micrometers per cut, until the first parts of the paint sample became exposed. Finer cuts were then made using a diamond ultramicrotomy knife (3.5 mm wet-cryo type) obtained from Delaware Diamond Knives, removing less than 1 micrometer per cut, while observing the process under a monocular microscope on an articulating arm (Specwell 10 × 30, 6°, with extra short focus). When an appropriate depth into the sample had been reached, exposing a “fresh” cross-sectional surface for analysis by ToF-SIMS, the sample and stub assembly was transferred to a custom-designed, home-built sample holder to ensure proper orientation of the exposed sample surface for ToF-SIMS analysis.

ToF-SIMS Analysis Conditions

The ToF-SIMS instrument used for analysis was a TOFSIMS IV, upgraded to the capabilities of a TOFSIMS V (ION-TOF, GmbH). The instrument is housed in the Surface Analysis Facility at the University of Delaware. It was equipped with a bismuth/manganese primary ion beam. Mass spectra and images were taken in the high-current “bunched” mode, utilizing 25-keV Bi₃⁺ ion clusters having a pre-bunched pulse width of 640 ps and an estimated spot size of

less than 5 micrometers in diameter, producing a sample current of ~ 0.27 pA. A low-energy (75 eV) electron flood gun was used to stabilize the sample's surface-charge state for the insulating samples analyzed here. The time-of-flight mass analyzer used an extraction voltage of ± 2 kV, depending on ion polarity, and post-acceleration voltage of 10 kV.

All spectra were acquired to the static SIMS limit of 1×10^{12} ions/cm². The mass scales of positive-mode spectra were calibrated with the following ions: H⁺, H₂⁺, H₃⁺, C⁺, CH⁺, CH₂⁺, CH₃⁺, C₂H₃⁺, C₃H₅⁺, C₄H₇⁺, C₅H₅⁺, C₆H₅⁺, and C₇H₇⁺; the mass scales of negative-mode spectra were calibrated with the following ions: H⁻, H₂⁻, C⁻, CH⁻, CH₂⁻, CH₃⁻, C₂⁻, C₂H⁻, C₃⁻, C₄⁻, C₅⁻, C₆⁻, C₇⁻, and C₈⁻. All data analysis was performed on ION-TOF software, version 6.2. No quantitation of TOF-SIMS signal intensities was used in this work, and thus no discussion of normalization is necessary. A forthcoming publication will focus on the quantitative analysis of these and similar cultural heritage objects (Voras, *et al.*, 2014). Lastly, it is important to note that all fragment peaks are identified by both exact-mass position and by the expected isotopic distribution profile of the fragment.

ToF-SIMS Mass Resolution, Mass Accuracy, and Mass Precision

Mass resolving power, also frequently called mass resolution ($m/\Delta m$) mass precision, and mass accuracy all affect the analyst's ability to interpret ToF-SIMS spectra, i.e. with confidence. Over approximately 228 different ToF-SIMS peaks, measured from 30 different samples, an analysis of peak position accuracy (m/z) and peak position precision (m/z) was made in this study. Peak position *precision* averaged 46 ± 10 parts per million (ppm), with a low of 36 ppm for some amino acid fragments and a high of 62 ppm for other amino acid fragments. That is, the ToF-SIMS instrument was able to reproducibly obtain the same m/z values of all peaks in all samples in repetitive measurements, to within 46 ppm on average. Peak position *accuracy* was calculated by examining the difference between the observed m/z value in atomic mass units (AMU) of a particular mass fragment and that fragment's theoretical m/z value. The absolute value of the peak position accuracy averaged $1.8 \pm 2.3 \times 10^{-3}$ AMU, with a low deviation of -3.8 mAMU and a high deviation of +3.5 mAMU. That is, the ToF-SIMS instrument was able to reproducibly obtain the correct m/z value for a given mass fragment, making its identification unambiguous.

Using the above 228 different ToF-SIMS peaks, measured from approximately 30 different samples, an analysis of mass resolving power ($m/\Delta m$) was also performed. The mass resolving power averaged $m/\Delta m = 6,360 \pm 1,300$, with a low of 3,720 and a high of 9,260. This relative wide range of $m/\Delta m$ values highlights the importance of a sample preparation technique that allows for reproducible ToF-SIMS performance to resolve analyte peaks. Prior to analysis of samples, a clean silicon wafer was used to optimize conditions. Such an optimization typically resulted in a mass resolving power of $m/\Delta m = 8,700$ at m/z 29 (²⁹Si⁺) for a clean silicon wafer.

Contrast in ToF-SIMS Images

ToF-SIMS images are usually presented with image contrast represented by a false-color scale (usually a thermal scale ranging from from bright yellow or white to black). Locations within

the image that have the brightest color (white) are indicative of the emission of the greatest number of ions represented in that image, whereas locations from bright yellow or white to black). Locations within the image that have the brightest color (white) are indicative of the emission of the greatest number of ions represented in that image, within the image that have the darkest color (black) are indicative of the emission of the lowest number of ions represented in that image, usually zero.

Sample Information

The embedded paint sample obtained from the Matteo di Giovanni painting was prepared in resin in 1990, while the Raphael sample was prepared in resin in 1963. The embedding resin used for the samples provided by Walters Art Museum is not known, although it was not a cyanoacrylate-based resin, based on its ToF-SIMS spectrum.