BINDING MEDIUM ALTERATION AND ITS EFFECT ON FINE ART PAINTINGS AS OBSERVED BY SURFACE ANALYSIS

by

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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 Chemistry and Biochemistry

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ABSTRACT

This dissertation covers research done to study the chemical phenomena related to the degradation of binding media as found in fine-art paintings. An introduction into the collaboration between surface analysis and cultural heritage research opens, and is followed by an extensive description of the experimental techniques used herein. The proceeding four chapters pertain to original research undertaken to identify, understand, and mimic the effects of degradation of binding media. The first set of results covers the analysis of Renaissance-Era artwork and the transition from egg tempera-based to oil-based painting technique. It was with this work that the novel identification of fatty acid depletion was observed in historic cross-sectional samples. This knowledge was then applied to the analysis of Fauvist-Era artwork, where the observation of pigment-binder interactions was crucial to understanding the chemical pathways of alteration of both pigment and binding media. The final research chapter combines the Renaissance-Era and Fauvist-Era results and attempts to mimic the degradation of egg tempera to observe which environmental factor(s) contributes to egg tempera degradation. This study is also the first use of gas-cluster ion sputtering to analyze binding medium degradation as a function of depth for thin films. Lastly, the appendices provide results of three independent studies that relate to the identification of soft materials and their degradation for cultural heritage materials.
Chapter 1
A REVIEW OF SURFACE ANALYSIS AND CULTURAL HERITAGE SCIENCE

1.1 Introductory Remarks

This dissertation, entitled “Binding-Medium Alteration and Its Effect on Fine Art Painting as Observed by Surface Analysis” stems from a much larger idea – using the fundamental theories and practices of the surface science community and applying them to those questions that exist in cultural heritage science. It is through collaboration that the combined effort of scientists of various expertise can come together to solve scientific problems, which is certainly not exclusive to these two fields. Herein lies the specific goal of this work, to use state-of-the-art surface analytical instrumentation to address the problem of binding medium degradation found in fine art paintings. While previous literature has combined the two fields for new methods of paint cross-section characterization, the intended purpose of this research was to use surface analysis to answer fundamental questions that involve probing new chemical systems observed in historic samples, adding to the knowledge gained as a result of the collaboration. The specific gap in knowledge concerning the identification of various organic materials used in binding media as well as degradation of these materials is the focus of this work.
1.2 Introduction

The collaboration between surface science and cultural heritage science has provided meaningful insights into complex chemical systems allowing for a greater degree of understanding into the systems encountered in cultural heritage science while pushing the limitations of current generation surface analytical instrumentation. There are three major goals in the collaboration of surface analysis and cultural heritage science; the analysis of historic samples to observe chemical phenomena, the elucidation of chemical mechanisms of failure found in cultural heritage science, and investigating the interaction between treatment methods and the object to be treated. For this review of the implementation of surface analytical techniques in the field of cultural heritage science, the above three listed goals will be covered, as well as ideas for future directions for the continuation of collaborative efforts.

The surface analytical techniques that will be in focus are the complementary techniques of time-of-flight secondary ion mass spectrometry (TOF-SIMS, or herein SIMS) and x-ray photoelectron spectroscopy (XPS). These techniques have been chosen based on their respective use in the surface science community for characterization of elemental and molecular signals present on a sample surface. These complementary surface techniques provide a wealth of insight into a chemical system, and when combined with non-surface techniques offer a complete characterization of the chemistry involved in cultural heritage science. SIMS allows for simultaneous analysis of both inorganic and organic components within a sample, albeit there is a
lack of quantitation due to the matrix effect inherent to the technique. The ability to observe a wide variety of mass fragments (from 0 – 1kDa with conventional bismuth metal cluster primary ion sources) provides molecular information pertaining to a sample. XPS serves as a quantitative technique for elemental and oxidative-state information present on a sample surface. The current technology available for both instrumental platforms allows for seamless operation in spectral, imaging, and depth profiling modes.

Previously, several reviews concerning the implementation of surface analytical instrumentation have been published in both article and book format. Adriaens and Dowsett have covered the initial studies involving SIMS and cultural heritage science, and have taken a look at the benefits and limitations of its use. The use of SIMS for molecular analysis and isotope analysis shows great promise in the field, albeit beam characteristics must be carefully selected for a proper analysis. Likewise, careful surface preparation is of importance to remove any traces of sampling bias, although given that SIMS would be used in conjunction with typical analytical techniques a synergistic approach to problem solving is ideal. Lastly, a review by McPhail of SIMS use in conservation science, archaeometry, and cosmochemistry provides insight into the difficulty in preparation of non-uniform surfaces typically found in cultural heritage science, but also suggests that the information provided by SIMS analysis is unparalleled in understanding a chemical system.

While several books have been published concerning the use of analytical instrumentation in the field of cultural heritage science, there are a few worth noting
for their particular details concerning surface analysis. Edited by Janssens and Van Grieken, *Non-Destructive Microanalysis of Cultural Heritage Materials* is a thorough presentation of microanalysis techniques applied to the field of cultural heritage science up through 2004.\(^4\) A more recent example of a SIMS review was written by Mazel and Richardin as a chapter in *Organic Mass Spectrometry in Art and Archaeology*, edited by Colombini and Modugno.\(^5\) These published materials cover a wide variety of uses of surface analytical instrumentation with cultural heritage materials up to 2009. The purpose of this review is to present the current literature, although a few key publications with significant contributions to surface science and cultural heritage science from previous reviews will be presented herein.

### 1.2.1 Sample Preparation

While the current trend of non-destructive and non-invasive analysis is preferred for the reduction of material sampling, the need for direct measurement is required when inferred information does not fully answer the intended question, such as molecular information in regards to material degradation. Through the use of surface analytical techniques that require minimal sample preparation (such as polishing, ultramicrotomy, or ion milling) the use of semi-destructive techniques can provide a large amount of chemical information on extant samples. Through careful analysis, surface analytical techniques damage only the uppermost portion of a sample and removal of damage post-analysis is simple through the preparation methods listed above, effectively returning an extant sample to its original condition.
There are various methods useful in the preparation of samples for analysis via SIMS and XPS. As both techniques analyze only the uppermost surface of a sample, it is imperative that the sample is free of contamination from storage, handling, and preparation materials, as well as uniformly flat. As such, hand polishing, a common preparation technique for ambient spectroscopies and microscopy, is usually avoided, as the residue left behind from the abrasive material is concentrated at the sample surface, especially with soft samples. Microtomy (or ultramicrotomy) is a well-known preparation technique, which originated in microscopy, has been used for preparation of soft materials (such as paint cross-sections) in cultural heritage science and is commonly found throughout the literature. While collecting intact thin sections of material for analysis is not always possible due do the friability of the cut material, the remaining top sample surface is adequately smooth and clear of contamination for SIMS and XPS.

The use of argon (monoatomic) ion milling for surface analysis has been known for many years, and the use of it in the specific case of cultural heritage science has been detailed by Boon. Ion milling is usually performed in the same chamber just prior to analysis, and so adventitious ambient contamination is negligible. This technique in comparison to various surface preparation methods (such as polishing and solvent cleaning) has been shown to increase signal intensity and decrease contamination. A downside of ion milling is the beam-induced damage to soft materials that would inhibit molecular analysis, and so ion milling is typically reserved for hard materials (such as metals and glasses). The recent development of gas-cluster ion beams (GCIB) has shown great promise in the field of cultural heritage science as the beam-
Figure 1.1: Results of an independent inter-laboratory study of a multilayered Irganox (1010 for thick layer, 3114 for thin layer) test sample that has been depth profiled using a variety of soft sputtering sources shown in Shard et al.9 Profile is given for tracking the Irganox 3114 component; note the well-defined layer structure and no significant loss of signal due to sputter-induced damage. Reprinted with permission from [9] Shard, et al. Copyright 2012 American Chemical Society.
induced degradation of soft materials is significantly reduced, and given correct optimization of the cluster size and acceleration is considered nonexistent.\textsuperscript{9-11} Figure 1.1, taken from Shard et al. highlights the use of argon-cluster sputtering beams as a depth profile source for Irganox, a soft-sputtering standard used to demonstrate any beam-induced damage from sputtering.\textsuperscript{9} Vermeulen et al. studied the use of interlaced monoatomic-argon and cluster-argon milling for contamination removal from paint cross-sections, however they did not specify any effects due to selective sputtering that has been observed with GCIB milling.\textsuperscript{12}

### 1.2.2 Analysis of Historic Samples

A requisite component of cultural heritage science is the analysis of historic materials for the reasons of provenance, state of degradation, and efficacy of prior treatments. As the ability to analyze historic samples is severely limited to the number of extant samples taken during treatment, it is necessary to establish historically accurate standards that will mimic the materials that may be observed in historic samples. Through careful examination of these standards, conclusions regarding an entire work from just a few extant samples may be possible. The use of SIMS and XPS (in conjunction with other surface and non-surface sensitive instrumentation) is highlighted for the provided chemical information that would otherwise not be possible.
1.3 Metals

The analysis of metals and their corrosion is commonly found in the literature in regards to corrosion of sculpture and coinage, including the use of treatments in the form of coatings. For these studies XPS is the dominant technique for its ability to provide oxidative-state information pertaining to metal corrosion, a key factor in the treatment and preservation of metal materials in cultural heritage science. By identifying the failure mechanisms of metal corrosion, artifacts from a very wide timeline can be preserved for future generations. In 2013, a book edited by Dillman, Watkinson, Angelini, and Adriaens offered as a comprehensive review of the corrosion and conservation practices for metal artifacts. The use of inorganic and organic coatings for the conservation of metal objects was discussed, although the use of surface analytical instrumentation was not specifically highlighted.

1.3.1 Non-Precious Metals

Starting with a 2009 study by Balta et al., the role of copper patinas on artistic bronze was identified for both composition and stratigraphy using XPS and dynamic (depth profiling) SIMS measurements. The study was able to identify patina coloration due to trace elements within the layers, as well as kinetic information pertaining to patina growth. A similar study on nano-sized films on brass alloys was conducted in 2016 by Cocco et al., where exact alloy composition was identified using XPS and x-ray Auger electron spectroscopy (XAES). Figure 1.2 is from Cocco et al. that shows the composition of the nanofilms on brass and highlights the various oxidation components found in the zinc LMM Auger region as observed by XPS.
Figure 1.2: Fitted high-resolution spectra from Cocco, et al. of zinc LMM Auger region of nano-films on brass alloys.\textsuperscript{15} Assignments A through E relate to the complex oxidation structure of the zinc component as found in the films. Reproduced from [15] Cocco, et al with permission of The Royal Society of Chemistry.
In cultural heritage studies, metals can also exist as architectural elements as found in a study by Miszczyk et al. By using XPS, SEM, x-ray diffraction (XRD), potentiodynamic polarization and electrochemical impedance spectroscopy the team was able to monitor steel corrosion at the Holocaust concentration camps at the Auschwitz-Birkenau sites.\textsuperscript{16} The study concluded with an establish corrosion rate of the original steel structures as well as identification of corrosion products for the possibility of treatments. Lastly, there are many collections of historic (ancient) metal artifacts from archaeological sites around the world containing objects that have been buried for several hundreds of years or more. Angelini et al. used XPS, XRD, and SEM to investigate degradation of ancient artifacts found in the Mediterranean basin.\textsuperscript{17} The study investigated a wide variety of objects, ranging from a shield and quiver, to bronze and gold coins, and also a gilded-copper object. The team found that the surface analytical techniques used were comprehensive enough to establish corrosion products from both soil and environmental exposure.

1.3.2 Precious Metals

While surface analysis is certainly useful for corrosion of common materials, the corrosion and treatment of precious metals is certainly an extensive field of study due to the commodity associated with precious metal artifacts. While a large amount of literature exists for precious metal artifacts, there are only a few that use surface analytical techniques in their investigations. Angelini et al. published in 2012 concerning the degradation mechanisms associated with precious metal artifacts, such as jewelry and coins.\textsuperscript{18} Using XPS, XRD, and SEM they were able to discern degradation mechanisms resulting in insoluble chloride and sulfide films that develop
due to soil-based burial. Additionally, they provided evidence that the purity of the object is correlated to stability; the higher quality of the initial production of the artifact, the less susceptible to corrosion due to burial. A study by Mezzi et al. provided evidence of micro-chemical degradation of silver-based archaeological artifacts. Using XPS, XRD, and SEM the team was able to identify chemical and morphological changes due to environmental degradation of historic silver objects due to copper impurities that enhance chloride and sulfur tarnish products. The study successfully identified a variety of degradation products, including chloroargyrite, atacamite, and paratacamite. In a similar study performed on Roman-era silver coins, Keturakis et al. detailed the layered structure of corrosion products using XPS, Raman spectroscopy, and high sensitivity-low energy ion scattering (HS-LEIS). Using static and dynamic measurements the layering of the chloride and sulfide corrosion products was observed and associated with preferential oxidation of the copper impurities in the artifact.

Lastly, surface analytical techniques have been used for monitoring cleaning and storage methodologies of silver objects. Palomar et al. subjected silver coupons to various mechanical, chemical, and electrochemical cleaning methods and observed the resulting surfaces using XPS, atomic force microscopy (AFM) and SEM. The team was unable to provide an optimal procedure for cleaning as each subgroup of cleaning methods provided various results based on initial silver composition, chemical identity of the corrosion, and also the tarnishing/patination of the coupon after cleaning. Figure 1.3 provides a summary of the observations from XPS and AFM analysis of the
Figure 1.3: Fitted XPS high-resolution spectra and AFM images from cleaned silver coupons as shown in Palomar, et al.\textsuperscript{21} XPS spectra (above) shows the decrease of sulfur concentration and AFM images (below) show the surface roughness from cleaning as observed in the tarnished silver (a, P1) and sterling silver (b, P1). MC/MP/MT relate to mechanical polishing; CP/CF relate to chemical cleaning; EN/ES relate to electrochemical cleaning. Reproduced from \textit{Palomar et al. Journal of Cultural Heritage} 2016; 17:20-26. Copyright 2016 Elsevier Masson SAS. All rights reserved.
cleaning methods for silver and sterling silver. Faraldi et al used the combination of XPS, XRD, and SEM analysis to assess changes in sulfur and chloride content of silver artifacts under storage conditions. By observing chemical changes due to fine particulates and aggressive chemical compounds found in museum atmospheres typical to Mediterranean indoor environments, the study was able to identify sulfur and chloride tarnish layers forming on the silver coupons under ideal conditions.

1.3.3 Metal Treatments and Coatings

Conservation of metal artifacts poses a particular challenge as cleaned metal surfaces tend towards high reactivity (such as oxidation) within their environment. Additionally, metal artifacts are usually intended to have a specific luster and color, either as a bare surface or as a patina layer of which corrosion can quickly discolor. An ideal coating on a metal artifact would be able to: (i) provide protection from environmental corrosion; (ii) be transparent to any intended surface finishes; and (iii) be removable as an established practice in cultural heritage science. Over the past decade, several different methods of metal coatings have been developed and studied, from polymers to deposited inorganic thin films.

Working with organic coatings offers several advantages over inorganic coatings that are detailed in the following articles, however surface analysis of organic coatings has traditionally been limited due to difficulties in depth profile studies of organic materials. One such method for producing coatings is to use self-assembled monolayers (SAMs) to produce transparent thin films on a metal surface. Mohammed et al. investigated the use of monocarboxylate SAMs for the conservation of lead
objects where they characterized the coating using XPS, SEM, XRD, Fourier-transform infrared spectroscopy (FTIR), and electrochemical measurements. The team concluded that the use of SAMs is feasible, with a reliable performance under salt-spray conditions. Another common method of organic coatings on brass and bronze is to use Incralac, a blend of polymethyl methacrylate (PMMA), polyethyl acrylate (PEA), and the copper corrosion inhibitor 1,2,3-benzotriazole (BTA). A recent paper by Grayburn et al. uses a combination of XPS, SIMS, and GCIB depth profiling to investigate the effectiveness of BTA as well as Incralac failure during outdoor weathering. The team found evidence for BTA migration to the copper surface as well as oxidation at the metal/polymer interface to indicate the source of coating failure. While these studies show the effectiveness of organic (soft) coatings that are easily applied and removable, they do not provide a coating with a long lifetime.

The use of inorganic (hard) coatings may provide an initial framework for which thin, transparent protective films have a longer useful lifetime than soft coatings due to their hard structure and inert properties. Unlike organic coatings that can be applied under ambient conditions using spray or dip methods, inorganic coatings will typically require specialized instrumentation for deposition through sputter, vapor, or electrochemical processes. While highly specialized, these coatings will generally be relatively thinner than their organic counterparts. One major concern of inorganic coatings is their effect on appearance of an object. Faraldi et al. investigated the use of diamond-like coatings for their aesthetic on metal objects. By using chemical vapor deposition (CVD) to produce diamond-like coatings, the team was able to produce
Figure 1.4: Derivative spectra of XPS high-resolution regions of carbon KLL Auger regions shown in Faraldi, et al. Shift spacing measured as “D” indicates the presence of diamond-like coatings resulting from the CVD process where sample “a” was collected in anodic mode with hydrogen gas present, and sample “b” was collected in anodic mode without hydrogen gas. Reprinted with permission from [26] Faraldi, et al with permission of Springer Publishing. Copyright 2014 Springer Publishing.
useful films against preliminary barrier tests that have minimal aesthetic effects on the metal objects as characterized by XPS, SEM, and Raman spectroscopy. Figure 1.4 shows the production of diamond-like coatings from CVD processes by measuring the peak spacing in the carbon KLL Auger region. For precious metals, the surface appearance is extremely important and so atomic layer deposition (ALD) is used as it can produce very thin, uniform films. Marquardt et al. used ALD for the protection of 3-dimensional silver objects. After one year ambient aging the group investigated the surface tarnish using XPS, AFM, Raman spectroscopy, and porosity measurements, finding that the complex structure of three-dimensional objects pose a unique challenge in ALD films for the protection of precious silver objects due to imperfect deposition of the initial film.

1.4 Stone Objects

While related to metals in cultural heritage science due to their use as architectural elements, stone objects have a unique challenge in their observation and treatment due to their complex composition and porous structure. Stone objects are typically among the oldest surviving materials due to their inertness to their environment, although susceptibility to microbial and freeze/thaw deterioration make them prime candidates for study via surface analytical instrumentation. The current research focuses on the observation of deterioration and the use of hydrophobic films in the treatment of stone and resin objects.
1.4.1 Coatings for Stone Objects

For stone objects, a common theme for treatment is to reduce the surface porosity to create a physical barrier to limit diffusion of contaminants into the bulk of the objects. By limiting the degradation and corrosion to the upper surface, the lifetime of the object will be increased. Fermo et al. investigated the properties of hydrophobic coatings in the form of siloxane resin applied to the surface of stone objects in architectural applications, where the applied resin was characterized using XPS, AFM, SEM, and attenuated total reflectance (ATR) FTIR.28 The team found that the siloxane resin was able to form homogenous layers that infill the porous stone and created a hydrophobic surface. By using a hydrophobic coating, the treatment offers the diffusion limitation of water into the porous stone, decreasing degradation while minimizing any effects on the appearance of the stone. Another coating used for its hydrophobic properties is titanium dioxide, TiO$_2$. Stranges et al. deposited transparent TiO$_2$ films onto stone objects to mimic outdoor and marine environmental corrosion.29 The films were characterized using XPS, x-ray fluorescence spectroscopy (XRF) and contact angle measurements. The team concluded that the coatings were hydrophobic as expected however the deposition process that requires an ultra-high vacuum (UHV) system is only applicable for small objects and not large, architectural objects.

Another area of interest in developing new treatments for stone is to limit damage incurred by microbial attack as microbial films produce local environments with varying pH and moisture content, both of which play a role in stone corrosion. The role of sol-gel synthesis N-doped TiO$_2$ for self-cleaning applications was studied by Bergamonti et al. using XPS, Raman spectroscopy, UV-Vis spectroscopy, and XRD.30
By depositing films of nanostructured TiO$_2$ onto stone surfaces using sol-gel synthesis methods, the team was able to produce photocatalytic TiO$_2$ which underwent self-cleaning as measured as a function of oxidation of a dye placed onto the treated surface, giving insight into the role of self-cleaning films for use on cultural heritage objects. This use of photo-induced oxidation could play a pivotal role in treatments intended for outdoor stone that are in areas prone to microbial attack. When doped with metal earth anions, “M”- TiO$_2$ will also behave as a biocide, which was then deposited using the sol-gel method onto mimics of monument stone by la Russa et al.$^{31}$ By varying the identity of the metal dopant, the study was able to show an increase in biocide activity in comparison to undoped TiO$_2$, as characterized by XPS, SEM, UV-VIS spectroscopy, and microbial tests. Lastly, zinc oxide (ZnO) nanocomposites have also been shown to provide decreased biological activity, as well as being co-deposited with hydrophobic siloxane-based coatings.$^{32}$ Ditaranto et al. has shown the use of ZnO nanocomposites for the control of biodeterioration of patrimonial stoneworks. The electrodeposited films were characterized by XPS, inductively coupled plasma mass spectrometry (ICP-MS), and SEM with their effect on microbial diversity analyzed via microbial cultures. The study concluded that the synergistic effects of the ZnO biocide and hydrophobic siloxane provided a net positive impact on limiting biodeterioration for samples taken both immediately after deposition as well as one year naturally aged samples. Figure 1.5 shows the mobility of the ZnO nanomaterial to the film surface after curing for 60 days for inhibition of biological growth.
Figure 1.5: High-resolution XPS spectra of Zn 2p region as shown in Ditaranto et al. The figure shows the increase of ZnO nanoparticle mobility to the surface of the nanocomposites coating over a curing period of 60 days. Reproduced from [32] Ditaranto et al with permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association and the RSC.
1.5 Glass

Glass objects, which typically cover the range of traditional stained glass, ceramics, porcelain, and volcanic glasses, have a wide variety of appearances in cultural heritage collections. Depending on the object, most conservation and preservation is limited to the pigmentation and bulk composition of the object, which is normally analyzed using optical/electron microscopy and Raman spectroscopy due to their inorganic composition. However, any corrosion products that form on the objects’ surface are well suited for analysis via SIMS and XPS as well as any possible interface interactions with proposed treatments. For the work presented here, the glass objects will be classified as either archaeological glass or modern glass.

1.5.1 Archaeological Glass Objects

Archaeological glass is generally classified as glass that was produced or modified before industrialization. Beginning with an ancient source of natural glass, obsidian, Laskaris et al. studied the cation composition and surface roughness of obsidian using depth profiling SIMS and AFM.\(^{33}\) The study found that the combination of SIMS and AFM was sufficient for establishing provenance of archaeological obsidian. Figure 1.6 is a SIMS depth profile as published in Laskaris et al. showing the distribution of atomic species in obsidian glass, highlighting the defined hydration layer at the uppermost surface. Duckworth et al. investigated the production of opaque Late Bronze Age glasses to identify both raw materials and glass production techniques.\(^{34}\) Using TOF-SIMS the team was able to identify molecular species attributed to various
Figure 1.6: Distribution of cationic species in obsidian glass as shown in Laskaris et al.\textsuperscript{33} The depth profile highlights the hydration layer at the uppermost surface where silicates and hydrates displace sodium and magnesium. Reproduced from \textit{Laskaris et al. Journal of Cultural Heritage 2016; Article in Press}. Copyright 2016 Elsevier Masson SAS. All rights reserved.
opacifiers found in Bronze Age glass production. An additional insight from the study was the relative heterogeneous mixture of opacifiers in comparison between the upper surface and the bulk of the glass, most likely resulting from improper glass melting techniques. Moving on to the Greco-Roman era, Elnaggar et al. focused on the laser removal of corrosion products resulting from burial of Greco-Roman glass objects. The team used a Q-switch Nd YAG laser to clean various objects that were then characterized via FTIR, focused ion beam (FIB)-SIMS, and SEM analysis showing that removal of the corrosion layer resulting from burial is possible through laser irradiation. Ending in the Medieval Ages, Mocioiu et al. characterized the composition and preservation of lead silicate glasses using XPS, ICP-MS, and SEM analysis, with sol-gel preparation of a silica coating. The team was able to identify the role of water for corrosion processes on lead silicate glasses and showed the effectiveness of sol-gel silica coatings to increase hydrophobicity of the resulting treatment layer to minimize water-induced corrosion.

1.5.2 Potash-Lime Glass Objects

The team of de Bardi et al. provided a broad work on the composition, corrosion, and protection of potash-lime-silica glasses. Potash-lime-silica glasses can be found across a wide variety of cultural heritage materials as well as having modern applications. In 2013, the team began with publishing an article concerning the leaching of medieval stained glass under acidic conditions for environmental degradation. Using depth profiling SIMS and SEM, this first study concluded the observation of leached cation components under acidic conditions. Next, the use of sol-gel synthesis silica coatings
Figure 1.7: SIMS depth profile (above) and 3D reconstruction (below) as shown in de Bardi et al.\textsuperscript{39} Sample has been treated by a sol-gel coating and left to gaseous weathering for 1 week. The sol-gel coating was effective for the inhibition of sulfur mobility into the potash-lime-silica glass. Reprinted as general use under open access guidelines.
for the protection of potash-lime-silica glasses was investigated, with the coatings being characterized by depth profiling SIMS and optical microscopy after weathering.\textsuperscript{38} In agreement with previous literature, the sol-gel silica coating does provide effective protection against acid-induced leaching due to the hydrophobic silica layer. Lastly, the team followed up with a 2015 study by using known gaseous reactants in their weathering conditions to test the effectiveness of their sol-gel silica coating on potash-lime-silica glass.\textsuperscript{39} Figure 1.7 Shows a SIMS depth profile and resulting 3D reconstruction of a potash-lime-silica sample from the 2015 study. After gaseous weathering, the composition of the coatings were analyzed with depth profiling SIMS and SEM that found the coatings to be effectively resistant to chemical change due to the gaseous reactants.

### 1.6 Non-Categorized Cultural Heritage Objects

A large portion of cultural heritage objects does not fall within a pre-defined category, or would rather fall across several highly unique categories. For modern surface analytical instrumentation, technologies related to surface-charge compensation, camera-assisted alignment, high-accuracy stages, and cryogenic cooling allow for the analysis of almost any type and shape of object or sample, given that the object or sample will fit into the analysis chamber. Having this flexibility in the type of material that can be analyzed allows for highly unique samples to be analyzed with SIMS and XPS.

Starting in 2006, Mazel et al. used SIMS, SEM, and FTIR analysis to analyze surface materials found on African wood statuettes.\textsuperscript{40} The team was able to conclusively show
Figure 1.8: Distribution of protein and starch mass fragments as found in a statuette sample as shown in Mazel et al. Images “a” and “b” show the SIMS mass fragment for protein (m/z 44.05) in positive ion mode and the infrared amide II band (1540 cm$^{-1}$), respectively. Images “c” and “d” show the SIMS mass fragment for polysaccharides (m/z 59.01) and the infrared starch band (1079 cm$^{-1}$), respectively. Reprinted from Mazel et al, Analytica Chimica Acta 2006, 570:34-40, with permission from Elsevier.
evidence for a wide range of materials such as proteins, lipids, starch, urate salts, and minerals using the listed complementary techniques on the surface of the statuettes, adding to the understanding of the ethnological role of the statuettes. Figure 1.8 shows the distribution of protein and starch as found on a sample taken from a statuette. Tortora, Notaristefani, and Ioele published another study involving the cultural and religious significance of an object in 2014 concerning the investigation of gilt and painted leather from an altar frontal from the church of San Domenico in Orvieto, Italy. Using SIMS and FTIR, the team was able to distinguish between oil paint layers containing indigo dye and lead white paint, as well as resins from the gilt and painted leather artifact. A follow-up study published in 2016 by Tortora et al. provided a method to distinguish between dammar and mastic resins using multivariate methodologies applied to SIMS spectra. Using principal components analysis (PCA) the team was able to distinguish between the isomeric components consisting of triterpenoids that distinguish between the chemically very similar dammar and mastic resins.

Continuing with natural materials found in cultural heritage objects, Sodhi et al. focused on Palaeogene European amber in a 2012 study. The study provided preliminary results in using SIMS analysis and PCA processing to distinguish between various Class 1A ambers that are found in cultural heritage collections. Lee et al. investigated natural Asian lacquers in a 2016 study using SIMS, XPS, and FTIR analysis. Asian lacquers are used in a wide variety of applications, from binders and surface coatings to adhesives, and SIMS analysis provided spectral differences in polymerization across lacquers prepared from various tree saps and resins. Figure 1.9
Figure 1.9: High-resolution XPS and SIMS spectra taken from three Asian lacquer films for identification as shown in Lee et al. The XPS spectra on the left (d, e, and f) correlate to their respective SIMS spectra on the right (a, b, and c). The SIMS spectra shown were taken in positive-ion mode. Reprinted from [44] Lee et al with permission from John Wiley & Sons, Inc.
is taken from Lee et al. and shows the use of high-resolution XPS and high-resolution SIMS to identify materials that are chemically very similar. Another method of distinguishing materials by chemical variability is through isotopic ratios. While SIMS is not considered a quantitative technique due to matrix effects, isotope ratios are a property inherent to the atomic species in a sample and not their concentration, meaning the isotopic abundances will not change due to matrix effects. Isotopic analysis was the focus of a study by Othmane et al. where hydrogen and copper isotopes were used for calibration of instrumental mass fractionation (IMF) for SIMS isotopic analysis of turquoise materials. Complementary analysis by SIMS, XRD, and FTIR, mineralogical differences in turquoise are distinguished via copper isotopic analysis that are beneficial for identifying turquoise objects for provenance.

One of the most unique objects to be analyzed over the past decade was described in a 2012 paper published by Cersoy, Richardin, Walter, and Brunelle in which they used SIMS imaging for the analysis of samples from a South-Andean mummy. The team used SIMS and SEM analysis to observe biological and mineralogical components found on the skin of the mummy to establish the current state of degradation of the mummy, as well as provide any ethnological observations pertaining to the culture of the mummy. Visualization of a wide variety of materials was possible, including amino acid distributions for dermis and epidermis, degradation of subcutaneous fats, mineral deposits, and collagen and keratin fibrous tissue. Figure 1.10 is shown as it highlights the differences in expected fatty acid residues between unaged skin and mummy skin.
Figure 1.10: High-resolution SIMS spectra of fatty acid residues found in unaged and mummy skin samples as shown in Cersoy et al.\textsuperscript{46} The spectra show a clear distinction between the expected fatty acid mass fragments when comparing between unaged and mummy skin samples, an explanation for the drastic difference in outer skin layers found in mummified samples. Reprinted from [46] Cersoy et al with permission from John Wiley & Sons, Inc.
1.7 Modern Polymers

Many works of modern art and culture include components consisting of polymers or plastics that pose a considerable challenge in their preservation. There have been many papers relating to the treatment of modern polymers and plastics, and a handful of those include surface analytical instrumental methods. In 2007, Abel and Coppiters published a study in which they used XPS, SIMS and SEM to characterize a variety of plastics in their use for cultural heritage.\textsuperscript{47} By considering the identity of additives to the plastics, they conclude it may be possible to predict chemical and physical degradation of the plastics in order to best assess treatment options. While several papers are forthcoming, a thesis has been written by Fricker to establish the conservation and treatment of polymer materials, of which several analytical methods were employed to assess the current and predicted degradation of a variety of polymeric materials.\textsuperscript{48} SIMS and AFM were used to establish surface chemical and physical changes due to cleaning protocols common in the cultural heritage field for polymeric materials.

1.8 Dyes, Textiles, and Documents

Due to the typically friable nature and high organic content of dyes, textiles, and documents, the use of surface analytical instrumentation has been limited in the past. Traditionally, textiles are colored through the use of organic dyes that adhere to the natural fibers to a greater extent than inorganic pigments. The inks used for writing on documents can be a combination of organic inks and inorganic pigments bound in a variety of aqueous-soluble binding media. These materials have traditionally been
analyzed by FTIR, Raman spectroscopy, and XRF as ambient spectroscopies do not require sampling, and for when organic analysis is required gas chromatography-mass spectrometry (GC-MS) has been the analytical technique most commonly employed. Surface analytical instrumentation has advanced past previous limitations where dyes, textiles, and documents are now able to undergo routine analysis, assuming small microsamples can be removed prior to analysis.

1.8.1 Dyes and Textiles

The initial production and chemical preparation of textiles for either wear or decorative use consisted of several harsh treatments that will negatively impact the lifetime and deterioration of the textile. Tapestries, the subject of a 2006 study by Batcheller et al., were the preferred decorative textiles of choice during the 15th-17th centuries by the wealthy elite. The SIMS investigation into the preparation methods and resulting chemical byproducts to establish degradation processes of fine wool and silk tapestries concluded the effects of cleaning with “wool wax” was characterized. Figure 1.11 shows two negative-mode SIMS spectra resulting from two different cleaning protocols for wool. Another interesting finding was that a result of natural dying found the removal of covalently linked lipids on the wool surface leading to decreased fiber strength leading to faster deterioration rates.

A large body of work into the analysis of dyes and textiles was published by a collaborative project headed by Lee, J. and Lee, Y. at the Korea Institute of Science and Technology. Beginning in 2008, Lee et al. investigated the use of natural dyes on ancient textiles using SIMS analysis to establish mass fragments associated with the
Figure 1.11: Negative SIMS spectra comparing modern cleaning methods with historic urine-scouring methods for wool as shown in Batcheller et al., where the triangle distinguishes expected mass fragments for wool. The modern methods (above spectrum) show a decreased background compared to that of the historic methods (below), indicating greater residues remaining from the urine-scouring process. Reprinted from Batcheller et al. Applied Surface Science 2006, 252:7113-7116, with permission from Elsevier.
natural dyes to use in future research.\textsuperscript{50} In 2012 the group published a follow-up article with SIMS and FTIR analysis of traditional dyes used for textile coloration.\textsuperscript{51} By using the FTIR and SIMS complement, the group was able to identify indigo dye on several ancient textiles. A third article was published in 2014 that use XPS along with SIMS and FTIR to establish color changes from burial conditions in contrast to the theorized original dye color from production.\textsuperscript{52} XPS analysis was able to show the shift in oxidation of the dye marking the color change of blue to brown on the ancient textiles.

1.8.2 Documents

Document analysis provides a unique challenge for sample preparation for SIMS and XPS analysis. While flat to the eye, documents are rarely flat on the micro-scale as the alignment of wood fibers are not uniform at the level expected for SIMS and XPS analysis. Secondly, documents are relatively thin which will make cross-sectional analysis difficult given spatial limitations for SIMS and XPS imaging. Nonetheless, articles pertaining to document analysis have been published which contain observations concerning document provenance and deterioration. Benetti et al. published a 2011 paper concerning the provenance of papers manufactured in the 18\textsuperscript{th} century across various paper mills in Tuscany, Italy.\textsuperscript{53} The study focused on SIMS and XPS analysis to deduce relevant minerals to the manufacturing process as well as sizing material found on parts of the paper. Figure 1.12 shows SIMS images and high-resolution XPS of the C 1s region of one of the papers studied by Benetti et al. In 2014, a study by Szczepanowska and Goreva characterized the effects of fungal biodeterioration on papers using SIMS and SEM.\textsuperscript{54} The preliminary results from the
Figure 1.12: SIMS images and high-resolution XPS spectrum of Italian papers as published in Benetti et al. The SIMS images (above) depict various cationic species from manufacture as well as the animal glue ($C_4H_8NO^+$) that co-localize with the cellulose species. The use of animal glue (gelatin) is further identified in the high-resolution XPS spectrum shown below. Reprinted from Benetti et al, Applied Surface Science 2011, 257:2142-2147, with permission from Elsevier.
study show that fungal growth through the film with distinguishing molecular fragments pertaining to fungal attachment on the paper fibers.

1.9 Paintings

An extensive area of research using surface analytical instrumentation for cultural heritage science is the study of paintings. While the exact reason for the higher number of literature citations for paintings is unclear, paintings offer a highly complex chemical system consisting of multiple layers of mixed organic/inorganic materials. The combination of binders and pigments from a multitude of manufacturing processes allows for a large amount of degradation to occur, each with unique chemical processes to be observed and characterized. Additionally, as modern conservation practices emerge with the newest chemical technologies, treatments and their interactions with historic materials need to be studied to ensure the best combination of aesthetics and protection. As mentioned in Section 1.1, several reviews and books have been published that show the feasibility of surface analytical instrumentation in the analysis of paintings and related materials. In the past decade, several papers have been published which take these initial studies into the realm of understanding fundamental chemical processes, whether it be degradation of binding media or the kinetics and dynamics of pigments mobilizing across a paint layer.

1.9.1 Analysis of Paintings

A major use of SIMS in paintings analysis is for binding medium identification as the technique allows for simultaneous organic and inorganic mass fragments to be
collected and imaged. Binding medium analysis is possible through identification of mass fragments related to the material to be analyzed, such as amino acid fragments for proteinaceous binders and fatty acid fragments for oil binders.

A 2009 study by Keune et al. into the “added value” of SIMS measurements in regards to Naples yellow oil paint reconstructions considered SIMS as a complementary technique for the analysis of paint cross sections.\textsuperscript{55} In the study SIMS was used in direct comparison to a variety of mass spectrometry techniques such as GC-MS, electrospray ionization mass spectrometry (ESI-MS), and direct-temperature resolved mass spectrometry (DT-MS), as well as FTIR, optical microscopy, and SEM. The conclusions discuss that while SIMS is unable to observe large molecular ions seen in the other mass spectrometry techniques (which are not imaging techniques), SIMS does have the advantage of detecting co-localization of pigment and binder species. Figure 1.13 highlights the ability to co-localize the lead signal from the various deprotonated fatty acid signals, which is a unique observation found using SIMS imaging. Tognazzi et al. published an article on SIMS characterization of pigments and binders as found in \textit{The Martyrdom of St Catherine}, a painting attributed to Francesco Cassarino.\textsuperscript{56} The SIMS analysis was used in complement to SEM, Raman, FORS-VIS, and FTIR analysis taken of the same painting to confirm pigment identity and provide information pertaining to the oil and
Figure 1.13: SIMS spectra and images taken from Keune et al. showing the use of weathering on Naples Yellow pigment bound in lead.\textsuperscript{55} The spectra (above) shows the differences between natural (A) and artificial (B) weathering on a Naples Yellow bound in oil paint film, where the artificial weathering underwent significant degradation. The SIMS images (below) taken in positive-ion mode show the naturally-aged sample as a cross section to identify (A) total ion intensity, (B) lead, (F) azelaic, (G) palmitic, (H) oleic, and (I) stearic fatty acids to co-localize the lead signal to the oil binder. Reprinted from Keune et al, \textit{International Journal of Mass Spectrometry} 2009, 284:22-34, with permission from Elsevier.
Figure 1.14: Identification of copper-carboxylate complexes in Renaissance paintings as published in Richardin et al. The spectra (above) show the higher mass region as seen in negative-ion mode (a) and positive-ion mode (b). The inset in (a) highlights fatty acid (FA) complexes of copper to myristic (M), palmitic (P), and stearic (S) acids. The SIMS images (below) are reconstructed based on the positive-ion spectrum in comparison to the copper signal (j) and copper-carboxylate complexes (k-m). Reprinted from Richardin et al, *Journal of the American Society of Mass Spectrometry* 2011, 22:1729-1736, with permission from Elsevier.
Figure 1.15: Summary of findings of the chemical composition of a cross-sectional sample taken from a Rembrandt painting as published by Sanyova et al. the optical image (above) is use for orientation of the SIMS image (below). Reprinted with permission from [58] Sanyova et al. Copyright 2011 American Chemical Society.
resin binders used in the work. Richardin et al. published an examination of copper green pigments as found in Renaissance paintings in 2011 that combined results as seen in SIMS and SEM.\textsuperscript{57} The study was able to show the organometallic complexes formed during degradation of the copper green pigments of atacamite and copper carboxylates. Figure 1.14 shows the identification of the copper-carboxylate complexes indicative of metal-soap formation.

Another publication from 2011 written by Sanyova et al. concerns unexpected materials found in \textit{The Portrait of Nicolas van Bambeeck} painted by Rembrandt van Rijn in 1641.\textsuperscript{58} The publication details a wide variety of organic materials found in a cross-sectional sample that was imaged using SIMS in comparison to SEM, FTIR, micro-Raman spectroscopy, and GC-MS analysis, exemplifying the workshop practice and inventive techniques of Rembrandt van Rijn. Figure 1.15 shows a SIMS image in summary of the findings in the study by Sanyova et al. Atrei et al. used the approach of SIMS, SEM, and GC-MS in their investigation of the reworked painting \textit{Madonna with Child} attributed to Pietro Lorenzetti in a 2014 publication.\textsuperscript{59} The team concluded that the original and reworked portions of the painting were consistent with the previously described literature, and SIMS was able to identify the proteinaceous binder as confirmed by GC-MS. Another publication by Atrei et al. published in 2014 expands on their previous publication by using PCA methods to distinguish between collagen, egg yolk, and casein proteins used as binders in Renaissance era painting.\textsuperscript{60} Through careful peak selection, the study was able to distinguish between collagen and egg yolk, with casein identification proving difficult to distinguish due to complications due to the matrix effect present in SIMS.
Figure 1.16: Comparison of proteinaceous binding media using multivariate analysis as shown in Benetti et al.\textsuperscript{61} The above scores plot identifies historic samples (5-7) compared to pure and mixed proteinaceous binding media films. The below scores plot compares historic samples (8-9) to unaged to aged protein films to assess degradation of the historic samples. Reprinted from Benetti et al, \textit{International Journal of Mass Spectrometry} 2015, 392:111-117, with permission from Elsevier.
In 2015, a study by Benetti et al. characterized the proteinaceous binders found in *Madonna and Child enthroned with Saints* by Ambrogio Lorenzetti using SIMS and high-pressure liquid chromatography (HPLC) analysis, including differentiation between aged and unaged proteinaceous materials. By using PCA for spectral processing the group was able to distinguish between egg, collagen, and casein proteins (or mixtures), as well as identify glue as a restoration component and not in the original artwork. Figure 1.16 shows a PCA scores plot of unaged and aged protein binders in comparison to a collected cross-sectional sample as shown in Benetti et al. Voras et al. published a 2015 paper that used SIMS and GC-MS analysis of *Bonheur de vivre* by Henri Matisse to compare results of cadmium yellow alteration as observed by a variety of synchrotron-based spectroscopy techniques. Through careful examination of the expected compounds associated with cadmium yellow alteration, the study was able to co-localize altered pigment with a drastic loss of oil binding media, an observation not possible through synchrotron-based measurements. Figure 1.17 details the use of isotopic ratios for identification of compounds with similar exact mass. A 2016 study published by Biocca et al. focused on identification of the gilding technique in the fresco *Vela della Castità* by Giotto’s school. By combining SIMS, SEM, and FTIR analysis the study was able to identify gold- and tin-leaf and their adhesives as well as a possible identification of cochineal dye.

Voras et al. published a comprehensive analysis of egg and oil binding medium as observed in Renaissance-era artwork using SIMS analysis. The study detailed observations of fatty acid depletion observed in both egg and oil paintings leading towards upper surface friability as observed during conservation efforts. Figure 1.18
shows SIMS images observing the fatty acid depletion as detailed in Voras et al. Noun et al., featuring the use of delayed extraction techniques for SIMS imaging, published a 2016 paper investigating a cross section form the painting *Rebecca and Eliezer at the Well* by Nicolas Poussin. The study was effective in providing higher levels of detail in pigment identification due to the higher observed spatial resolution due to delayed extraction. Figure 1.19 summarizes the use of high-resolution imaging for cross-sectional analysis from Noun et al. Lastly, a 2017 paper by Radovic et al. investigated using MeV ion excitation sources for SIMS analysis to identify various modern paints. Modern paints pose a particular challenge for cultural heritage research, as their chemical composition can be highly complex due to a multitude of additives from manufacturers leading to unknown materials compromising their lifetime stability. Figure 1.20 shows the use of MeV primary ions for the use of SIMS imaging of modern lead-based paints.

Sano and Cumpson performed XPS and SEM analyses of gum binders for their use in watercolor paints. The study was able to effectively differentiate between a variety of gum binders using the chemical speciation provided by XPS as well as inorganic components by both XPS and SEM. In 2014, Sano et al. performed XPS on a set of aged oil paints containing modern organic pigments with the purpose of using multivariate analysis to distinguish the various chemical components related to aging effects. The observation of oxidation products in the binding oil resulting from aging was a major factor in the degradation of modern organic pigments bound in oil. Figure 1.21 shows the use of partial least-squares (PLS) models for the identification of modern organic pigment degradation.
The expected isotopic ratios (above) are shown in comparison to collected spectra from standard powders and a historic cross-sectional sample taken from Le Bonheur de vivre (1905-1906) by Matisse. The inset shows the detail of the low-signal cadmium chloride peaks. Reprinted from Voras et al, *Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
Figure 1.18: Observation of fatty acid depletion in uppermost paint layers as shown in Voras et al (2016). Sample is taken from Pentecoste (1480-1489) by Matteo di Giovanni. Upper optical images are in visible (left) and UV (right) exposure showing the layered structure of the ground (4), underdrawing (3), inner paint layer (2) and upper paint layer (1). Note in the SIMS images (below) the distinct lack of fatty acid signal in layer (1) in contrast to the homogenous protein signal (CN⁻). Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
Figure 1.19: Summary of the advantages of delayed extraction techniques to increased spatial resolution for SIMS imaging as shown in Noun et al.\textsuperscript{65} An optical image (a) of the cross-sectional sample taken from \textit{Eliezer and Rebecca} (1664) by Nicolas Poussin; (b) a diagram of the identified layers; (c) a high-spatial resolution SIMS image of the various lead oxides observed; (d) SIMS spectrum of the area indicated by the red circle in (a); and (e) a y-area profile of the identified materials across the two green lines in (a). Reprinted from [65] Noun et al with permission from John Wiley & Sons, Inc.
Figure 1.20: SIMS spectra and images showing the use of MeV primary ions for the analysis of modern paints as shown in Radovic et al. The spectra (above) is of phthalocyanine pigments in an alkyd binder showing the free pigment (PB 16) and complexed pigment (PB 15:1 and 15:3). The SIMS images (below) are of the cross-sectional samples showing the distribution of the same mass fragments. Reprinted from Radovic et al, Nuclear Instrumental Methods B 2017, Article in Press, with permission from Elsevier.
Figure 1.21: Results of XPS analysis of aging experiments of modern organic pigments as shown in Sano et al. \(^{68}\). The upper plots are for naturally aged samples where (a) plots the change in carbon chemical shift as a function of aging and (b) plots the observed O/C ratio. The lower plots show the results of a partial least-squares (PLS) model applied to a set of samples exposed to UV exposure where (a) shows the correlation between predicted and actual aging and (b) the regression coefficients showing the predicted change in chemical shift. Reprinted from [68] Sano et al with permission from John Wiley & Sons, Inc.
1.9.2 Treatments and Conservation of Paintings

Another application of surface analytical instrumentation in the field of paintings analysis is that of observing the use of modern treatments (such as gels) for cleaning and preservation purposes. SIMS and XPS are ideal candidates, as their surface sensitivity will ensure analysis at the exact interface of treatment and painting. A 2013 paper by Willneff et al. covers the conservation of artists’ acrylic emulsion paints by wet cleaning methods. The study used XPS, near-edge x-ray absorption fine structure (NEXAFS), and FTIR analysis to characterize wet cleaning methods used in the conservation of acrylic emulsion paints. XPS analysis of the paint film surface concluded that wet cleaning methodologies tend towards selective extraction of aqueous film components as well as pigment alteration and cleaning residues that would all contribute to paint film stability and longevity. Figure 1.22 shows high-resolution XPS spectra of the paint films after cleaning to show changes in surface chemistry due to solvent-based extraction and chemical modification. Recently, the book *Gels in Conservation* (2018 expected publication) has a focus on the use of gels for conservation and treatment of paintings. A chapter written by deGhetaldi et al. focuses on the use of aqueous solvent gels for the cleaning of *The Triumph of David* housed at Villanova University. By comparing results of SIMS, GC-MS, and FTIR with cleaning tests, the decision of using a primarily aqueous gel was determined due to the proteinaceous overpaint layers as observed by SIMS. Figure 1.23 highlights the analysis of a cross-sectional sample taken from *The Triumph of David* that was used to identify a glue-based prior treatment that was only removable with aqueous gels.
Figure 1.22: High-resolution XPS spectra showing changes in chemical shift due to solvent-based surface modification as shown in Willneff et al.\textsuperscript{69} The top spectra show differences observed in the Cl 2p region across various cleaning solvents. The bottom spectra show the differences observed in the C 1s region across the same cleaning solvents. Reprinted as general use under open access guidelines.
Figure 1.23: Optical and SIMS images of a cross-sectional sample taken from The Triumph of David as shown in de Ghetaldi et al.\textsuperscript{70} (A) is a UV image showing a significant fissure and infill. (B) is the total ion image from the positive-ion mode; (C) is an overlay of the identified pigments; amino acid peaks for hydroxyproline (D), proline (E), and alanine (F) identify the infill as animal glue; (G) is palmitic acid and (H) is stearic acid. Reprinted with permission from Kristin DeGhetaldi and Villanova University
1.10 Conclusions

Surface analytical instrumentation, such as SIMS and XPS, has provided significant contributions to the field of cultural heritage research as shown over the past decade. The use of SIMS and XPS provide highly unique information regarding cultural heritage systems, whether in the form of chemical observation and characterization, understanding of fundamental chemical processes such as degradation, and the effects of conservation cleaning and treatments. While the use of surface analytical instrumentation is limited due to instrument access and vacuum considerations, the benefits of surface analysis will outweigh the initial concerns, as well as providing unique collaborations across museums and research institutions around the globe.

As such, the use of surface analytical instrumentation must be carefully guided to ensure that cultural heritage science is at the forefront of emerging technologies. The past decade has seen a large expansion of surface analysis technologies, and its use in cultural heritage science should undoubtedly follow. The following list is not all encompassing, but rather suggested based on the author’s experience;

i. Proper sample handling and preparation. As discussed by several above papers, surface analysis can have a bias due to surface preparation as only the top surface (3-10 nm) is observed during analysis. For example, cultural heritage materials are highly subject to solvent extraction and contamination from polishing.

ii. The use of multivariate analysis when applicable. Multivariate methods should only be used in cases when univariate data processing simply will not work. In
which case the chemical constituents related to the particular multivariate
technique must be determined.

iii. The use of modern materials and techniques to develop stable, high-lifetime coatings. Mentioned above, the use of techniques such as atomic layer desorption (ALD) and modern polymeric materials should not be discouraged for their use in cultural heritage research. Weathering studies of these coatings as characterized by SIMS and XPS will ascertain how and why the coatings are failing and will lead towards higher quality coatings for future preservation methodologies.

iv. Implementation of gas cluster ion beam (GCIB) sputtering. The commercialization of GCIB sources has allowed for the cleaning and depth profiling of organic materials without any loss of chemical information due to beam-induced degradation. With these sputter sources it should be possible to provide an entire 3-dimensional analysis of the complex systems found in cultural heritage research. This includes 3-D imaging (from varnish to canvas of a paint sample) or buried interfaces (polymer coating degradation on metals). However, bias due to sputter effects (such as selective sputtering) should be monitored.
REFERENCES


Chapter 2

EXPERIMENTAL OVERVIEW

2.1 Introductory Remarks

For the work discussed in this dissertation, various instrumental and experimental techniques have been used towards binding medium analysis in fine art paintings. A major goal of this research is to identify the materials that were present within a cross-section sample removed from a painting. This includes producing a method of analysis for identification of materials found across all eras and painting techniques. Another goal of this research is to develop a method of distinguishing the pathways of degradation that are present in paintings and various cultural heritage materials. The following instrumentation and sample preparation techniques played unique roles necessary for completion of these research goals.

2.2 Preparation of Inorganic and Organic Thin Films

To aid in surface analysis, preparing thin films of inorganic and organic materials was necessary for standards analysis prior to the analysis of irreplaceable historic samples. To prepare thin films of inorganic materials such as pigments and organic materials such as binding media, there are three main methods; drop-casting, spin-casting, and thermal evaporation. While each method can produce a usable surface for analysis, there are limitations that must be considered prior to preparing the thin film. The
sample must be placed onto a clean, uniform substrate that will not interact chemically during the experimental process and analysis of the standard sample. The majority of the time the substrate used was a silicon wafer that was sonicated in isopropyl alcohol prior to use.

For the work detailed herein, both the methods of drop casting and spin casting were used for the majority of prepared samples. For inorganic pigment standards, drop casting or simply pressing the powder onto adhesive tape was used for analysis. For binding medium standards and various organic materials the preparation method of choice was spin casting, as the thin film produced was of an acceptable surface flatness. Preparation by thermal evaporation was not necessary for any standard sample as spin casting produced samples of sufficient quality in a quicker timeframe, however thermal evaporation did provide thin films of organic materials that were of the highest quality.

2.2.1 Drop Casting

Drop casting is the simplest method of the three preparation methods and allows quick sample preparation on the benchtop without any equipment, except for glassware. The material to be tested is dissolved in an appropriate solvent (such as water for a water-soluble protein or toluene for an organic-soluble binder) that is then deposited onto an appropriately cleaned substrate (such as a silicon wafer) with the use of a glass pipet. The drop is allowed to dry which removes the solvent and leave a thin film of just the intended material on the substrate. To increase the coverage of the material, additional drops may be dispensed onto the substrate and allowed to dry between each layer. To
facilitate fast dry times, the substrate may be heated to increase the evaporation rate of the solvent. This technique of producing thin films has the benefit of quick preparation, however the sample coverage on the substrate depends on the original solution concentration. Additionally, the resulting thin film may have a rough surface and inconsistent film thickness from sample to sample.

2.2.2 Spin Casting

Spin casting (or spin coating) is a modification of the drop casting technique by which the substrate is rotated during the solvent drying process. The substrate is placed on a rotatable drum and held in place by a vacuum seal where the sample is then spun for a desired amount of time until the solvent has completely evaporated from the sample. The substrate may or may not be rotated during the initial drop cast of the sample, typically for a fast drying solvent the sample is rotated, while for a slow drying solvent the substrate is stationary until all material is drop cast and then rotated. Altering the rotation speed and time, as well as using slower or faster evaporating solvents can control sample thickness. By rotating the sample during drying the resulting thin film has an increased uniformity and flatness compared to traditional drop casting. If the sample is prepared by drop casting using the exact same volume of dissolved material and spun at identical rates and times, the sample to sample variation in uniformity and flatness should be very similar. This is especially important for preparing a set of sample for analysis or degradation.
2.2.3 Thermal Evaporation

The third technique that was tested to prepare inorganic or organic samples relevant to cultural heritage materials is thermal evaporation. Thermal evaporation is dissimilar to the above casting techniques as it involves preparation of samples under high vacuum conditions instead of ambient benchtop conditions, allowing less atmospheric contamination within the bulk layer of the thin film. Thermal evaporation works by lowering the temperature of sublimation of a material by placing it within a vacuum environment. To prepare a sample for thermal evaporation, the material of interest must first be drop cast or placed (if a powder or pellets) onto a heating boat (typically made of tungsten or tantalum). The heating boat is then placed into the thermal evaporation chamber where it is connected to a voltage-limited power supply. The cleaned substrate of choice is placed in direct line of sight of the heating boat within the same chamber and then the whole thermal evaporation chamber is placed under vacuum, typically below $1 \times 10^{-6}$ mbar. After positioning a shield between the heating boat and the substrate, a voltage-limited power supply is turned on the heating boat to slowly increase the temperature of the heating boat to begin sublimation of the sample. When the sample has begun to sublime at a steady rate, as measured by a quartz crystal microbalance, the shield is removed and the sample is exposed to the sublimated material until the desired thickness is achieved. The shield is again placed between the heating boat and the sample and the applied power is removed from the heating boat. The chamber is then vented and the sample removed. While this technique produces very uniform samples and highly reproducible sample thicknesses, thermal evaporation is time-consuming as vacuum pumping and venting is required.
for each sample (unless multiple substrates can be loaded at the same time in direct line of sight of the heated boat).

2.3 Paint Cross-Sectional Sample Analysis Techniques

A major factor in the analysis of paint cross-sections is the ability to prepare an existing sample such that previous and future analyses are not affected by the current analysis. This concept is to help maximize the amount of collected information per sample with the ability to co-localize chemical information across multiple analytical techniques. Figure 2.1 shows the role of using an embedding resin to fix a very small cross-sectional sample for instrumental analysis. One major concern of TOF-SIMS analysis of a paint cross-section is the destructive nature inherent to any mass spectrometry technique where the sample is consumed to produce mass fragmentation patterns. However, TOF-SIMS has the benefit compared to traditional gas- and liquid-chromatography mass spectrometry methods (GC-MS and LC-MS) as both positive-mode and negative-mode spectra can be taken on the same sample surface. Additionally, the damage left behind after TOF-SIMS analysis is both from damaged surface species (top 3-10 nm) and embedded primary ions (< 5 µm) is easily removed with techniques such as hand-polishing or microtome techniques as discussed below.
Figure 2.1: Schematic of resin embedding of a cross-sectional sample. The sample (2D shown top, 3D bottom left) is affixed into a cube of resin prior to instrumental analysis and storage. Note that the 2D diagram includes a ‘substrate’ whereas the 3D does not as it is not common to include the cross-sectional substrate (canvas, panel, stucco, etc.) when collecting a sample.
2.3.1 Traditional Polishing Method

The traditional method of preparing paint cross-sections for analysis is through hand polishing. After embedding the micro-sampled cross-section in an appropriate polymer resin (such as polyester) and allowing the resin to cure, the cross-section must be brought to or near the surface for analysis. After finding the correct face for analysis, the resin cube (or cylinder) is either hand-trimmed using a jeweler’s saw (or other appropriate fine-toothed cutting blade) or polished using coarse polishing cloth or sanding paper. After rough removal of resin to expose the cross-section, the surface is polished with finer-grade polishing cloth in an iterative manner to produce a smoother surface to prepare a smooth surface for analysis. This is done by either holding the resin block by hand or by using a holding device to ensure a flat, uniform polish across the entire resin surface. While this method of cross-section preparation is viable for bulk-analysis methods such as optical microscopy, electron microscopy, FTIR, and Raman spectroscopy, the remaining surface layer of embedded polishing residue (such as silicon carbide or alumina) is too thick for surface analytical instrumentation such as TOF-SIMS and XPS to gather analytical information pertaining to the cross-sectional sample.

2.3.2 Ultramicrotomy Method

The surface sensitivity of TOF-SIMS and XPS require that the exposed surface be that of the cross-section and not of any contamination and/or residue remaining from sample storage, handling, or preparation. By combining sample preparation techniques common to electron microscopy and surface probe microscopy, a technique was
developed to prepare a paint cross-section for surface analysis. While the initial sample embedding and rough trim is completed in a similar fashion to hand polishing, the final surface preparation is different than the above described method. Figure 2.1 details the process of producing a viable surface for TOF-SIMS analysis of a cross-section of an historic sample. A summary of this process is the following: After rough trimming, the resin cube (or cylinder) is further trimmed of excess resin and affixed onto a specimen pin as shown in Figure 2.2 parts (A) through (C). After drying, the specimen pin is placed into a custom-built sample holder designed to hold the pin at a desired height and rotation for placement in both a microtome and sample holders of the ToF-SIMS and XPS to minimize sample handling. This holder is shown on the right-hand side of Figure 2.2. Once in the microtome the sample is trimmed using a steel knife (or other suitable trimming knife). When the cross-section is nearly visible at the surface, the trimming knife is replaced with a fine-cutting diamond knife for final cutting and exposing of the cross-section surface. Diamond ultramicrotomy knives are specially prepared as cleaved and ground crystalline diamond to have an extremely hard and sharp cutting blade. These knives are capable of cleaving thin films of a few hundred nanometers and leaving behind no residue because the diamond is an intact crystal and no polishing compound is required for cutting. While the friability of the paint cross-sections and the specific choosing of a resin that does not penetrate through the cross-section will hinder the production of a thin film for analysis, the remaining exposed surface is usable for surface analysis.
Figure 2.2: Detail of the paint cross-sectional sample mounting process used for ToF-SIMS analysis. (A) is the original embedded sample. (B) and (C) show the trimming and subsequent mounting of the sample on a specimen pin prior to microtome trimming. (D) shows the direction of cut for the microtome. The two images on the right show the detail of the specimen pin holder used for both microtome and ToF-SIMS analysis to hold the sample in at a given height and orientation. (A) through (D) are reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
2.4 Weathering Chambers for Thin Film Degradation

To understand the chemical degradation seen in historic paint cross-sections, weathering chambers that precisely control and measure heat, humidity, light exposure, and any atmospheric conditions as critical to producing consistent results. Due to the complex nature of fine art paintings, the major sources of degradation may be classed as i) degradation due to reactions involving original, intended paint materials without external influence (in-to-out); ii) degradation due to previous cleaning and restoration materials, and iii) degradation due to environmental exposure (out-to-in). The observed degradation that is discussed in the chapters of this dissertation has no singular cause, and the focus of the weathering chambers is to elucidate the initial interactions of binding media with its environment. As the degradation of paint films is very complex, weathering experiments were limited to unpigmented thin films of egg tempera, a common binding medium used since antiquity. Additionally, because of the complexity of the alteration pathways, it is imperative to provide the highest amount of useful data per sample in each sample set, to reduce any bias due to sampling, leading to a maximum of data collection of minimal sampling. This setup allows for three individual XPS depth profiles to characterize changes in chemical environment as a function of depth as well as sufficient area for TOF-SIMS analysis of the upper surface to find evidence of molecular alteration from weathering.
2.4.1 Rudimentary Weathering Chambers

Initial experiments with rudimentary weathering chambers that various environmental factors (such as heat, humidity, and light exposure) showed a significantly different chemical pathway as observed by TOF-SIMS and XPS analysis on thin films of egg tempera. These chambers consisted of glass jars that could be placed within a heating oven and humidity controlled with glycerol/water mixtures. However, there was no direct measurement of heat or humidity inside of the glass jars during the weathering. For light exposure, samples were placed in a glass dish on the benchtop and exposed to 254 nm UV light. Using these experiments it was evident that a system that could control these various environmental conditions while providing in-situ measurements of the chamber conditions was required for accurate observation of the chemical pathways of degradation of egg tempera thin films. Also, this chamber would become a platform for testing the degradation pathways for various cultural heritage materials and so a system to accommodate many different samples was ideal. Figure 2.3 shows schematics for both types of rudimentary weathering chambers.

2.4.2 Design of Environmental Chamber

To meet the above listed specifications, an initial small chamber was built from a UV-vis gas flow cell to control heat, humidity/atmosphere, and UV exposure for weathering of spin-cast binding media samples. This chamber is detailed in Figure 2.3b. From this initial test chamber, a full-scale chamber was built which provided a
Figure 2.3: Schematics of rudimentary weathering chambers used as testing platforms for controlling various environmental weathering conditions. ‘A’ is the jar-in-an-oven technique that includes atmosphere controlled by a water/glycerol mixture. ‘B’ uses a UV-vis flow cell that has been wrapped in heating tape with atmosphere bubbled through with dry nitrogen gas. UV exposure is done with a handheld UV lamp through a CaF$_2$ window on the flow cell.
platform for testing a variety of environmental factors. Figure 2.4 provides a schematic of the final chamber design. The design allowed independent control over chamber temperature, relative humidity, illumination, and atmosphere. The system was purged with dry nitrogen to for maximum flow over the sample surface and to remove any unwanted condensation on the sample. Temperature was measured via a thermocouple placed near the sample tray, and controlled with heating of the chamber sidewalls. Relative humidity was measured using a humidity sensor placed in close proximity to the samples. Illumination was done using a 254-nm Hg lamp. Lastly, the atmosphere was controlled through a combination of a glass jar located at the bottom of the chamber which was independently heated and stirred, as well as any gaseous components leaked in through the nitrogen purge line.

2.5 Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is an ultra-high vacuum (UHV) surface analytical technique used to observe atomic and molecular species present on a sample surface. The technique involves a primary ion source that is focused and accelerated towards a sample, where the resulting collision produces ablated secondary ions that are directed into a mass analyzer (specifically a time of flight (TOF) mass spectrometer). The collisional cascade converts the potential energy of the primary ion into kinetic energy of the ablated fragment where the proximity of the ablated material to the epicenter of the initial collision to determine mass fragment size.
Figure 2.4: Final design of weathering chamber for environmental aging of thin films of binding media. The system provides for self-contained control and measurement of various conditions for aging. Chamber heat is applied through heating tape and measured using thermocouples both on the chamber wall and near the sample tray. The atmosphere is where chamber humidity is created and measured with an RH sensor. UV exposure is from a 254-nm Hg lamp. Lastly, dry nitrogen is purged through the chamber to maintain steady temperature and RH conditions during the weathering experiment.
The general equation (2.1) that relates the ionization of secondary ions for SIMS is

\[ I_s^m = I_p y_m \propto^\pm \theta_m \eta \]  (Equation 2.1),

where \( I_s^m \) is the secondary ion current of species \( m \), \( I_p \) is the primary particle flux, \( y_m \) is the sputter yield, \( \propto^\pm \) is the ionization probability of either positive ions (+) or negative ions (−), \( \theta_m \) is the concentration of species \( m \), and \( \eta \) is the transmission of the analysis and detection system.\(^{72}\) Because the primary and secondary ions require a high level of control for optimal signal rate and mass resolution, the instrument is held at UHV conditions to ensure minimal mean-free path collisions beginning in the primary source region and ending in detection of mass fragments, a path of over 1 meter. Figure 2.5 provides a general overview of the TOF-SIMS technique for surface analysis. By optimizing the primary beam energy and identity it is possible to maximize the yield of secondary ions produced from a single collisional event. While TOF-SIMS is able to characterize a material on a surface by observing both atomic and molecular ions, it is possible to reduce residual damaged material by using cluster ion sources as discussed below.

2.5.1 Dynamic and Static SIMS

The original instrumental setup involved a focused monoatomic primary ion beam that was used to etch through a sample to analyze their elemental composition as a function of depth.\(^{73-75}\) This process, known as dynamic SIMS, would quickly consume the upper surface layers of the sample and would be highly destructive to both metallic and nonmetallic material surfaces. Through the work of Alfred Benninghoven and his research group, advancements in optics related to beam focusing, primary ion
Figure 2.5: Overview of the ToF-SIMS technique. In the bottom-right corner is a schematic of the primary ion colliding with a surface, thereby producing secondary ions/neutrals as a result of transferring the kinetic energy from collision. Detailed is the relative size of the fragment as related to distance from the collision epicenter. From the top-right of the image is the general scheme of the experiment, a source of primary ions (for this example, a liquid metal ion gun [LMIG]) that is rastered across a surface each square is a spot that the TOF-SIMS will analyze, and the resulting secondary ions are directed into a mass analyzer. Depending on the resolution provided by the mass analyzer, resulting spectra may either have nominal mass resolution up to high-mass resolution, although the mass resolution is a function of the primary ion beam (as either a continuous beam or a pulsed beam).
bunching, and primary ion identity, the ability of SIMS to be a surface-sensitive technique known as static SIMS was developed in the 1960’s.\textsuperscript{76} By producing tightly bunched packets of primary ions, the beam could be rastered over a given area to produce an X/Y image. As the average surface monolayer has $1 \times 10^{15}$ atoms/cm$^2$, by controlling the primary ion beam dosage to $1 \times 10^{12}$ ions/cm$^2$ (the ‘static SIMS limit’) there is a 0.1% probability that, over the entire sample area, no surface site would collide by the beam twice during the lifetime of the measurement.\textsuperscript{72} The static SIMS limit is used to guarantee that the analysis only analyzes ‘fresh’ species and not previously sampled species. Figure 2.6 shows the main differences between dynamic and static SIMS. An important distinction between the different modes of SIMS is the collection of secondary ions during the experiment, where dynamic SIMS has the collection of mass fragments from a continuous beam of primary ions and static SIMS has the collection from the result of a pulsed primary beam. For this reason, dynamic SIMS, while it has a higher sensitivity due to higher data rates, is typically limited to low mass resolution where static SIMS is capable of high mass resolution. For depth profiles where high mass resolution is required, it is possible to combine the two techniques to allow for a sputter beam (dynamic beam) to remove bulk material, and then a pulsed primary ion is able to collect a static analysis of the resulting exposed surface.

\subsection*{2.5.2 Time-of-Flight Mass Analyzer}

To achieve high mass resolution, time-of-flight (TOF) mass analyzers are commonly used for SIMS as they a suitable counterpart to the pulsed primary ion
Figure 2.6: Schematic showing difference between *dynamic* and *static* SIMS experiments. Dynamic SIMS is used for tracking of elemental signals through the bulk materials of a sample, and static SIMS (also referred as ‘imaging SIMS’) is used for analysis of just the upper 3-5 nm of a surface. Historically, the two modes were independently ran, however modern instruments are capable of combining the two modes to provide the ability to image a surface as a function of depth.
beam. TOF analyzers function by accelerating an incoming ion through a drift tube, where the ion will strike a detection device (commonly a microchannel plate).\textsuperscript{77} To ensure optimal mass resolution, the pulsing of the primary ion beam and extraction/acceleration stages of the mass analyzer must be perfectly synced.\textsuperscript{78} Additionally, the relatively small pulse width of the bunched ions must be as short as possible (less than 1 ns) to further maximize mass resolution.\textsuperscript{79} Lastly, in comparison to other mass analyzers such as those based on quadrupole and magnetic-sector, TOF mass analyzers have the highest transmission and sensitivity, a requirement for achieving data rates sufficient for static SIMS analysis.\textsuperscript{72}

2.5.3 Molecular SIMS and Current Generation TOF-SIMS

In order to analyze intact large mass-fragment and molecular species using SIMS, it is important to discuss the relationship between the disappearance cross-section and the damage cross-section. Equation 2.2 relates the secondary ion current $I_s^m$ from Eq. 2.1 to the disappearance cross-section

$$I_m = I_m^o e^{-\sigma I_p} \quad \text{(Equation 2.2)}$$

where $I_m^o$ is the initial secondary ion current ($I_m^o$ in Eq. 2.1), $\sigma$ is the disappearance cross-section, and $I_p$ the primary ion flux to predict the final secondary ion current $I_m$.\textsuperscript{72} For molecular species, the damage cross-section is related to the disappearance cross-section as induced damage from the primary ion beam, as damaged material is left on the surface during monatomic primary ion beam analysis. If it is possible for all of the damaged material to be removed, the value of damage cross-section is essentially insignificant in regards with the disappearance cross-section.
The current generation of TOF-SIMS instruments involves the use of “cluster” primary ion sources, typically in the form of $M_n^z$, where $M$ is the identity of the ion, $n$ is the number of atoms per cluster, and $z$ is the charge of the cluster. This new technology, combined with modern TOF electronics and pulsing techniques has been labeled molecular SIMS as the analysis of intact molecular species is possible with cluster-based sources with a minimal damage cross-section. A common example is $\text{Bi}_3^+$ which is a liquid metal cluster ion consisting of a single charge being placed on three bismuth atoms. The development of cluster ion sources has allowed the analysis of “soft” materials such as polymeric and biologically relevant surfaces. In general, by having a primary ion source with lower eV/atom than traditional monatomic beams, the resulting collision imparts more energy to the upper surface, leading to higher desorption rates and larger intact secondary ions. The available cluster sources for TOF-SIMS primary beams range from liquid metal polyatomic ions to large gaseous clusters ($\text{Ar}_{500-2000}^+$), and each source has its own advantages and limitation for sputter yield and spatial resolution, among others. Liquid metal ion guns (LMIG) comprise the most common primary ion beam sources for current generation TOF-SIMS experiments. Among the various beams, bismuth clusters currently have the overall highest combination of sputter yield, spatial resolution, and high mass desorption, making it the preferred primary ion beam for current generation TOF-SIMS instruments. By combining depth profile experiments, imaging capabilities and high-resolution mass information, TOF-SIMS has become a very powerful analytical technique for the analysis of surface, interfacial, and bulk information.
2.5.4 TOF-SIMS Data Processing

Modern TOF-SIMS instrumentation provides highly complex, large datasets that can be processed using simpler univariate methods or more detailed multivariate techniques. Spectral processing begins with calibration of the high-mass resolution spectra using ubiquitous mass fragments found on samples exposed to ambient atmosphere. Table 2.1 lists the preferred mass fragments used for calibration in both positive-ion mode and negative-ion mode. As the number of calibration peaks increases, the greater the accuracy of the calibration to compare calculated exact mass to observed exact mass of a mass fragment; in practice this accuracy is at or below 3.0 mAMU. Last, the spectra are normalized to minimize any matrix effects that occur during analysis. A typical normalization is by use of a reference peak or by the total ion intensity.

After the initial processing, TOF-SIMS data can be processed in a large multitude of methodologies, including univariate and multivariate methods on both spectral and image data. A common first approach is to identify mass fragments of interest using calculated exact mass and isotopic ratio information. After the analyte peaks are identified, the areas and ratios of the various peaks can be compared across a sample set, although care must be made to account for all matrix effects inherent to the sample system. If a sample has a defined surface structure or pattern, these analyte fragments can be used to reconstruct images based on chemical identity. These images can be further processed through normalization to a reference image (i.e. total ion image), summed, or have X/Y linescans performed to identify unique areas present on the sample surface. Lastly, assigned analyte peaks can be used to reconstruct depth
Table 2.1: List of mass fragments commonly used for calibration of TOF-SIMS data in both positive-ion and negative-ion mode. The ‘Exact m/z’ column are calculated values for each mass fragment.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Nominal m/z</th>
<th>Exact m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Mode</td>
<td>Negative Mode</td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>55</td>
<td>55.0549521</td>
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<td>91.0549521</td>
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</table>
profiles as either a line profile or a 3D image given the quality and data rate collected of the analyzed sample.

TOF-SIMS data is limited in the multivariate analysis techniques that can be applied, as matrix effects obscure some quantification aspects relevant to the intended results. However, techniques such as principal components analysis (PCA), multivariate curve resolution (MCR), and hierarchical clustering methods can be applied to highlight variance within a TOF-SIMS dataset, albeit from a qualitative standpoint. TOF-SIMS datasets should be thoroughly preprocessed to account for matrix effects when possible, as well as being placed through time-warping algorithms to ensure a high level of peak precision across the entire dataset.

2.6 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), originally named electron spectroscopy for chemical analysis (ESCA) by Kai Siegbahn in 1954, is a surface analytical technique that is useful in the characterization of elemental and oxidative state information pertaining to a sample surface. Currently, the common setup for XPS includes either a monochromatic aluminum X-ray source or non-monochromatic magnesium and/or aluminum X-ray sources and the photoelectrons are resolved with a hemispherical analyzer. Because of the relatively long path of travel of the incoming X-rays and the energy resolution required for the emitted photoelectrons, XPS is usually conducted in an UHV environment, although ambient-pressure XPS experiments have been conducted. The work herein was conducted in UHV regimes.
2.6.1 XPS Instrumental Details

XPS works by having a beam of incident X-rays directed towards a sample where both valence and core-shell electron orbitals are probed. As described by the photoelectric effect, emitted photoelectrons are then analyzed for their kinetic energy. Figure 4 shows a useful schematic for the typical setup of an XPS experiment. A source of X-rays is directed towards a sample, and the emitted photoelectrons are collected in a hemispherical analyzer. Equation 2.3 relates the incident X-rays and detected photoelectrons from an analysis

\[ BE = hν - KE - \phi_{sp} \]  

(Equation 2.3)

that relates the difference of the energy of the x-ray source \( (hν) \) and the work function of the instrument \( (\phi_{sp}) \) to the measured kinetic energy \( (KE) \) of the emitted photoelectrons, which calculates the binding energy \( (BE) \) of the probed electron orbitals.

The most common x-ray generation technique is through the use of an electron gun (such as one based on W or LaB_6) that is directed towards an anode coated in the desired material, such as aluminum for 1486.6 eV X-rays (Al Kα X-rays). These sources provide X-ray spot sizes from 500 µm to <50 µm.\(^{85,86}\) The emitted fluorescence X-rays are sent directly towards the sample (non-monochromatic) or into a crystal monochromater before being directed towards the sample. The photoelectrons emitted from the sample are sent through a series of optical lenses to focus the photoelectrons into an energy-resolving analyzer and finally into a detector. A hemispherical (dispersive) analyzer as shown in Figure 2.7 is preferred as the transmission and
Figure 2.7: General overview of the XPS experimental setup. A beam of x-rays is directed towards a surface that will probe the valence and inner-shell electron orbitals of the atoms comprising that sample (detailed in the bottom-right). The emitted photoelectrons are focused into a hemispherical analyzer for detection. Usually, any photoelectron lines seen in the survey scan are then used for high-resolution scans of the quantitative peak of that element. In this schematic, the “Ar⁺” source refers to a sputter source used for a depth profile experiment, however this source is not unique to XPS instrumentation.
resolution provided by the curvature of concentric hemispheres is sufficient for resolving the emitted photoelectrons.\textsuperscript{87} Generally, the larger the radius of the hemisphere the higher the possible resolution of the spectrometer. After dispersive resolution in the hemispherical analyzer, an electron-multiplying detector such as a channel plate detects the photoelectrons, whether as a one- or two-dimensional detector.\textsuperscript{88} Lastly, since the loss of emitted photoelectrons produce a buildup of positive-charge states on the sample surface, charge compensation is required for insulting and semi-conductive samples.

With control over the electronics of the analyzer it is possible to adjust both the pass energy and eV resolution of the spectrometer. For initial analysis, a survey scan is used to detect all elemental species on a sample surface from a binding energy of 0 eV up to the kinetic energy (KE) of the X-ray source. This scan is done at higher pass energies to increase data rate and typically eV increments for a quick resolution. After identifying all elements from the survey scan, the analyzer can be setup to collect high resolution scans. High resolutions scans are taken at the quantification peak for the elements found in the survey scan. Low pass energies are used to increase spectral quality and typically 0.1 eV or lower energy steps for maximum energy resolution. The number of high resolution scans taken per region can change depending on the preferred signal-to-noise ratio for the region.

\textbf{2.6.2 XPS Chemical Shift}

While elemental analysis was the intended use of ESCA and certainly a useful characterization for a sample surface, the added benefit of XPS is the ability to probe
the oxidation state of the elements present on a surface. Because the binding energy of a valence or core-shell electron has a slight, but significant energy shift based on local chemical environment due to adjacent bonding atoms and electronegativity differences, the emitted photoelectrons have a KE shift that is resolvable in the hemispherical analyzer.\textsuperscript{82} The ability of XPS to produce high-resolution scans that contain information about all oxidation states of a material provides an ideal complement to the atomic and molecular information provided by TOF-SIMS.

Since the technique involves the direct measurement of emitted photoelectrons, the peaks seen in XPS spectra are inherently quantitative given the correct relative sensitivity factors for the incident angle of the incoming X-rays, transmission function, and provided every element present in sufficient concentration is accounted for.\textsuperscript{89,90} While there is ongoing discussion in the literature on the methods of curve-fitting of XPS spectra, a common theme can be found for the analysis of soft materials with XPS. If the materials are well known and if their elemental ratios carefully controlled (such as in a prepared polymer), the various oxidation states per functional group can be determined and individual chemical shifts can be assigned to these oxidation states. If the identity of a material is not well known (such as a complex biological material that is commonly seen in the study of cultural heritage materials), an \textit{ad hoc} approach to chemical speciation is more prevalent. As it may not be possible to know the exact oxidative state composition of a sample, it is useful to speciate the sample based on the observed shifts (such as by assigning functional groups) using the observed elemental ratios (such as carbon to nitrogen) to determine if any overlapping shifts are present. This method of speciation is particularly useful in the analysis of degradation
as any change in the high-resolution scans is observed as a loss/gain of a functional group that can be correlated with TOF-SIMS analysis for exact molecular identification.

2.7 Gas Cluster Ion Beam (GCIB)

A major advance in the analysis of soft materials is through the development of gas cluster ion beams (GCIB) for use as a sputter beam. Traditionally, a depth profile is conducted by using a sputter beam comprised of a metal ion (similar to a dynamic SIMS experiment), a monoatomic argon ion, or by an ionized oxygen beam. While these sputter beams have good performance in both control and etch rate for hard materials such as metals or metal oxides, they quickly degrade soft materials due to their high impact energy per atom. A common feature of soft material sputtering with a monoatomic beam is the removal of all higher oxidized functionalities present, effectively reducing the soft material to graphite. Through the use of current gas cluster ion beams (GCIB), soft material sputtering is possible with no evidence of beam-induced degradation. Figure 2.8 is a schematic showing the use of GCIB (or other sputtering beam) for the use of analyzing a buried interface, in this example the change from the red region into the blue region.

When an ion strikes a surface, the resulting penetration depth and collisional cascade are a function of initial beam energy, the ion size, and the incident angle. The further the penetration depth of the directed ion, typically an increase in degradation of a sample is observed. There are several measures for the ability of a sputter beam to remove secondary fragments for a depth profile as discussed in section 2.5. The
Figure 2.8: General overview of the information gained from a profile through a thin film of material with a degraded surface (red) and an unaltered bulk (blue). The use of a GCIB allows for the removal of organic material without any change in chemical composition of the remaining surface, therefore allowing the ability to track chemical components as a function of degree of degradation.
sputter yield indicates the number of fragments, or volume, removed from a surface after a single ion collision. Additionally, the sputter threshold indicates the amount of energy required to remove a secondary fragment from a surface. The penetration depth is a measure of how far the sputter ion travels into a sample. These factors are all dependent on the chemical composition of a sample and the composition of the sputter beam.\(^72\)

A recently developed source is argon clusters (Ar\(_n\)). Ar\(_n\) clusters have shown to be one of the most effective cluster sources for overall reduced degradation of soft materials upon sputtering.\(^95,96\) These clusters can be varied in size where \(n = 60\)-3000 and acceleration energy. The cluster size is selected via a separate mass analyzer prior to incidence with the sample surface. Generally the argon clusters have a lower sputter yield than the clusters or bismuth, but a constant sputter rate regardless of cluster size, and lower sample damage.\(^97\) Large argon clusters have the benefit of very low kinetic energy per atom, allowing for the removal of intact molecular species, such as insulin and cytochrome C.\(^98\) Argon clusters have shown the ability to depth profile and also create secondary fragments of pure amino acids (along with their dimers/trimers/multimers) with almost no beam damage.\(^99,100\) Argon cluster sources have been shown to have a large role in the surface and interface analysis of complex soft materials, such as polymers and biological materials.\(^101,102\) Cluster sources have been widely sold commercially and have been used in many experimental platforms to successfully depth profile through soft materials.

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REFERENCES


75. P. Williams; *Surface Science* **1979**, *90*, 588.


Chapter 3

INITIAL STUDY OF HISTORIC PAINT MATERIALS

3.1 Introductory Remarks

The first year of research was conducted to establish the feasibility of TOF-SIMS for the analysis of historic paint materials that previous literature had identified as problematic. This chapter covers two main types of paint materials; i) lead-soaps and ii) egg-oil emulsions. Additionally, a comparison between the use of FTIR and biological staining methods to identify oil- and egg-based binding media is discussed. This initial study was beneficial in that the preparation methods and results were used as a framework for historical cross-section analysis, as well as to provide a small library of typically observed mass fragments related to egg- and oil-based binding media. Last, a brief discussion of the use of principal components analysis to aid in the observation of egg-oil emulsions is included.

3.2 Introduction

Over the past decade, time-of-flight secondary ion mass spectrometry (TOF-SIMS) has shown great potential as a characterization tool used in the field of cultural heritage.\textsuperscript{103-105} There are three main advantages to using TOF-SIMS on samples collected from artworks or culturally significant objects. First, the instrument can be used to simultaneously collect chemical information from both inorganic and organic
Inorganic species originate from pigments and inert fillers or extenders while the organic components stem from a much wider range of materials.\textsuperscript{109-111} Secondly, TOF-SIMS is capable of performing high-resolution chemical imaging as the primary ion beam can be focused to 1-2 \( \mu \)m. This enables the simultaneous identification of both organic and inorganic species present in discrete areas within a sample, specifically those located in individual layers or as distinct particles. Finally, like LA-ICP-MS, TOF-SIMS is one of the few mass spectrometric techniques that allows the user to directly analyze the surface of the solid sample. The sample therefore is not subjected to an extraction protocol prior to analysis or to the addition of a matrix.

Paint samples collected from complex and/or multi-layered painted surfaces (\textit{e.g.} easel paintings, wall murals, polychrome sculpture) can be challenging to fully characterize. Easel paintings executed before the 20\textsuperscript{th} century typically contain binders consisting of collagen (animal glue), egg yolk (egg tempera), drying oils (linseed, walnut, or poppyseed), and natural resins (\textit{e.g.} dammar, mastic), among other organic materials.\textsuperscript{110,111} It can be difficult to confirm whether these materials, sometimes applied in layers only a few microns thick, exist as mixtures, emulsions, glazes, or surface coatings within these complex multi-layered paint systems. Even ATR-FTIR mapping allows the characterization of only those layers or layer components that are spectrally active within the mid-infrared region.\textsuperscript{112,113} Further complications also arise due to a) insufficient sample size b) the presence of non-original materials from previous restoration campaigns, and c) the interference of pigments when attempting
to identify organic components. Many of these challenges can be overcome with the application of SIMS techniques to the study of paint cross-sections.

Over the past decade, new developments in TOF-SIMS technology has improved total ion detection and greater overall spatial resolution for the analysis of biological materials. Previous studies have also published molecular ion maps corresponding to compounds of particular interest found in paint cross-sectional samples. Not only does this assist with identifying the materials and techniques used by the artist, but imaging can also identify compounds associated with pigment or binder alteration or non-original materials that may be present from previous restoration campaigns.

Only a handful of studies focusing on the analysis of inorganic and organic components from historically representative reference paint samples using TOF-SIMS have been published. By preparing paint samples that contain historically accurate materials (e.g. historic pigments, animal glue, etc.) and subjecting them to short-term and long-term aging we can gain better insight into the current capabilities and limitations of the TOF-SIMS technique before attempting to analyze samples from artworks that contain unidentified components. This chapter outlines two experiments using paint reference samples that demonstrate the ability of TOF-SIMS to overcome challenging analytical obstacles associated with the identification of both inorganic and organic art materials.
The first study focuses on the analysis of lead soaps found in a series of artificially aged paints bound in linseed oil. Metal soaps (a complex between a metal cation and a deprotonated fatty acid) have been identified in a number of easel paintings using TOF-SIMS and other analytical techniques.\textsuperscript{103,108} The mobility of these soaps are associated with film stability and aesthetic problems including the formation of agglomerates that erupt from the surface of the oil painting leaving spherical voids in the paint film.\textsuperscript{108,118,129-131} A considerable number of studies have focused on the identification and formation of metal soaps within paint films.\textsuperscript{103,107, 108,117-127} While metal soaps have been found in films containing lead, zinc, copper, and cobalt, the precise mechanisms involved in the formation, propagation, and agglomeration of these complexes are not entirely understood. Previous studies have led to a better understanding of pigment-binder interactions.\textsuperscript{126-139} Extreme environmental conditions (i.e. high temperature and humidity) have been linked to the increased formation of metal soaps as well as the general reactivity of the pigments.\textsuperscript{130,135,141} The presence of metal soaps can lead to an increased transparency of the paint and can cause weakening of the paint as well as the development of unsightly aggregates that rise to the painting’s surface.\textsuperscript{127-129, 133,142,143} More research is needed to determine the precise mechanisms involved in metal soap formation in order to address questions and concerns posed by art conservators.

The second study focuses on the identification of markers associated with egg yolk, animal glue protein, and a drying oil (linseed) in a number of references samples that have been subjected to short-term artificial aging. One of the earliest uses of TOF-SIMS technology for paint cross-sectional analysis was the attempt to determine
whether Rogier van der Weyden’s *Descent from the Cross* was executed using oil paint over an egg tempera underpainting. While the authors found no protein markers, they did see markers for phosphate and cholesterol in a reference paint sample of lead white egg tempera.

In recent years TOF-SIMS has been increasingly used in protein studies to identify amino acid fragments. Drying oils (linseed, walnut, or poppyseed oil) and egg yolk (the primary binder for egg tempera paints) both contain similar types of fatty and carboxylic acids, namely palmitic, stearic, azelaic, suberic, and sebacic acids. Chromatographic studies have routinely used these organic components as chemical markers to identify types of drying oils and to determine whether both egg and oil are present as binders on a single painting. The presence of egg protein can be further confirmed by identifying a number of amino acids including leucine, isoleucine, proline, valine, alanine, lysine, and glycine while animal glue proteins additionally contain hydroxyproline. Table 3.1 lists the particular amino acids that have been shown to be fairly stable when subjected to artificial aging, making them reliable markers for determining the presence of proteinaceous material on 500 year old works of art.

Recent studies have shown the problems associated with the previously described methods of interpretation for GC-MS. There is no current standard operating procedure for the analysis of aged paint samples using chromatographic techniques, and more research is greatly needed to assess and compare the efficacy of protocols.
<table>
<thead>
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<th>Species (Mode)</th>
<th>Formula</th>
<th>m/z</th>
<th>Egg Yolk (Rel. Percentages)</th>
<th>Animal Glue (Rel. Percentages)</th>
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<td>Glycine, GLY (+)</td>
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<td>Alanine, ALA (+)</td>
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<td>Valine, VAL (+)</td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
<td>C₅H₁ₑN</td>
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<td></td>
<td></td>
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<tr>
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<td>12.1%</td>
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<td>Palmitic Acid, PA (-)</td>
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<td>Stearic Acid, SA (-)</td>
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<td>--</td>
</tr>
<tr>
<td>Generic Protein (-)</td>
<td>CN</td>
<td>26.003</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 3.1: Specific ion fragments observed during TOF-SIMS imaging and the expected relative percentages as reported in the literature for aged egg yolk and aged animal glue (rabbit). Percentages are given as mole percent of stable amino acids as determined by remaining total protein content after artificial aging at 50°C and 50% relative humidity for 500 hours. Amino acid mass fragments are compiled using similar TOF-SIMS analysis parameters.
used for sample preparation and various derivatizing/silylization reagents. Furthermore, detection limits are a critical factor to consider when dealing with samples that are on the order of 0.5-1 mg. The reliance on the presence and quantity of certain fatty acids and amino acids is problematic as complex mixtures can lead to misinterpretation and reactive pigments can alter overall yields of such markers.\textsuperscript{123,176-179} A handful of chromatographic studies have turned to monolithic sorbent tip technology in an attempt to avoid unwanted pigment interference. More studies are greatly needed to demonstrate the success of this technology for the characterization of binding media mixtures when used in conjunction with other protocols and with a wide range of aged paint samples.\textsuperscript{180-182} In addition, the various historical and modern methods of refining oils such as water-washing, sun bleaching, acid and alkali treatment, and heating can alter fatty acid ratios greatly complicating data interpretation.\textsuperscript{145}

Previous studies using TOF-SIMS to image cross-sections have proven relatively unsuccessful at detecting markers for proteins, specifically proteins associated with egg-based materials.\textsuperscript{103,104,108,125} However, more recent techniques have been used to identify blood on the surface of African sculptures and a protein-containing ground in a sample collected from a painting by Rembrandt van Rijn using TOF-SIMS technology.\textsuperscript{106,133} Finally, chemometrics can be used successfully to extract relevant information from the data set. Chemometrics have recently been used in the analysis of organic media of cultural heritage in an effort to overcome some of these challenges and aid in final data interpretation.\textsuperscript{180-184} Principal components analysis is helpful in both confirming the presence of certain molecular species and their relative amounts.
3.3 Experimental

This section covers the preparation of naturally- and artificially-aged reference paint samples for TOF-SIMS, FTIR, optical imaging, and biological staining, as well as instrumental details for analysis of these materials. The lead soap samples were naturally aged while the egg-oil emulsion samples were artificially aged.

3.3.1 Paint Reference Samples

Paint samples used for the analysis and identification of lead soaps were created at the Smithsonian’s Museum Conservation Institute under the direction of Marion Mecklenburg and Dr. Stuart Croll. Pigments and cold-pressed Swedish linseed oil were purchased from Kremer Pigments, Inc. and mixed with cold-pressed linseed. The Naples yellow paint was prepared in May 1992. The lead white 90 and 99 paints were created in February 1990 and November 1999, respectively. All paint outs were prepared on polyester film and were stored at ambient humidity and temperature levels. Lead white 5 was prepared on a glass slide at the National Gallery of Art in Washington, DC in January 2008 (the lead white was obtained from Rublev/Natural Pigments) and was stored at ambient humidity and temperature levels for comparison of a shorter-term natural aged oil sample.

Paint samples used for the analysis and identification of protein and oil markers were created at the National Gallery of Art in Washington, DC in January 2008. Yellow ochre (Natural Sienna Monte Amiata), calcium sulfate (Terra Alba-Natural Selenite) and Swedish cold-pressed linseed oil were purchased from Kremer Pigments, Inc.
azurite (fine grade), vermilion (dry process), and lead white (prepared using the Dutch stack method) were obtained from Rublev/Natural Pigments. Egg yolks were collected from USDA organic brown eggs from free-range hens. Collagen was extracted by boiling parchment scraps (from skins of calf, sheep, and goat) purchased from Talas. All paints were subjected to short-term aging at the National Gallery of Art using the Atlas Ci4000 Weather-ometer, equipped with a xenon light source (75,000 lux) using the ASTM Gamblin oil paint parameters (45% RH and 25º C for 400 hours). For the purposes of this experiment, a series of egg-oil “gradients” were created using historically representative pigments like those available to 15th century artists (azurite, vermilion, lead white, and yellow ochre) and painted out onto a panel coated with several layers of traditionally prepared gesso (collagen glue mixed with calcium sulfate dihydrate). Paint references ranged from 100% egg yolk binder to 100% cold-pressed linseed oil, with step-wise mixtures of egg and oil to serve as tempera grassa reference samples, as diagramed in Figure 3.1. Prior to analysis, each sample was embedded in a polyester resin and allowed to fully cure before preparation. It is crucial to note that each pigment has different physical and chemical properties and will inherently require a slightly different amount of binding medium to create a stable paint film. Cold-pressed linseed oil was chosen as this process subjects the flax seeds to the least amount of heat and chemical refinement during oil extraction. More is known about the use of heat-bodied and refined oils in Northern Europe, however, it remains unclear the extent to which heat processing was used in the 15th century Italy.¹⁵⁶
Figure 3.1: Schematic of egg-oil paint gradient prepared for cross-sectional analysis and FTIR analysis. A total of four gradients were prepared using vermilion, lead white, azurite, and yellow ochre. All samples were painted atop a traditional gypsum-glue ground.
3.3.2 Cross-Sectional Microscopy

All cross-sections 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 using a Canon EOS-1 Ds Mark II Digital camera in conjunction with EOS Canon Utility and Capture Software. A “D” filter cube was used to examine the cross-sections under ultraviolet illumination (excitation range: UV & blue BP 355-425 - excitation filter/ RKP455 - beam-splitting mirror/ LP 460 - suppression filter). Staining reactions using the Alexa Fluor 488 stain were observed using and I 2/3 cube (excitation range: blue BP 450-490 - excitation filter/ RKP510 - beam-splitting mirror/ LP 515 - suppression filter).

Alexa Fluor 488 succinimide (Invitrogen) is prepared as a 0.02% aqueous solution at a pH of 9 (0.05M borate) with a 5% DMF addition. The stain is typically left on the surface of a cross-section for up to 3 minutes after which time the excess stain is removed. A positive reaction color for the presence of proteins is green or yellowish-green when viewed with the appropriate filter cube (excitation 450-490 nm and a barrier filter between 515-520 nm). Amido Black is a pre-made aqueous solution (Staining solution, 2X concentrate, Sigma: A-8181) that dilutes to 500 mL (in water) and consists of approx. 25% (v/v) isopropanol and 10% (v/v) acetic acid. The stain is typically left on sample for approximately 5 minutes, after which the excess stain solution is blotted and the surface of the sample rinsed with 1% (v/v) acetic acid. A positive reaction color for proteins is a dark blue when viewed under normal visible light.
3.3.3 Sample Surface Preparation

One of the challenges in preparing paint cross-sections for analysis is the effect of sample smearing and/or contamination of the sample surface. Since TOF-SIMS is a surface sensitive technique, every effect of sample preparation will be observed during analysis. Additionally, any oils resulting from sample handling and plastic residue from storage will be noticed in the TOF-SIMS spectra if left unprepared. To reduce these artifacts, microtomy is the preferred method of preparation for the current analysis as noted in recent publications. A detailed description of this preparation technique is given in Chapter 4 of this dissertation, however a summary is provided here. First, the embedding resin must be trimmed to remove all excess material. Next, a trapezoid shape is cut onto the sample surface to lessen the mechanical stress on the sample during cutting. A series of cuts is then made by a trimming knife followed by a diamond ultramictromy knife (Delaware Diamond Knives, Wilmington, DE) to expose a “fresh” surface for analysis in the TOF-SIMS. Since the ability to consistently remove intact sample thin-sections is highly dependent on the friability of the cut section, analysis was performed on the remaining sample block-face.

3.3.4 Instrumentation

Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet Nexus 670 optical bench equipped with a continuum microscope (128 scans at 4 cm$^{-1}$ resolution; the spectral range is 4000-650 cm$^{-1}$). The samples were compressed between two windows of a diamond cell (Spectra Tech) and compared to spectra from
the IRUG database (Infrared and Raman Users Group). The TOF-SIMS instrument used for analysis was a TOFSIMS IV (ION-TOF, GmbH) equipped with a bismuth primary ion beam. Mass spectra and images were taken in the “high-current bunched” mode utilizing 25 keV Bi$_3^+$ primary ion clusters at 0.27 pA target current. A low-energy electron flood gun was used to compensate the  insulting property of the casting resin surrounding the sample. The TOF analyzer had an extraction voltage of 2 kV and post-acceleration of 10 kV. All spectra were acquired to the ‘static SIMS limit’ (1x10$^{12}$ ions/cm$^2$) to minimize sample degradation due to beam effects. Positive mode spectra were calibrated with the following ions: H$^+$, H$_2^+$, H$_3^+$, C$^+$, CH$^+$, CH$_2^+$, CH$_3^+$, C$_2$H$_3^+$, C$_3$H$_5^+$, C$_4$H$_7^+$, C$_5$H$_5^+$, C$_6$H$_5^+$, and C$_7$H$_7^+$. Negative mode spectra were calibrated with the following ions: H$^−$, H$_2^−$, C$^−$, CH$^−$, CH$_2^−$, CH$_3^−$, C$_2^−$, C$_2$H$^−$, C$_3^−$, C$_4^−$, C$_5^−$, C$_6^−$, C$_7^−$, and C$_8^−$. All spectral reconstruction was performed on ION-TOF software including peak area assignments, and all principal components analysis was done in MATLAB using the PLS Toolbox.

3.4 Lead Soaps TOF-SIMS Results

The primary goal of this study was to compare the relative amount of lead soaps and other elemental/molecular species in a series of naturally aged paint films containing the lead pigments lead white, 2 PbCO$_3$.Pb(OH)$_2$, and Naples yellow, Pb$_3$(SbO$_4$)$_2$. While TOF-SIMS is a technique that is highly sensitive to matrix effects that can alter ion yields, it may be possible to observe trends with samples that are prepared and stored in similar conditions. Particular attention was devoted to the Naples yellow paint film since little is known about its role in the creation of metal soaps. TOF-SIMS has been used previously to compare both new and artificially aged paints containing
Naples yellow, however the pigment used in a recent study was found to contain zinc oxide and lead chloride components not found in the historical product. Four paints containing cold-pressed linseed oil and the following pigments were analyzed (as discussed in section 1.3.1): A) lead white or basic lead carbonate (2 PbCO₃·Pb(OH)₂), naturally aged 23 years; B) pure Naples yellow or lead(II) antimonate (Pb₃(SbO₄)₂), naturally aged 21 years; C) lead white, naturally aged 14 years and D) lead white, naturally aged 5 years. Table 3.2 summarizes the useful mass fragments and their assignments for the analysis of fatty acids, whether unbound (free), glycerols, or metal-bound.

3.4.1 Negative-Ion Mode TOF-SIMS Analysis of Lead Soaps

Negative-ion mode is useful to obtain information relating to free fatty acids and free diacids within a paint sample. The youngest lead-white paint film (D) and the Naples yellow film (C) appear to contain the higher amounts of free palmitic and stearic acid as compared to the older lead white paint films. Oleic acid as well as its hydroxy-derivative (m/z 295) could also be detected in all four samples, although in much smaller quantities. The absence of oleic acid in paint samples is generally linked with extremely aged films; therefore, it is not surprising that it is still present to a certain extent in these relatively young samples. Previous studies using TOF-SIMS have had difficulties detecting free diacids or dicarboxylic acids, however suberic, azelaic, and sebacic acids were observed in all four paint films (Figure 3.2). Interestingly,
Table 3.2: Summary of notable ions (e.g., fatty acids, diacids, and lead-soaps) and their associated exact m/z values found in samples A through D (monoacylglycerols are denoted by MAG). Peaks are assigned both by their observed m/z value and also by isotopic ratios.

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<th>Species (mode)</th>
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<th>m/z</th>
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<td>Lead Oxides (-)</td>
<td>PbO, Pb_{2}O, Pb_{3}O_{2}</td>
<td>223.972, 431.948, 655.920</td>
</tr>
<tr>
<td>Lead-Bound Hydroxides (-)</td>
<td>PbOH, Pb_{2}O_{2}H, Pb_{3}O_{3}H</td>
<td>224.979, 448.951, 672.923</td>
</tr>
<tr>
<td>Lead-Bound Palmitate (+)</td>
<td>PbC_{16}H_{31}O_{2}</td>
<td>463.210</td>
</tr>
<tr>
<td>Lead-Bound Stearate (+)</td>
<td>PbC_{18}H_{35}O_{2}</td>
<td>491.240</td>
</tr>
<tr>
<td>Lead-Bound Acylum Ion of Azelaic Acid (+)</td>
<td>PbC_{9}H_{13}O_{3}</td>
<td>377.063</td>
</tr>
<tr>
<td>Lead Oxide-Bound Palmitate (+)</td>
<td>Pb_{2}C_{16}H_{31}O_{3}</td>
<td>687.181</td>
</tr>
<tr>
<td>Lead Oxide-Bound Stearate (+)</td>
<td>Pb_{2}C_{18}H_{35}O_{3}</td>
<td>715.212</td>
</tr>
</tbody>
</table>
the Naples yellow paint (C) produced the highest amount of free diacids, with the youngest paint film (D, containing basic lead white) producing the lowest amount. In all four samples, peaks corresponding to the aliphatic moieties of the free fatty acids were also detected (m/z 99, 113, 127, 141, 155, 169, 183, 197) while shorter fatty acids chains were observed in smaller amounts (m/z 143, 157, 171). Peaks associated with monoacylglycerols of palmitic and stearic acids (m/z 311, 339) could be observed in samples A-C.

Overall these observations suggest that the amount of free fatty acids present in lead white paints diminishes over time. This is most likely explained by a) the relative increase in the amount of metal soaps (corroborating the results obtained using positive mode) as the paint films continue to oxidize and age in the presence of the reactive lead(II) carbonate and/or b) the migration and subsequent loss of fatty acids near the surface of the film. Previous research has also shown that oxidative and hydrolytic reactions are linked to higher amounts of diacids in aged paint films. This trend is also observed in the lead white containing paints, with youngest lead-white paint (D) containing the lowest amount of suberic, azelaic, and sebacic acids. Conversely, the higher amount of dicarboxylic acids in the oldest lead white paint (A) can also be correlated to a higher degree of oxidation and saponification. It is interesting to note that the Naples yellow paint (C) appears to have a significantly higher amount of free fatty acids and diacids. One explanation would be a lower reactivity of the Naples yellow pigment compared to lead white. The observed reactivity difference could be due to thermodynamic or kinetic factors. The samples
Figure 3.2: Fatty acid components of the naturally aged oil-based samples A-D. Overlays of unbound (free) major components of pigmented linseed oil are shown on the top row. Specific molecular structures of the [M]- peaks are given in Table 3.2. The [M+2] peak for oleic acid is not shown as the [M]- peak of stearic acid interferes with identification. Overlays of the diacid components of pigmented linseed oil are shown on the bottom row. The peak below nominal mass 187.0 in sample C of the azelaic acid region is not a contributor to the [M]- peak intensity.
studied are insufficient to probe the kinetics of $\text{Pb}_3(\text{SbO}_4)_2$ reactivity versus that of $2 \text{PbCO}_3\cdot\text{Pb(OH)}_2$ as the bond dissociation energies are not available for the relevant moieties at this time.\textsuperscript{145,146} The irreversible release of carbon dioxide upon degradation of lead white may be a driving force for the reactivity of this pigment with free fatty acids as compared to lead antimonate. As no depth-profiling was performed during this experiment, the relative amounts of the ions are only representative of the compounds present at the surface of the paint films.

3.4.2 Positive-Ion Mode TOF-SIMS Analysis of Lead Soaps

Positive-ion mode is more suitable at detecting metal-soaps and related cationic species in paint films. Figure 3.3 provides a summary of results given as TOF-SIMS spectra overlays for positive-ion mode analysis of the oil films A-D. For samples A-D, isotopic ratio patterns of lead (m/z 207) were used to confirm the presence of lead pigment in the naturally aged paints, as well as related lead oxides/hydroxides (see Table 3.2). Lead palmitate (m/z 463) and lead stearate (m/z 491) were identified in samples A and B while negligible amounts were found in samples C and D (Figure 3.3 top row). Analogous trends were observed with the lead-bound acylium ion for azelaic acid (m/z 375) as shown in Figure 3.3. Lead oxide ($\text{Pb}_2\text{O}$) -bound palmitate and stearate (m/z 685, 714) were visible as shown in Figure 3.3, bottom row. Peaks related to monoacylglycerols associated with palmitic and stearic acids were found to be absent in the youngest paint film (D) and in moderate amounts in samples B and C while significant peaks were observed in the Naples yellow paint (C).
Figure 3.3: Summary of positive-ion TOF-SIMS results for naturally aged oil-bound paint films. Overlays of lead-bound fatty acid and diacid components of linseed oil are shown in the top row. Exact masses of [M]+ species are in Table 3.2. Due to low signal, the spectra have been smoothed using 2nd order polynomial Savitzky-Golay smoothing. Both Samples B and D have minimal to no signal present for azelate. Sample D also has no signal present in the palmitate and stearate regions. Overlays of Pb$_2$O bound to stearic and palmitic acid are shown in the bottom row. Samples C and D have been omitted as they have no identifiable doubly bound species. The Pb$_2$O-palmitate species shows an example of the isotope distribution resulting from an ion containing two lead atoms. Both regions have been smoothed using 2nd order polynomial Savitzky-Golay smoothing.
The increase in the amount of lead-bound species in the older paint films (samples A and B) suggests an overall increase in metal-soap formation over time even when stored at ambient conditions. These observations correspond with results obtained from previous studies using TOF-SIMS, DTMS, and other analytical techniques such as FTIR imaging.\textsuperscript{123,126,138,145} Older paint films also contained a higher amount of free lead and lead oxides/hydroxides, most likely related to the gradual disassociation of \( \text{Pb}^{2+} \) from the lead white pigment. The relative amount of monoacylglycerols exhibited expected trends when comparing the three lead white containing paints (with sample A containing the highest amount) as their presence indicates that the film has undergone a higher degree of oxidation and hydrolysis. Interestingly, the Naples yellow sample (C) contained a greater amount of these compounds than any of the lead white samples. Again, this is most likely explained by the stability of the lead (II) antimonate pigment as compared with that of the more reactive lead (II) carbonate.

3.5 \textit{Tempera Grassa} Egg-Oil Emulsion Comparison

Paintings that contain both egg and oil as mixed binders can be particularly challenging to analyze. These paints were used in 15\textsuperscript{th} century Italy and more recently in the tempera revivalist movement in the late 19\textsuperscript{th}/early 20\textsuperscript{th} century.\textsuperscript{146-150} The 15\textsuperscript{th} century was a transitional period in Italy when artists were beginning to move away from traditional egg tempera paints and incorporate drying oils into their workshop practice. These mixtures can manifest as true emulsions (\textit{tempera grassa}) or as layered systems (oil glazes atop egg tempera).\textsuperscript{151} Some of the more common analytical techniques that have been used to identify complex paint systems like egg-oil paints include cross-section (biological and fluorochrome) staining, Fourier transform
infrared spectroscopy (FTIR) and an abundance of chromatographic methods (e.g. GC-MS, HPLC). \(^{152-155}\)

Reference gradients were prepared by combining historically accurate pigments (lead white, yellow ochre, azurite, vermilion) with a binding medium (ranging from 100% egg yolk to 100% linseed oil; see Figure 3.1) and applying the paints over a traditional gesso ground. Samples were collected from the reference gradients and subjected to cross-section biological and fluorochrome staining and FTIR analysis for comparison prior to being analyzed using TOF-SIMS. The primary goals of this study were to a) obtain spatial information using TOF-SIMS relating to both the inorganic and organic components of the paint films b) assess whether SIMS could effectively differentiate between two commonly used protein sources in the 15\(^{th}\) century (egg and glue) and c) evaluate whether SIMS could identify emulsions as well as layered paint systems.

### 3.5.1 Cross-Sectional Staining

Biological stains and fluorochrome have been used for the identification of binding media in cross-sectional samples since the 1950s and continue to be used in a number of conservation laboratories. \(^{147}\) However, many factors can interfere with staining protocols and results. Biological stains may not produce successful results if a paint sample is considerably degraded or aged and contaminants that come in contact with the surface can yield false positive or false negative reactions. Furthermore, some stains are delivered in solvents that may dissolve sensitive materials in a cross-section. The presence of certain pigments can also cause false positives during the attempted
characterization of the paint binding media. Despite these drawbacks, cross-sectional fluorochrome stains remain popular, as they are relatively inexpensive and simple to prepare, allowing for immediate results.

Tests performed on fourteen egg-oil reference samples revealed that two different protein stains (Amido Black II and Alexa FLUOR 488®) were unable to characterize the egg protein binder as protein-containing. While the stains both showed a positive reaction for the collagen in the gesso ground layers, both produced false negative results for the egg proteins present in the paint layers (Figure 3.4). This result was not only true of samples containing trace amounts of egg yolk in the paint layer but also of paints bound in pure egg yolk containing either lead white or yellow ochre. This discrepancy is probably best explained by pigment interference, which may cause false positives during the attempted characterization of the paint binding media.

Another possibility is that the small amount of oil naturally found in egg yolk may be inhibiting a positive stain or that these particular stains are simply more sensitive to glue-based materials. Based on these observations, cross-sectional staining does not appear be a reliable system to confirm the presence of egg yolk in paint cross-sections.

### 3.5.2 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR is often used as a first step in the molecular analysis of the materials in a paint sample. Samples can then be compared to over 1500 reference spectra obtained from artists’ materials (e.g. pigments, binders, etc.) in the IRUG database (Infrared and Raman Users Group). In addition, multiple spectra can be obtained from the same
Figure 3.4: Cross-sectional analysis demonstrated the ineffectiveness of the fluorochrome stain Alexa FLUOR® 488 and an amino acid diazo stain, Amido Black (pictured above). A reference sample containing lead white/egg tempera paint over a gypsum-glue ground (100x) is shown in normal visible light (A) and stained with Amido Black (B). The same procedure was performed on a reference sample containing a yellow ochre/egg tempera paint sample in images (C) and (D).
sample which may ultimately give a more accurate representation of the disparate materials present. Recent studies using Imaging Attenuated Total Reflectance-FTIR (ATR-FTIR) have successfully characterized inorganic and organic components of paint cross-sections that are spectrally active in the mid-infrared.\textsuperscript{112,113}

FTIR analysis was only partially able to confirm the presence of protein in the paint layers (Figure 3.5). Protein containing materials are often characterized by the C-N-H stretching band (1565-1500 cm\textsuperscript{-1}) and two C=O stretching bands (1750-1600 cm\textsuperscript{-1}) while oil containing materials give rise to a sharper C=O stretching band around 1750-30 cm\textsuperscript{-1}.\textsuperscript{156} Characterization of protein in the emulsions of egg and oil became problematic when the oil component was over 50\% of the total volume of the binding medium. In addition, pigments were found to interfere with the “fingerprint” region in the 1500-400 cm\textsuperscript{-1} range or mask peaks within the area of interest, as was found with lead white.\textsuperscript{58} FTIR may also give a false positive for protein in the paint layer if red lake was used by the artist as these pigments may be made by extracting the organic dye from proteinaceous textiles such as wool or silk.\textsuperscript{161} Finally, FTIR cannot distinguish between types of proteins, namely animal glue from egg yolk, a distinction that is critical from an art historical standpoint.

3.5.3 TOF-SIMS

In positive mode, molecular species consistent with amino acid residues, as well as the cationic portions of pigments were expected secondary ions. The amino acid residues used for analysis have been established in the literature and provide unique masses for
Figure 3.5: The series of FTIR spectra shown above correspond to the range of egg-oil mixtures containing yellow ochre and demonstrate the detection issues often encountered when proteinaceous materials are present in complex mixtures. For all of the egg-oil paints, the peaks associated with protein (area circled in red) became increasingly difficult to detect with univariate methods when the egg yolk consisted of half or less than half of the overall binding medium. Protein containing materials are often characterized by the C-N-H stretching band (1565-1500 cm$^{-1}$) and two C=O stretching bands (1750-1600 cm$^{-1}$) while oil containing materials give rise to a sharper C=O stretching band around 1750-30 cm$^{-1}$. Note that pigments typically interfere with the “fingerprint” region in the 1500-400 cm$^{-1}$ range.
TOF-SIMS imaging.\textsuperscript{162-166} These residues were established with a TOF-SIMS instrument with analogous analysis parameters. Previous studies using harsh artificial aging conditions have shown that seven of these residues (glycine, alanine, valine, leucine, isoleucine, proline, and hydroxyproline) are able to withstand various degradation and oxidation reactions and can therefore serve as reliable markers for historical works of art.\textsuperscript{171} These seven residues should be visible in historical artwork as they survived artificial aging in a weathering chamber at 50°C and 50% relative humidity for 500 hours under illumination by a xenon lamp. Hydroxyproline is especially significant as it is mainly found only in collagen, the protein comprising animal glue. To distinguish between the collagen and egg yolk proteins, a principal components analysis (PCA) was performed on the data. PCA is a technique that uses redundancy to establish significant axes of variance (principal components) within a multivariate dataset. When plotted against these new principal components, groupings within a dataset can be visualized typically corresponding to chemical variables. In negative mode, the molecular species seen are mostly longer aliphatic chains with electronegative functionalities (fatty acids), and also the anionic portion of pigments. Depending on the embedding resin surrounding the paint cross-section, it is possible to use CN\textsuperscript{−} as a marker for protein, however this is not usable to distinguish between types of protein.

Figure 3.6 highlights the images associated with various positive and negative ions in a cross section containing a 50% egg yolk/50% linseed oil paint layer over an animal glue ground. Images were reconstructed by selecting the fragment peaks falling at the exact masses of the amino acid residues in Table 3.1. In the case that peaks were not
Figure 3.6: ToF-SIMS images of a yellow ochre paint layer (bottom layer in TOF—SIMS image) bound in a tempera-oil emulsion (50%/ 50% by wt.) over a traditional glue ground (top layer in TOF-SIMS image). The image at the top left is a video capture taken after analysis with the square indicating the analysis area. Exact masses of all organic species are given in Table 3.2. Images collected in “high-current bunched” mode with Bi$_3^+$ primary beam with beam dosage to the static SIMS limit. Notice the “pocket” of material in the top left corner of the images. This is most likely displaced material resulting from embedding which was uncovered with the microtome.
perfectly resolved from background noise or adjacent peaks, the selected peak areas were kept within an estimated 20% peak height. There was no scaling of images to reduce background noise. The ability of the instrument to observe mass resolved peaks are shown by imaging the residues for hydroxyproline (C₄H₈NO⁺, 86.061 m/z) and isoleucine/leucine (C₃H₁₂N⁺, 86.097 m/z). The images are significantly different from each other, with minimal to no peak interference observed. Also, for both valine and proline there are two possible residue fragments that can be used; valine was observed with fragments C₅H₇O⁺ at 83.050 m/z and C₄H₁₀N⁺ at 72.081 m/z, while proline was observed with fragments C₄H₆N⁺ at 68.050 m/z and C₄H₈N⁺ at 70.066 m/z. In Figure 3.6 this is referenced with the nominal mass in the images. The three pigment images demonstrate the location of the gesso ground (top) and paint layer (bottom). Hydroxyproline, a significant marker in animal glue, was detected in the ground layer with minimal crossover to the paint layer. This capability allows for the distinction between animal glue and other proteinaceous materials using TOF-SIMS. The fatty acid fragments used for imaging (palmitic acid and stearic acid) in negative mode are not able to distinguish between egg yolk and linseed oil, as fatty acids are found in egg yolk. Interestingly, there seems to be a separation between the oil and egg yolk, with the oil being between the ground layer and the egg layer. The amino acid residue images appear to have the expected relative amounts of each residue given in Table 3.1, but since TOF-SIMS is a technique highly sensitive to matrix effects that can alter ion yields, there was no quantitation produced from the peak intensities of each fragment.
The last images in the set are taken in negative mode on a different spot on the sample (to the right) of the positive mode images. Palmitic and stearic acid fall in the egg yolk/linseed oil layer, and the CN⁻ image has a strong collagen response above the egg yolk. The “pocket” of material in the upper left portion of the images most likely resulted during embedding of the paint chip and exposed during subsequent cutting with the diamond knife. Figure 3.7 contains a series of overlaid images from three samples in the iron gradient. Pure linseed oil and pure egg yolk paint layers are contrasted against each other with the 50/50 mixture shown from Figure 3.7. Each of the images have been oriented to have the paint layer on the top, and the ground gesso layer on the bottom. CN⁻ is shown in green as a marker for generic protein response and is highlighting both collagen and protein. \( \text{C}_{16}\text{H}_{31}\text{O}_2^- \), which is a fragment for palmitic acid, is shown in red as a marker for fatty acids found in both linseed oil and egg yolk. \( \text{CaSO}_4^- \) is a marker for the gesso ground layer, and is shown in blue. In the first image of 100% pure linseed oil paint layer, there is a discrete separation between the two cross-section layers. The middle image shows the presence of the CN⁻ in the top paint layer, corresponding to the egg component of the emulsion. The last image in the set shows the complete infiltration of protein signal into both layers with the only the palmitic acid and \( \text{CaSO}_4^- \) signals being useful in determining layer structure.

To understand if matrix effects have an effect on the TOF-SIMS ability to observe an entire binding medium gradient, PCA was performed on the dataset. To reduce the amount of complexity within the system, PCA was only done on a gradient of a single pigment. Tracing the outlines on the layers with a polygon and then reconstructing the mass spectrum of each layer first selected the regions of interest. To normalize for the
Figure 3.7: Overlays of three yellow ochre paints (oil, egg-oil, egg) in negative mode. Bottom layer is the glue ground; top layer is the yellow ochre paint layer. Green is CN\(^-\) showing generic protein response, red is palmitic acid showing oil response, and blue is calcium sulphate for gesso area. The TOF-SIMS is able to establish both “pure” layers and also mixed layers based on organic content. Note the unexpected layer separation in the 50/50 egg-oil mixture, as the red and green signals are not completely intermixed.
varying sizes of the layers, CH₃⁺ was chosen as a reference peak prior to further processing of the data. This peak was chosen because the fragment will be found in all binding media, hopefully with minimal bias due to matrix effects, so that the PCA will establish grouping based on peak intensity, not on ion yield. Because the peaks can have closely interfering peaks, Gaussian-type peaks were fit to each amino acid residue and the reference peak prior to exporting the peak areas to MATLAB. Figure 3.8A shows the PCA scores plot of just the “pure” components (collagen, 100% oil paint layer, 100% egg yolk paint layer) and the 50% oil/50% egg yolk layer in the iron gradient. The plot has a clear grouping of the four components. Figure 3.8B is a PCA scores plot with a data point originating from each layer of the entire iron gradient. Each of the paint layers has been marked. The gradient is observed in the spread from pure oil to pure egg yolk, although the spread of the gradient is strictly qualitative, as strict calibration standards are required to perform quantitative measurements with TOF-SIMS. While the scores plot does not show error, it is unclear if the differences due to minimal changes in binding media (such as between 0% and 5% of oil in egg yolk) are reproducible as the method of preparation of paint films was not strictly controlled for this initial study. Lastly, although not shown here, the loadings for the first few components relate to expected variations (see Table 3.1) between egg yolk and collagen proteins (i.e. proline and hydroxyproline for collagen) as the dataset only included amino acid mass fragments.

Lastly, to understand if TOF-SIMS can produce similar images from a multi-layered sample consistent with 15th century Italian artwork, cross-sections were created
Figure 3.8: Scores plot resulting from PCA of reference *tempera grassa* paint films. ‘A’ is a plot of “pure” layers taken as reconstructed regions-of-interest (ROIs) for the 100% egg yolk, 100% linseed oil, and 50% mixture of the two paint binding media. ‘B’ is a plot comparing the entire iron-pigmented gradient set, with the resulting gradient coming from the relative abundances of the amino acid mass fragments.
consisting of an oil glaze (mixed with lapis lazuli) atop a 50% egg yolk/50% linseed oil egg tempera paint (mixed with azurite). Both layers were applied over the same traditional collagen-containing ground. Figure 3.9 shows the resulting TOF-SIMS images from analysis. $[\text{Ca}]^+$ is used to identify the ground layer, $[\text{Cu}]^+$ identifies the egg tempera layer, and the combination of $[\text{Al}]^+$, $[\text{Si}]^+$ and $[\text{NaO}_3\text{H}]^+$ identifies the glaze layer. There appears to be a silica-based impurity in the azurite layer, and conversely the faint silicon signal in the lapis lazuli layer is indicative of higher-quality lapis lazuli. Analogous with Figure 3.6, the amino acid residues fall within the ground and egg tempera layers, with some uptake of egg yolk protein into the glaze layer. The uptake is shown in the valine and isoleucine/leucine images. Hydroxyproline is again observed only in the collagen-containing ground layer. The negative mode images again show the fatty acid fragments falling only in the egg yolk- and oil- containing layers, while $[\text{CN}]^-$ has a response only in the ground and egg tempera layers.

3.6 Conclusions

TOF-SIMS continues to show great promise as a tool for the analysis of objects of cultural importance. The improvements in primary ion beam technology have allowed for an overall improvement in total ion yield and spatial resolution. The two experiments discussed in this Chapter demonstrate that TOF-SIMS is capable of simultaneous identification and characterization of inorganic and organic components within a cross-sectional sample. Analysis of reference materials containing historically accurate pigments and binding media (e.g. oils, egg yolk, etc.) can improve our
Figure 3.9: TOF-SIMS images of a mock multi-layered paint system. The sample contains lapis lazuli in linseed oil (top) over azurite in egg tempera (middle) over a traditional glue ground (bottom). The image at the top left is a video capture taken just after analysis with the square indicating the analysis area. Exact masses of all organic species are given in Table 3.1. Images collected in “high-current bunched” mode with Bi$_3^+$ beam to the static SIMS limit. The major components of lapis lazuli (Al, Na, and Si) are overlaid in the top row. Notice the less intense CN$^-$ signal in the egg layer in the bottom right image.
understanding of detectable secondary ions and spatial resolution associated with the TOF-SIMS technique. This study suggests that the trend in metal soap formation is a highly time dependent process, however further research is needed to assess whether ionization using similar parameters produces a significant difference secondary ion yield for metal soap mass fragments during TOF-SIMS analysis. Protein fragments bound within paint reference samples can be detected even when present at low amounts. TOF-SIMS imaging coupled with principal component analysis can not only differentiate between various classes of organic compounds, but it can also distinguish between protein sources (e.g., animal glue vs. egg yolk). However, this is also accomplished using careful selection of unique mass fragments. Multivariate analysis will be of greater importance to chemically similar proteins (or other binding media) that can not be differentiated using unique mass fragments. Further studies are needed in order to compare these preliminary findings with aged paint samples collected from works of art.

3.7 Acknowledgements

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Chapter 4

COMPARING OIL AND EGG TEMPERA PAINT SYSTEMS AS FOUND IN RENAISSANCE-ERA ARTWORK USING TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

4.1 Introductory Remarks

For the observation of binding medium degradation on historical samples, the comparison between oil and egg tempera is an ideal candidate as the chemical difference between the two media allow for a high degree of chemical variability. For this study, differences in the spatial distribution of mass fragments relating to pristine and altered binding media were imaged across the cross-sectional samples. Observations due to the spatial distribution of these mass fragments relate to the status of binding medium degradation for each sample. This work was published in the journal Studies in Conservation in 2016.\(^\text{185}\) The author list was Zachary Voras, Kristin deGhetaldi, Brian Baade, Eric Gordon, Glenn Gates, and Thomas P. Beebe, Jr.

4.2 Abstract

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is quickly becoming a critical tool in the field of art conservation. This technique provides high-resolution spatial maps of both inorganic and organic components located within cross-sectional samples collected from works of art. 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 oils. For example, the
detection of the ion fragment associated with the amino acid hydroxyproline can be
used to confirm the use of animal glue in a paint sample. As an analytical technique,
TOF-SIMS avoids the need for derivatization/silylation reagents, with no interference
by the presence of reactive or unreactive pigments. Furthermore, the layered systems
that are often encountered in historical paint samples remain intact throughout the
analytical procedure. This allows 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 correlated to previous studies of the same preserved samples. In this
study, TOF-SIMS was used to analyze a paint cross-section obtained from a painting
attributed to Raphael, as well as a sample collected from a painting by the Sienese
painter Matteo di Giovanni.

4.3 Introduction

It has long been a goal of conservation scientists and art historians of early
Renaissance paintings to identify and distinguish between the animal proteins in egg
yolk and collagen, and to do so in a spatially resolved manner for the various layers. If
such a determination were possible, conservation scientists and art historians could
then identify the boundaries of the various layers that artists were known to use, or
could possibly reveal previously unknown techniques by artists thought to adhere to
certain practices. Furthermore, such a determination would greatly assist in
establishing a painting’s provenance. For example, if animal glue (i.e., collagen) is
known to be the binding agent in the ground layer of an artist’s paintings, and egg tempera (i.e., egg yolk) is known to be the binding agent in the paint layers of that artist’s paintings, then it would be important to confirm these practices with scientific accuracy, and correlate the findings with the artist’s journal and other historical contexts.

4.3.1 Analysis of Complex Multi-Layered Paint Samples

The use of “bulk” analytical techniques has played a major role in the establishment of our current knowledge base in art conservation and history. The ability to dissolve a complex heterogeneous art specimen, followed by gas chromatography-mass spectrometry (GC-MS) analysis has certainly provided ample evidence for the presence of certain proteins, oils, and pigments in such samples. Nevertheless, the original location (and function) of those species in the specimen must then be inferred, and the sample will have been destroyed, making further analysis of the same sample in the same location impossible.

Paint samples collected from complex and/or multi-layered painted surfaces (e.g., easel paintings, wall murals, polychrome sculpture) can be challenging to characterize fully. Easel paintings executed before the 20th century typically contain binders consisting of animal glue, egg yolk, drying oils (e.g., linseed, walnut, or poppyseed), natural resins (e.g., dammar, mastic), among other organic materials. Despite recent advancements in analytical procedures, it remains difficult to confirm whether the various component materials, sometimes applied in layers only a few micrometers
thick, exist as mixtures, emulsions, glazes, or surface coatings within these complex multi-layered paint systems.

For example, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) provides information about specific chemical groups, while TOF-SIMS provides more molecular and structural information.\textsuperscript{193,194} Further complications can also arise when using chromatographic methods such as insufficient sample size, the presence of non-original materials from previous restoration campaigns, and the interference of pigments when attempting to identify organic components.\textsuperscript{188,189,192,195} While some of these issues are also encountered using TOF-SIMS, the technique has the added benefit of providing spatial maps to help distinguish between unoriginal/original materials and to characterize discrete layers.

4.3.2 Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and Cultural Heritage Objects

Over the past decade, time-of-flight secondary ion mass spectrometry has shown great potential as a characterization tool in the field of cultural heritage.\textsuperscript{196-198} There are four main advantages to using TOF-SIMS on samples collected from artworks or culturally significant objects. First, the instrument can be used to simultaneously collect chemical information (both elemental and molecular information) from inorganic and organic materials found in works of art.\textsuperscript{199-201} Inorganic species originate from pigments and inert fillers or extenders while the organic components stem from a much wider range of materials.\textsuperscript{186,191,202} Secondly, 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. This enables the simultaneous unambiguous identification of both specific organic and inorganic species present in discrete areas within a sample, specifically those located in individual layers or as distinct particles. Third, cross-sectional samples can be used for future analysis. Finally, TOF-SIMS is one of the few mass spectrometric techniques that allows the user to analyze directly the surface of the unmodified solid sample. The sample is therefore not subjected to an extraction protocol prior to analysis, nor to the addition of a matrix.

4.3.3 TOF-SIMS and Paint Cross-Sections

Over the past decade new developments in TOF-SIMS technology (specifically ion beam technology and detection systems) has allowed for an improved total-ion yield and better spatial resolution for the analysis of biological, organic, and other “soft” materials. Previous studies have also published molecular-ion maps corresponding to compounds of particular interest found in paint cross-section samples. Imaging not only assists with identification of the materials and techniques used by the artist, but also it can assist with identification of compounds associated with pigment or binder alteration, or non-original materials that may be present from previous restoration campaigns.

Previous studies using TOF-SIMS to image cross-sections have proven relatively unsuccessful at detecting markers for proteins, specifically proteins associated with egg-based materials. However, more recent techniques have been used to identify blood on the surface of African sculptures, and a protein-containing ground in
a sample collected from a painting by Rembrandt van Rijn using TOF-SIMS.\textsuperscript{196,199} Previous studies using GC-MS have shown that, over time, approximately seven amino acids are able to withstand oxidation and other degradative processes.\textsuperscript{189,195,215,216} These relatively stable amino acids were chosen as the primary markers for this study.

### 4.3.4 Goals of the Present Study

This study focuses on the simultaneous identification of specific markers associated with egg yolk, animal-glue protein, and a drying oil (linseed) in two paint cross-sections collected from Italian panel paintings in the collection of The Walters Art Museum. Cross-sections associated with the historic panel paintings were prepared more than 20 years prior to analysis with TOF-SIMS, and no additional samples were collected from the paintings. The primary goals were to: obtain spatially resolved TOF-SIMS information relating to both the inorganic and organic components of the historic samples; assess whether TOF-SIMS could effectively differentiate between two commonly used protein sources in the 15\textsuperscript{th} and early 16\textsuperscript{th} centuries: egg yolk (tempera) and animal glue (collagen); and evaluate whether TOF-SIMS could identify and distinguish between these materials in layered paint systems.

### 4.4 Materials and Methods

The observation of historical cross-sections required the use of carefully prepared standards for both chemical and historical accuracy. A discussion of TOF-SIMS
performance is also included to ensure optimal signal and minimal bias for correct observation of results.

4.4.1 Reference Materials

A set of historically accurate reference or standard paint samples was used to extract relevant information regarding positive- and negative-ion fragments observed in TOF-SIMS. Table 4.1 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. Literature-accepted amino-acid marker fragments are compiled from previous studies using TOF-SIMS applied to protein-containing materials and both the observed and calculated m/z values are reported.\textsuperscript{217-220} Paint reference samples used for the analysis and identification of protein and oil markers were created at the National Gallery 2008. Yellow ochre (Natural Sienna Monte Amiata), calcium sulfate (Terra Alba-Natural Selenite) and Swedish cold-pressed linseed oil were purchased from Kremer Pigments, Inc. Azurite (fine grade), vermillion (dry process), and lead white (prepared using the Dutch Stack Method) were obtained from Rublev/Natural Pigments. Egg yolks were USDA-grade organic brown eggs from free-range hens. Collagen was extracted by boiling parchment scraps (obtained from skins of calf, sheep, and goat) purchased from Talas.

All painted panel standards were prepared on glass by first applying a gesso ground layer, followed by drying, followed by brush application of the pigmented paint in
Table 4.1: Table of specific positive and negative ion fragments observed during TOF-SIMS analysis, and the expected molar percentages as reported by Shilling, 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. Reprinted from Voras et al, *Studies in Conservation* 2016, 61(4):222-235, with permission from the Taylor and Francis Group.

<table>
<thead>
<tr>
<th>Amino Acid Species Observed (ion polarity)</th>
<th>Empirical Formula of Indicator Ion</th>
<th>m/z of Ion Calculated (observed ± 0.001)</th>
<th>Egg Yolk (mole % ± 9%)</th>
<th>Animal Glue (mole % ± 9%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine, GLY (+)</td>
<td>CH₃N⁺</td>
<td>30.034 (30.034)</td>
<td>15.1 %</td>
<td>46.0 %</td>
</tr>
<tr>
<td>Alanine, ALA (+)</td>
<td>C₇H₈N⁺</td>
<td>44.050 (44.050)</td>
<td>23.1 %</td>
<td>17.0 %</td>
</tr>
<tr>
<td>Proline, PRO (+)</td>
<td>C₇H₈N⁺</td>
<td>68.050 (68.050)</td>
<td>10.5 %</td>
<td>16.1 %</td>
</tr>
<tr>
<td>Valine, VAL (+)</td>
<td>C₇H₁₈NO⁺</td>
<td>72.081 (72.084)</td>
<td>16.6 %</td>
<td>3.0 %</td>
</tr>
<tr>
<td>Hydroxyproline, HYP (+)</td>
<td>C₇H₂₀NO⁺</td>
<td>86.061 (86.065)</td>
<td>0.0 %</td>
<td>12.1 %</td>
</tr>
<tr>
<td>Isoleucine, ISO (+)</td>
<td>C₇H₁₂N⁺</td>
<td>86.097 (86.100)</td>
<td>12.4 %</td>
<td>1.9 %</td>
</tr>
<tr>
<td>Leucine, LEU (+)</td>
<td>C₇H₁₄N⁺</td>
<td>86.097 (86.100)</td>
<td>21.9 %</td>
<td>3.7 %</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>99.6</strong></td>
<td><strong>99.8</strong></td>
</tr>
<tr>
<td>Palmitic Acid, PA (-)</td>
<td>CH₁₅(CH₃)₃COO⁻</td>
<td>255.232 (255.231)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Stearic Acid, SA (-)</td>
<td>CH₁₇(CH₃)₃COO⁻</td>
<td>283.264 (283.261)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Generic Protein (-)</td>
<td>CN⁻</td>
<td>26.003 (26.005)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>
Figure 4.1: Diagram of the reference materials used for TOF-SIMS analysis of Renaissance-Era paintings. ‘A’ shows the binding medium gradient between egg tempera and linseed oil used for the paint layer of each sample set. ‘B’ is the layered structure of the four sample sets, with a description of the gesso ground and the pigmented paint layer. All samples were made atop a clean glass slide.
Figure 4.1 highlights the ground/paint layer structure as well as outlines the binding medium gradient used for TOF-SIMS analysis. Painted panel standards were subjected to short-term aging at the National Gallery of Art using the Atlas Ci4000 Weatherometer, equipped with a Xenon light source (75,000 lux) using the ASTM Gamblin oil paint parameters (45% RH and 25º C for 400 hours). Small triangular cross-sections of the reference paint samples were imbedded in Extec® polyester resin/hardener (approximately 10 mL/0.5 mL).

### 4.4.2 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.

### 4.4.3 Sample Mounting and Preparation

There are several challenges associated with the preparation of cultural heritage objects, and especially historical 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 oils (resulting from ungloved sample handling) and volatile polymeric residues (resulting from storage in improper containers) 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 encountered here. While sample preparation and microtomy have been discussed in previous literature, none have gone into the detail described herein.\textsuperscript{199,221,222} Cryomicrotomy, in which the sample is held at a low temperature during sectioning, is called for rather than cutting at room temperature if the samples are soft and prone to smearing. All sample cross-sections were microtomized at room temperature in this study.

The goal of microtomy, as practiced here, was to provide a flat \textit{remaining} sample surface, rather than to 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 4.2, starting from a roughly 1-cm resin cube (Figure 4.2A), the embedding resin was trimmed by hand using a Dremel\textsuperscript{®} tool and cut-off wheel to remove most excess resin material, leaving a 4-mm resin cube containing the sample near one face of the cube and oriented edge-on, such that the paint layer planes are perpendicular to the cutting plane (top of Figure 4.2A). The sample was then mounted on a Cryo Specimen Pin (part number 70446) obtained from Electron Microscopy Sciences,
Figure 4.2: Preparation procedure for either freshly embedded or extant 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 (Electron Microscopy Sciences, P/N 70446). (C) The sample is then hand-trimmed in preparation for microtomy. The cut direction is indicated by (D). Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
using cyanoacrylate-based glue (part number 15187) obtained from Pacer Technology (Figure 4.2B). Next, the embedding medium, now held firmly on the specimen pin, was tapered by hand using a fresh standard 0.009-inch-thick safety razor blade (part number 67-0238), obtained from Famous Smith Brand, to further reduce the resin area surrounding the future cross-section at the tip of the specimen (Figure 4.2C).

It was observed during microtomy that thin sections tended to fracture off (rather than cut cleanly) near the end of the cut 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). This tended to leave behind a rough specimen surface with an ill-defined sample cross-section. It is surmised that mechanical stress during cutting could be lessened if the tip of the specimen was shaped to reduce the width that the microtome knife encountered as it progressed through each cut. Therefore, to lessen the mechanical stress on the sample during the cutting of the flat-topped face of the resin and its embedded paint chip specimen, further hand-shaping of the resin was used to form a trapezoid-shaped tip having a wider end at the beginning of the cut, and a narrower end at the completion of the cut (Figure 4.2D; the direction of the arrow indicates the direction of microtome blade movement). The exposed surface is what was analyzed here, leaving the remaining of the precious sample (except for the loss of a few micrometers of one edge), in its original embedding matrix, for subsequent analysis by others.
4.4.4 Microtomy

A series of cross-sectional cuts were 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.

4.4.5 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 Bi$_3^+$ 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 insulting
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 $1 \times 10^{12}$ ions/cm$^2$. The mass scales of positive-mode spectra were calibrated with the following ions: H$^+$, H$_2^+$, H$_3^+$, C$^+$, CH$^+$, CH$_2^+$, CH$_3^+$, C$_2$H$_3^+$, C$_3$H$_5^+$, C$_4$H$_7^+$, C$_5$H$_5^+$, C$_6$H$_5^+$, and C$_7$H$_7^+$; the mass scales of negative-mode spectra were calibrated with the following ions: H$^-$, H$_2^-$, C$^-$, CH$^-$, CH$_2^-$, CH$_3^-$, C$_2$H$_3^-$, C$_3$H$_5^-$, C$_4$H$_7^-$, C$_5$H$_5^-$, C$_6$H$_5^-$, C$_7$H$_7^-$, and C$_8$H$_8^-$. All data analysis was performed using 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.

4.4.6 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 distinct 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 \( m/z 29 \) (\( ^{29}\text{Si}^+ \)) for a clean silicon wafer.

4.4.7 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 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.
4.4.8 Sample Preparation

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 The Walters Art Museum is not known, although it was not a cyanoacrylate-based resin, based on its TOF-SIMS spectrum.

4.5 Results and Discussion

For the specific work in this Chapter, a focus will be on the sample taken from Raphael’s *Madonna of the Candelabra* (1513) and Matteo di Giovanni’s *Pentecoste* (c. 1480-1489). These paintings were chosen as they exemplify the chemical differences between pure egg tempera and pure oil based technique to give a contrast in identification. Additionally, a brief discussion will follow of additional paintings from the Walters Art Gallery that demonstrate that the conclusions based on the Raphael and Matteo di Giovanni are cohesive across multiple artworks.

4.5.1 Reference Paint Samples

Cross-sections obtained from reference paint samples were analyzed using TOF-SIMS in order to a) confirm the presence of the ion fragments summarized in Table 4.1 and b) to assess whether certain pigments had an effect on the detection of these fragments. The characteristic markers for amino acids associated with animal glue (see Table 4.1) were detected in the gesso ground for all samples. Likewise, amino acid fragments (with the exception of hydroxyproline) associated with egg yolk were
detected in all egg containing paints. Characteristic markers for fatty acids (see Table 4.1) were also observed in both egg and oil bound paints.

4.5.2 Raphael’s Madonna of the Candelabra

The Madonna of the Candelabra in the collection of the Walters Art Museum dates to about 1513 and has been associated with Raphael’s Roman period.\textsuperscript{223,224} 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 and techniques used by the artist or those working within his workshop. A cross-sectional sample collected from the proper right arm of the Christ Child was prepared using a microtome equipped with a diamond knife prior to analysis by TOF-SIMS, as outlined schematically in Figure 4.2. Figure 4.3 shows an optical microscope image under both visible (left) and ultraviolet (right) illumination. In both images the paint layer appears to be extremely fractured, cleaving away from the layers beneath. A gap (arrow 2) was observed just beneath the paint layer (arrow 1), as well as a medium-rich, auto-fluorescent layer (arrow 3) immediately atop the ground layer (region 4). As shown in Figure 4.4A, these observations were confirmed in the TOF-SIMS all-masses image (often called the total ion image), revealing a lack of signal at the interface between the paint layer and the layer immediately below. Below this void, in Figure 3B, TOF-SIMS showed a strong Ca\textsuperscript{+} signal at \textit{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 (Pb\textsuperscript{+}, \textit{m/z} 207.977, Figure 3C; Pb\textsubscript{2}\textsuperscript{+}, \textit{m/z} 415.953, not shown;
Figure 4.3: Cross-section collected from proper-right arm of the Christ Child in the Madonna of the Candelabra attributed to Raphael as seen in optical micrographs of the same area, using visible illumination (left) and ultraviolet illumination (right). A void is present (2) between the paint layer (1) and the rest of the sample. An auto-fluorescent medium-rich layer (3) can be seen directly atop the ground layer (4). Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
Figure 4.4: TOF-SIMS images obtained from the cross-section in Figure 4.3, in positive-ion mode, showing (A) all masses (pixel of maximum counts (POMC) has 5,123 counts; total image counts (TIC) is $5.19 \times 10^5$); (B) Ca$^+$ distribution, POMC = 182; TIC = $7.84 \times 10^5$; (C) Pb$^+$ distribution, POMC = 100; TIC = $7.80 \times 10^4$; (D) PbOH$^+$ distribution, POMC = 19; TIC = $1.72 \times 10^4$; (E) Pb$_2$O$_3$H$^+$ distribution, POMC = 12; TIC = $4.42 \times 10^3$; (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 4.3 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
PbOH$^+$, \( m/z \ 224.979 \), Figure 3D; Pb$_2$O$_2$H$^+$, \( m/z \ 448.951 \), Figure 4.4E; and Pb$_3$O$_3$H$^+$, \( m/z \ 672.923 \), not shown) and their expected isotopic peaks were observed as well. 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 4.4B; and Ca$_2^+$, \( m/z \ 79.923 \), not shown), and associated characteristic fragments in negative-ion mode (CaOH$^−$, \( m/z \ 56.965 \), not shown; and CaSO$_4^−$, \( m/z \ 135.914 \), Figure 4.5B). 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) that confirmed an absence of iron and mercury. No markers associated with possible mordants (e.g. Al, Ca), however, could be detected using either technique. If present, the red lake pigment may be present in concentrations that are too low for either system to detect. Figure 4.5 depicts the TOF-SIMS images obtained in the same area from the negative-ion TOF-SIMS mode. 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/cm$^2$) the sample was not microtomized 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.

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 4.5C). As depicted in Figures 4.5D and 4.5E, negative molecular ions characteristic of the fatty acids palmitic acid (CH$_3$(CH$_2$)$_{14}$COOH) and stearic acid (CH$_3$(CH$_2$)$_{16}$COOH), observed at \( m/z \ 255.232 \)
Figure 4.5: TOF-SIMS images obtained from the cross-section in Figure 4.3, in negative-ion mode, showing (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) C_{16}H_{31}O_2 (Palmitic Acid, PA) distribution, POMC = 29; TIC = 2.10 × 10^4; (E) C_{18}H_{35}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 4.3 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
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 in TOF-SIMS due to the matrix effect, this negative-mode intensity overlay in Figure 4.5F may indicate a depletion of these mobile fatty acids in the uppermost layers of the paint surface.

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 4.6. These included glycine (CH$_4$N$^+$, m/z 30.034, Figure 4.6A), alanine (C$_2$H$_6$N$^+$, m/z 44.050, Figure 4.6B), proline (C$_4$H$_6$N$^+$, m/z 68.050, Figure 4.6C), valine (C$_4$H$_{10}$N$^+$, m/z 72.084, Figure 4.6D), hydroxyproline (C$_4$H$_8$NO$^+$, m/z 86.065, Figure 4.6E), and isoleucine/leucine (C$_5$H$_{12}$N$^+$, m/z 86.100, Figure 4.6F). Including the presence of regularly spaced voids, all proteinaceous ion-fragment images yielded spatial intensities that displayed a very similar pattern. This is as expected, since any given amino acid marker merely indicates the presence of quasi-random-sequence protein, without any enrichment of particular amino acids. The protein marker signals were found throughout the ground layer, and were more intense in the medium-rich layer.

The amino acid hydroxyproline (Figure 4.6F) is found in collagen, but not in egg yolk. Since hydroxyproline was found in both the medium-rich layer and in the gesso
Figure 4.6: TOF-SIMS images of amino acid fragments obtained from the cross-section in Figure 4.3, in positive-ion mode showing (A) CH\(_4\)N\(^+\) (glycine) distribution, POMC = 40; TIC = 8.19 \times 10^4; (B) C\(_2\)H\(_4\)N\(^+\) (alanine) distribution, POMC = 28; TIC = 6.40 \times 10^4; (C) C\(_4\)H\(_6\)N\(^+\) (proline) distribution, POMC = 55; TIC = 1.15 \times 10^5; (D) C\(_4\)H\(_{10}\)N\(^+\) (valine) distribution, POMC = 10; TIC = 1.40 \times 10^4; (E) C\(_4\)H\(_8\)NO\(^+\) (hydroxyproline) distribution, POMC = 31; TIC = 6.65 \times 10^4; (F) C\(_5\)H\(_{12}\)N\(^+\) (isoleucine/leucine) distribution, POMC = 10; TIC = 1.15 \times 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 4.3 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
ground layer, it can be concluded that the artist chose to size his gesso-glue ground with an additional, unpigmented 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 (c. 1510) at the National Gallery of Art in Washington, DC, using different methodologies also revealed the use of an animal-glue size layer atop the gesso ground layer.\textsuperscript{225} 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.\textsuperscript{226} 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.

4.5.3 Matteo di Giovanni’s Pentecoste

The Pentecoste by the Sienese painter Matteo di Giovanni (b. 1430-1495), also at the Walters Art Museum, 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.\textsuperscript{227} A sample collected from the Madonna’s blue robe near the bottom edge of the painting was prepared as above.
Figure 4.7: Cross-section collected from the Pentecost by Matteo di Giovanni as seen in optical micrographs of the same area, 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 (right) in the form of discrete black particles. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
Figure 4.8: TOF-SIMS images obtained from the cross-section in Figure 4.7 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) Pb\(_2\)O\(_2\)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 4.7 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
Optical examination under high magnification, as seen in Figure 4.7, revealed evidence of an underdrawing (Figure 4.7, left and right images, arrow 3) atop the ground layer (Figure 4.7, left, arrow 4), followed by a thick white layer of paint (Figure 4.7, left, arrow 2) beneath a rather thin degraded paint layer (Figure 4.7, left, arrow 1) containing blue lapis particles. Analysis of other paintings by this artist have also revealed the occasional use of a white imprimatura, or preparatory layer, atop a dark, pronounced underdrawing.228,229 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. This is shown in Figures 4.8 and 4.9, respectively. In positive-ion mode, Figure 4.8 shows signals for elemental aluminum (Figure 4.8F), which was found to co-localize with the blue particles in the optical images (Figure 4.7, left, arrow 1), confirming the presence of the pigment lapis lazuli (known to be comprised of Al, m/z 26.982; Na, m/z 22.990; Si, not shown).

Figure 4.9 shows the mass-resolved TOF-SIMS images for the observed prominent negative ions. A signal for CN\(^-\) (m/z 26.003), a generic protein marker, Figure 4.9C, was observed throughout the gesso ground layer in Figure 4.9B (CaSO\(_4\)\(^-\), m/z 135.914). However, a protein signal was also observed in the upper paint layers, as seen in Figure 4.9C. Figure 4.10 shows particular amino acid fragment signals for glycine (CH\(_4\)N\(^+\), m/z 30.034, Figure 4.10A), alanine (C\(_2\)H\(_6\)N\(^+\), m/z 44.050, Figure 4.10B), proline (C\(_4\)H\(_6\)N\(^+\), m/z 68.050, Figure 4.10C), valine (C\(_4\)H\(_{10}\)N\(^+\), m/z 72.084, Figure 4.10D), hydroxyproline (C\(_4\)H\(_8\)NO\(^+\), m/z 86.065, Figure 4.10E), and isoleucine/leucine (C\(_5\)H\(_{12}\)N\(^+\), m/z 86.100, Figure 4.10F). These protein signals were
Figure 4.9: TOF-SIMS images obtained from the cross-section in Figure 4.7, 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) C_{16}H_{31}O_2^− (Palmitic Acid, PA) distribution, POMC = 78; TIC = 9.49 × 10^4; (E) C_{18}H_{35}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 4.7 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
Figure 4.10: TOF-SIMS images of amino acid fragments obtained from the cross-section in Figure 4.7, in positive-ion mode showing (A) CH$_4$N$^+$ (glycine) distribution, POMC = 29; TIC = 3.73 × 10$^4$; (B) C$_2$H$_6$N$^+$ (alanine) distribution, POMC = 23; TIC = 3.39 × 10$^4$; (C) C$_4$H$_6$N$^+$ (proline) distribution, POMC = 21; TIC = 2.32 × 10$^4$; (D) C$_4$H$_{10}$N$^+$ (valine) distribution, POMC = 8; TIC = 7.51 × 10$^3$; (E) C$_4$H$_8$NO$^+$ (hydroxyproline) distribution, POMC = 10; TIC = 7.93 × 10$^3$; (F) C$_5$H$_{12}$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 4.7 to guide the eye. Reprinted from Voras et al, Studies in Conservation 2016, 61(4):222-235, with permission from the Taylor and Francis Group.
observed both in the ground layer and in the paint layer, except for hydroxyproline, which was detected only in the ground layer (Figure 4.10E). This corroborates the use of a gesso-glue ground layer, while the paint layers are most likely bound in egg tempera, as confirmed by the presence of fatty acid fragments found only in the paint layers. Fatty acid images are seen in Figure 4.9D (palmitic acid, CH$_3$(CH$_2$)$_{14}$COO$^-$, m/z 255.232) and Figure 4.9E (stearic acid, CH$_3$(CH$_2$)$_{16}$COO$^-$, m/z 283.264).

Dunkerton’s interpretation of samples collected from Matteo di Giovanni’s Judith or Tomyris of Scythia at the National Gallery of Art in London suggested the use of egg tempera. As stated previously, recent research has also shown that Matteo di Giovanni occasionally employed a white imprimatura layer consisting of lead white in egg tempera. Similar to the Raphael sample, a marked intensity gradient of the TOF-SIMS fatty acid marker signals (Figures 4.9D, 4.9E, and 4.9F) was seen to occur along the top surface of the paint, notably in the degraded top layer containing particles of lapis lazuli. Taken at face value, in the absence of a significant TOF-SIMS matrix effect, this result indicates a depletion of oil in the uppermost layers of the paint surface. Figure 4.11 provides a summary of the results discussed herein, showing an overlay of the TOF-SIMS image reconstructions of proteinaceous (CN$^-$), palmitic acid (CH$_3$(CH$_2$)$_{14}$COO$^-$), and stearic acid (CH$_3$(CH$_2$)$_{16}$COO$^-$) mass fragments.

In addition, two other early Italian egg-tempera paintings from the Walters collection (The Ideal City attributed to Fra Carnevale and The Entombment by Giovanni di Paolo) have been analyzed and found to display the same oil-depletion pattern. Figure 4.12 provides a summary of the results from these paintings, showing an overlay of
Figure 4.11: Summary of results for Raphael’s *Madonna of the Candelabra* and Matteo di Giovanni’s *Pentecoste*. The paintings with sampling location is the top image, the middle image is the optical microscopy image (with layer structure indicated by the bottom inset), and the bottom TOF-SIMS image is an overlay of the mass fragments for proteinaceous material (CN⁻) in red, palmitic acid (CH₃(CH₂)₁₄COO⁻) in green, and stearic acid (CH₃(CH₂)₁₆COO⁻) in blue.
Figure 4.12: Summary of results for Giovanni di Paolo’s *Entombment* and *The Ideal City*, attributed to Fra Carnevale. The paintings with sampling location are shown in the top image, the middle image is the optical microscopy image (with layer structure indicated by the bottom inset), and the bottom TOF-SIMS image is an overlay of the mass fragments for proteinaceous material (CN⁻) in red, palmitic acid (CH₃(CH₂)₁₄COO⁻) in green, and stearic acid (CH₃(CH₂)₁₆COO⁻) in blue.
the TOF-SIMS image reconstructions of proteinaceous (CN\(^-\)), palmitic acid (CH\(_3\)(CH\(_2\))\(_{14}\)COO\(^-\)), and stearic acid (CH\(_3\)(CH\(_2\))\(_{16}\)COO\(^-\)) mass fragments. From this summary it is obvious that upper paint layers that originally contained fatty acids (either in the form of egg tempera or pure drying oil) shows a significant depletion in comparison to paint layers underneath. This is not surprising since fatty acids have been shown to remain mobile until they form complexes with reactive pigments (such as metal soaps), although over time even these complexes can erupt through the surface of the paint layer.\(^{201,230-232}\) Furthermore, harsh chemicals were often used during past restoration campaigns and may have contributed to the leaching of these free fatty acids at the surface of the paintings. Finally, the mobility and volatility of free fatty acids under environmental degradation conditions (heat, humidity, and UV exposure) can allow for the migration and loss of fatty acids.\(^{230-232}\) Further research is needed in order to better characterize the mechanisms involved with fatty acid migration and depletion in egg and oil paints.

### 4.5.4 Conclusions

Recent advancements in imaging TOF-SIMS now allow for the mapping of amino acids and other organic materials with molecular specificity and high spatial resolution, without the need to consume or destroy precious art samples. This technique provides high-mass-lateral resolution that is dependent upon the sample and its preparation, both of which affect the amount of signal that the sample yields. This is not limited by the technology of the ion beam itself, which can be focused to a spot size of under 100 nm. Surface-sensitive information with 80-20 spatial resolution on
the order of 6 µm was routinely achieved here in going from one cross-sectional layer to the next.

As with any analytical technique, caution must be exercised by the analyst when making conclusions based on a cross-section from a single sample. When feasible, multiple samples should be collected and analyzed from an artwork in order to confirm analytical findings. However, TOF-SIMS images are not comprised of merely a single datum; consistency and spatial correlations between nearby image pixels greatly increase the confidence with which one can make conclusions using only a single sample. TOF-SIMS can not only be used to analyze extant samples (including samples obtained and prepared more than 50 years ago), but also can be used to distinguish between protein types (e.g., egg tempera and collagen glue) present within a single sample using the same cross-section of that sample. Complex, real-world samples rarely consist of single-component analytes in a given location. TOF-SIMS has the ability to identify multi-component organic and inorganic species that might happen to be co-located.

For the Raphael analyzed here, three distinct layers were conclusively identified: a paint layer, an imprimatura layer, and a ground layer. For the first time it was shown that the imprimatura layer was sized with collagen, implying the use of animal glue, as opposed to egg tempera. The uppermost paint layer was largely free of proteins, consistent with oil-only painting techniques. The ground layer consisted of gypsum-related compounds, consistent with a traditional animal-glue (collagen) gesso round layer. There appears to be a depletion of oil from the uppermost surface of the paint
layer, perhaps due to volatilization, previous restoration campaigns, other environmental factors, or some combination thereof.

For the Matteo di Giovanni analyzed here, three distinct layers were conclusively identified: a paint layer, a relatively thick *imprimatura* layer, and a ground layer. Co-localized in the paint layer were several inorganic marker ions consistent with lapis lazuli, as well as organic oil species, egg protein, and *not* animal glue. The thick, lead white containing layer (~50 µm) was found to be protein-rich, although marker signals for collagen were absent, suggesting that an egg tempera *imprimatura* layer was applied directly onto the sized panel. This *imprimatura* layer is consistent with the use of egg tempera in the Sienese style. Unlike the layers above it, the ground layer consisted of a traditional animal-glue *gesso* ground layer, like the Raphael. There was an even more pronounced depletion (relative to the Raphael) of oil from the uppermost surface of the lapis paint layer.

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REFERENCES


Chapter 5

MOLECULAR-LEVEL ALTERATION MECHANISMS IN *LE BONHEUR DE VIVRE* BY HENRI MATISSE

5.1 Introductory Remarks

While the identification of fatty acid depletion was significant in the context of binding medium degradation, the results were limited in focus to only deterioration of Renaissance-era binding media and similarly produced works. One major question concerned the interaction between pigment and binding media, as the extent of degradation will be closely linked to the unique chemical environment of the pigment-binding medium system. In order to establish trends of binding medium degradation for fugitive pigments such as cadmium yellow (cadmium sulfide, CdS), *Le Bonheur de vivre* (1905/06) by Henri Matisse was studied using TOF-SIMS imaging. The work as presented in this chapter was published as an invited paper in *Applied Physics A* in 2015. The co-authors included Kristin deGhetaldi, Marcie B. Wiggins, Barbara Buckley, Brian Baade, Jennifer L. Mass, and Thomas P. Beebe, Jr.

5.2 Abstract

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has recently been shown to be a valuable tool for cultural heritage studies, especially when used in conjunction with established analytical techniques in the field. The ability of TOF-
SIMS to simultaneously image inorganic and organic species within a paint cross-section at micrometer-level spatial resolution makes it an analytical technique that is uniquely qualified to aid in further understanding the processes of pigment and binder alteration, as well as pigment-binder interactions. In this study, ToF-SIMS was used to detect and image both molecular and elemental species related to CdS pigment and binding-medium alteration on the painting Le Bonheur de vivre (1905-1906, The Barnes Foundation) by Henri Matisse. Three categories of inorganic and organic components were found throughout Le Bonheur de vivre and co-localized in cross-sectional samples using high spatial resolution TOF-SIMS analysis: (1) species relating to the preparation and photo-induced oxidation of CdS yellow pigments (2) varying amounts of long-chain fatty acids present in both the paint and primary ground layer and (3) specific amino acid fragments, possibly relating to the painting’s complex restoration history. ToF-SIMS’s ability to discern both organic and inorganic species via cross-sectional imaging was used to compare samples collected from Le Bonheur de vivre to artificially aged reference paints in an effort to gather mechanistic information relating to alteration processes that have been previously explored using µXANES, SR-µXRF, SEM-EDX, and SR-FTIR. The relatively high sensitivity offered by TOF-SIMS imaging coupled to the high spatial resolution allowed for the positive identification of degradation products (such as cadmium oxalate) in specific paint regions that have heretofore been unobserved. The imaging of organic materials has provided an insight into the extent of destruction of the original binding medium, as well as identifying unexpected organic materials in specific paint layers.
5.3 Introduction

Henri Matisse’s *Le Bonheur de vivre* has long been recognized as an archetype of Fauvist technique, as the artist produced several works between 1905 and 1907 that demonstrate a bold use of line and color. In the past decade, however, scientific studies have revealed unforeseen problems associated with Matisse’s technique, notably the degradation of the synthetic cadmium yellow (CdS) pigment. These findings have prompted the art conservation and scientific communities to conduct further research on Matisse’s compositions in an effort to identify the various alteration mechanisms that have led to fading and chalking of passages that would have initially appeared a brilliant yellow. Questions relating to the preventative care of Matisse’s works, as well as other painters related to the Fauvist movement, can thus begin to be addressed by developing a better understanding of degradation processes related to CdS pigments.

During this industrial period of the 19th and 20th century, new synthetic pigments were on the market for these modern artists; however, many of those pigments are now showing signs of degradation. In addition to yellow cadmium sulfide paints, lead chromate yellow and emerald green have been studied by conservators and scientists due to their degradation. Like cadmium sulfide, lead chromate has been analyzed extensively with XANES and µXRF, showing evidence of photo-oxidative degradation. Emerald green, Cu(C_2H_3O_2)_2 \cdot 3 Cu(AsO_2)_2, on the other hand, has not been as extensively analyzed, but work with FTIR and Raman have shown reactions of free fatty acids to form copper soaps.
5.3.1 Prior Studies of CdS Pigment Alteration.

Previously, various scientific studies have sought identification of the inorganic components relating to synthesis and alteration of CdS pigment.\textsuperscript{236-240} These results are generally complicated because of the various sources of related cadmium compounds. The photo-induced oxidation products of CdS in cadmium yellow follow the path:

\[
\text{CdS} + 2 \text{O}_2 + \text{H}_2\text{O} \leftrightharpoons \text{CdSO}_4 \cdot \text{H}_2\text{O} \quad \text{(Equation 1)}
\]

where \(\text{CdSO}_4 \cdot \text{H}_2\text{O}\) has the relatively high solubility in water of 76.4 g/100 mL (3.37 M). This leads to the end-products:

\[
\text{CdSO}_4 \cdot \text{H}_2\text{O} + \text{CO}_2 \leftrightharpoons \text{CdCO}_3 + \text{H}_2\text{SO}_4 \quad \text{(Equation 2)}
\]

where \(\text{CdCO}_3\) is insoluble (\(K_{SP} = 1.8 \times 10^{-14}\)). While chemically distinct from CdS, these photo-oxidation products can be attributed to either residual material from pigment synthesis (\(\text{CdSO}_4\), wet process; \(\text{CdCO}_3\), dry process or indirect wet process) or as a paint additive/paint lightener (\(\text{CdCO}_3\)). Additional cadmium compounds have been identified, including \(\text{CdCl}_2\) (possible residual starting material from the wet process synthesis of \(\text{CdSO}_4\)), \(\text{CdC}_2\text{O}_4\) (possible paint additive or acid hydrolysis product), and \(\text{CdS}_2\text{O}_3\) (possible paint extender), increasing the chemical complexity in studies of the CdS pigment.
In prior studies, µXANES, SR-µXRF, and SR-µFTIR have identified the Cd\textsuperscript{II} compounds CdS ($K_{SP} = 1 \times 10^{-27}$), CdSO\textsubscript{4} (highly soluble), CdCO\textsubscript{3} ($K_{SP} = 1.8 \times 10^{-14}$), CdCl\textsubscript{2} and CdC\textsubscript{2}O\textsubscript{4} ($K_{SP} = 6 \times 10^{-3}$) in cross-sectional samples taken from Le Bonheur de vivre. These results indicate that CdS and CdCl\textsubscript{2} are residual starting materials, and that CdSO\textsubscript{4}, CdCO\textsubscript{3}, and CdC\textsubscript{2}O\textsubscript{4} are most likely photo-induced oxidation products. Also, the appearance of CdS\textsubscript{2}O\textsubscript{3} may be an additional by-product of photo-induced oxidation.\textsuperscript{239,240} Giacopetti has done theoretical work on the initial effects of air and humidity (as O\textsubscript{2} and H\textsubscript{2}O) on the surface of cadmium sulfide in order to understand the beginning of formation of hydrated cadmium sulfate and cadmium carbonate.\textsuperscript{244} Currently these same species have been mapped for cross-sectional samples taken from Le Bonheur de vivre by 2-D X-ray and SR-µFTIR. For the analyses presented herein, the same samples have been analyzed by TOF-SIMS imaging. It will be shown below that analysis by TOF-SIMS imaging produces data of a quality analogous to that observed by synchrotron-based analytical techniques. This is a beneficial finding, since TOF-SIMS imaging does not require allocated beam-time at a synchrotron facility.

5.3.2 Artistic Choices and Treatment of Le Bonheur de vivre

To create Le Bonheur de vivre, Matisse likely employed paints bound in a drying oil (e.g., linseed oil), paints that were either drained of their oil medium prior to application, or ones significantly thinned using a diluent such as turpentine.\textsuperscript{233-235} It appears that Matisse may have been experimenting with a range of organic media including distemper (e.g., collagen-based paints) and casein during this period of his career, something that, along with the drained-oil paints and cadmium sulfide
alteration, may be related to the flaking that has been observed on *Le Bonheur de vivre*. To date only a handful of studies have been conducted to characterize the organic binding media present in Matisse’s paints and grounds. The current hypothesis strongly supports a depletion of the fatty acids comprising the oil-based binding medium of the painting in the uppermost layers of the paint surface.\textsuperscript{235,236,245} It has also been hypothesized that the depletion of fatty acids should be inversely correlated with the formation of CdC\textsubscript{2}O\textsubscript{4}. Such a process could be viewed as a hydrolytic breakdown of the fatty acids in the presence of excess H\textsubscript{2}SO\textsubscript{4}, present either as a leftover reagent of CdS pigment synthesis, or as a byproduct of photo-induced oxidation of CdS.\textsuperscript{236}

A complicating factor for most research involving the analysis of art objects is the unavoidable presence of restoration materials. Due primarily to the lack of cohesion between the paint layers (chalking, spalling, etc.), *Le Bonheur de vivre* has had an extensive restoration history involving multiple campaigns, the first dating to even before Albert C. Barnes purchased the painting. Since then the canvas has been lined to an additional canvas support with a glue or glue-paste adhesive (e.g., collagen, starches), varnished with tri- and/or di-terpenoid resins (e.g., dammar), and locally consolidated using a wide range of poly-vinyl acetate and ethyl vinyl acetate polymers (e.g., PVA adhesives, BEVA 371) to stabilize insecure areas of paint (predominately the cadmium yellows) [from the Barnes Foundation conservation records]. A recent study performed on Matisse’s *Le Luxe II* painting series (1907) was also hampered by the presence of restoration materials, making it difficult to distinguish between the collagen used during a 1966 restoration and the protein-based paint that may have been used by Matisse.\textsuperscript{245}
5.3.3 TOF-SIMS Imaging

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is an ultra-high vacuum technique useful in identifying elemental information, including isotopic information, and molecular and chemical information inherent to a sample surface.246,247 The technique uses a focused, rastered beam of primary ions that collide with a sample surface, causing secondary molecular and atomic fragments of positive, negative, and neutral charge, to ablate into the vacuum. These are then directed into the time-of-flight mass analyzer where they are detected. The emitted secondary fragments are indicative of the sample surface’s composition, and have an escape depth of roughly 2-10 nm, with 95% of the emitted particles originating from the uppermost two monolayers, making the technique effectively surface-sensitive. When practiced in its so-called dynamic mode, TOF-SIMS can be used to erode the sample on atomic or molecular scales, producing a depth profile of a sample’s composition. When practiced in its so-called static mode, as was the case here, less than 0.1% of a sample’s surface is consumed or damaged, thus making it possible to do true analysis of the molecular fragments located on a sample surface, consisting in the present case of a paint cross-section. Because the primary ion beam is focused and pulsed, these analyses can be conducted in a point-by-point manner on the lateral plane of the sample, resulting in TOF-SIMS images, where each pixel contains information about the molecular fragments and/or elemental species present on the sample surface.

The current TOF-SIMS instrumentation allows for the routine analysis of soft materials.248-250 This is directly related to advancements in primary ion beams (cluster sources) that provide higher data acquisition rates and increased spatial resolution of
the rastered beam.\textsuperscript{251-254} Specifically, the use of bismuth clusters has drastically improved secondary ion yield while maintaining a high spatial resolution in the sub-micron level when the sample truly contains interfaces with such structural features.\textsuperscript{255-257} Using these cluster sources, TOF-SIMS has shown great promise in the analysis of proteins and various biological materials.\textsuperscript{258-262} Additionally, the advent of cluster TOF-SIMS analysis has allowed researchers to study the matrix effects and reproducibility as they relate to soft materials.\textsuperscript{263,264}

TOF-SIMS has previously been shown as a technique useful in the field of art conservation.\textsuperscript{265-268} The technique has been proven for its ability to co-localize the various components of paint, as well as show signs of binder and/or pigment degradation.\textsuperscript{269-271} The instrument’s ability to simultaneously image inorganic and organic species (atomic and molecular) provide a practical complement to the various techniques commonly used in the art conservation field, such as scanning electron microscopy, Fourier-transform infrared spectroscopy, and gas chromatography-mass spectrometry.\textsuperscript{265,272,273} Additionally, TOF-SIMS has the added benefit of providing analysis as-is permitting the return of extant samples without the need for additional derivitization or analyte extraction. This benefit allows for the sample to remain chemically unaltered and physically intact for further analysis.

A benefit to TOF-SIMS imaging is the ability to assign chemical identity based on exact mass fragment and isotopic distribution instead of chemical shift based on electronic structure or vibrational structure, such is seen in X-ray techniques, FTIR, and Raman spectroscopy. This can minimize spectral interference that leads to
ambiguity in assigning chemical identity. While secondary fragments can have similar masses, the high mass resolution \((m/\Delta m > 6500\) for most molecular fragments - see specific examples below) afforded by the time-of-flight mass analyzer is able to resolve most potential peak overlaps. Whenever an overlap of analyte peaks is not able to be resolved, it is generally possible to select a different but related analyte peak that corresponds to the chemical species of interest, based on fragmentation of the molecular ion. Similarly, it is beneficial to select and image multiple mass fragments resulting from the fragmentation of a single compound of interest to ensure the colocalization of the mass fragments is identical, providing higher confidence in the analysis. Examples of this are given below. Lastly, in direct comparison to the XANES technique that has been used to image the same cross-sectional samples from *Bonheur de vivre*, it is important to understand the benefit and limitation to each analysis. XANES, which requires a synchrotron facility, has the benefit of reliable quantitation but lacks a low detection limit, since the XANES technique requires a few ppm for detection.\(^{274}\) TOF-SIMS, a lab-based technique, can have higher sensitivity depending on the sample (on the scale of ppb or better), but is limited in its ability to quantitate absolutely, due to the matrix effect.\(^{247,275}\)

### 5.4 Materials

For this study, careful selection of unique mass fragments was required as the various original/degradation products of CdS had overlapping mass fragments, leading to false-positive results. The reference materials included both chemically-pure standards and historically-accurate recreations of the CdS paint system.
5.4.1 Cd-Containing Standards

To help identify pertinent exact-mass fragments, isotopic ratios, and to determine the effect of possible primary-ion-beam-induced chemical alteration, standards were purchased and analyzed by TOF-SIMS using the same parameters used for the analysis of cross-sectional samples taken from the *Le Bonheur de vivre* painting. The selected standards were: CdS (99.999% metals basis, Alfa Aesar); CdSO₄·8H₂O (99.996%, Alfa Aesar); CdC₂O₄ (> 98%, MP Biomedicals); CdCO₃ (99.998% metals basis, Alfa Aesar); and CdCl₂ (99.99% trace metals basis, Acros Organics).

5.4.2 Historically Accurate Paint Reference Standards

To generate comparable CdS paint reference samples, historically accurate materials were used to reproduce the paint stratigraphy observed on Matisse’s *Le Bonheur de vivre*. A canvas substrate was first prepared in a manner commonly used during the artist’s lifetime. The medium-weight linen artists’ canvas was first stretched and tacked onto a stretcher frame. Application of sizing layers to limit the absorption of oil into the fabric from subsequent layers followed this. Soaking one part by weight of rabbit-skin glue in 15 parts by volume of distilled water for a few hours, and then dissolving the glue in a double boiler created the sizing material. The warm sizing was then applied to the fabric using a hog’s hair brush. A second sizing layer was added after the first layer had dried and had been sanded to remove extraneous fibers and protruding slub threads. A specially prepared ground composed of 60/40 w/w lead white and barium sulfate in linseed oil was made to mimic that found on *Le Bonheur de vivre* in previous studies using SEM-EDS and FTIR.²³⁹ The ground was thinned to
a creamy consistency with a small addition of triple distilled English turpentine and was applied with a priming knife. A second layer was added after the first had dried. The canvas was then allowed to cure for a week before the reference paints were applied.

The five reference oil paints were made by first combining the appropriate dry pigments on a tempered sheet of clean glass. Cold-pressed linseed oil was then added dropwise, and the mixture was roughly mixed using a metal palette knife to create a barely workable paste. The pigments were then thoroughly dispersed into the oil using a glass muller. The reference paints were mulled for approximately 15 minutes until they were smooth, glossy and deemed suitable for application. Glass microscopy slides (Fisher Scientific, 12-544-1) were used to make drawdowns of the dispersed paint samples on the primed canvas. The paints were allowed to dry before analysis. Figure 5.1 details the prepared reference paint samples. The following linseed oil reference paints were created for the study: cadmium sulfide (1.2 g) which was prepared in-house by a precipitation reaction at 50°C in deionized water using CdSO$_4 \cdot 8$ H$_2$O (0.02 g/mL) and Na$_2$S $\cdot$ 9 H$_2$O (0.015 g/mL) solutions. The sodium sulfide solution was poured into the cadmium sulfide solution and stirred while the reaction mixture cooled to room temperature. The pigment particles were filtered and washed with deionized water repeatedly and gently dried. To prevent the formation of CdO on the surface of the particles, and to most closely replicate the known synthesis procedures followed at the turn of the 20$^{th}$ century, no calcinations were used.
Figure 5.1: Schematic of historically-accurate reference paint samples used for artificial aging of CdS pigments. A mixed lead white/barium sulfate ground was applied below hypothetical CdS containing paint layers.
Various mixtures of pigments were created to account for potential pigment-pigment interactions after a period of artificial aging. Lead white (2PbCO₃ • Pb(OH)₂), barium sulfate, and zinc white (ZnO) were sourced from Kremer Pigments (New York). Mixtures included 1:2 cadmium sulfide/lead white; 1:2 cadmium sulfide/zinc white; 1:1:1 lead white/zinc white/cadmium sulfide; and 1:2 cadmium sulfide/cadmium carbonate. The resulting cadmium sulfide particles were characterized by XRD and high-resolution transmission electron microscopy (HR-TEM) (data not shown here), and were observed to have an average crystallite size of 2.9 nm.

5.4.3 Sample Locations from ‘Le Bonheur de vivre’

Four samples from Le Bonheur de vivre were selected for TOF-SIMS imaging: S6, S112-2, S115, and S117. The sampling nomenclature used here preserves that used in all previous publications so that direct comparisons can be made. The locations on the painting are detailed in Figure 5.2. These samples were selected based on both their documented visual changes and because of the extensive synchrotron-based analysis performed on similar samples and regions. S6 was taken from yellow paint near the bottom edge of the painting. S112-2 was taken from the upper-left corner of the painting in the brown foliage area. S115 was taken from the yellow fruit/lemon of the tree on the right of the painting. S117 was taken from yellow paint island in the right foreground region, between the flute player and the reclining couple.
Figure 5.2: Sampling locations on *Le Bonheur de vivre*. Sample S6 and S112-2 were taken on the outer edges of the painting, while S115 and S117 were taken from the inner portion. Reprinted from Voras et al, *Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
5.5 Experimental Details

A key aspect of this work is to establish multiple reference standards for direct comparison to the historic paint cross-sections. This includes the use of artificial aging for weathering of the historically-accurate reference standards. Additionally, as a point of comparison with the TOF-SIMS results, binding medium analysis was also performed with GC-MS to validate the observation of fatty acids and amino acids in the paint layers.

5.5.1 Artificial Aging

The historically accurate paint reference samples were subjected to short-term aging at the Getty Conservation Institute using the Atlas Ci4000 Weather-Ometer. This was equipped with a Xenon light source (75,000 lux), and carried out using the ASTM Gamblin oil paint parameters (45% RH, 25°C, 400 hours). Visible-only and UV-only exposures were carried out on two identical sets of samples. Visible light exposure was carried out for 40 million lux hours, intermediate between ISO Blue Wool 5 and 6. Visual comparison to the reference set of samples at this point revealed no evidence of photo-aging. The samples were deemed to have surfaces that were too inhomogeneous to measure sub-visible delta E color changes.

5.5.2 Microscopic Examination

Reference and historical samples were analyzed under high magnification using a Nikon Eclipse 80i Binocular Microscope (4×, 10×, and 20× objectives), with a Nikon X-cite® 120 mercury lamp for reflected ultraviolet light. Under ultraviolet light, the
samples were viewed using a Nikon BV-2A cube (excitation wavelengths between 400 and 470 nm with barrier filter). Digital images were obtained using a Nikon Digital Eclipse DXM 1200f Camera in conjunction with Automatic Camera Tamer control software for PC operating systems.

5.5.3 Sample Preparation for TOF-SIMS Analysis

Sample preparation for TOF-SIMS analysis was performed as detailed in Chapter 4. Microtomy was used here to expose a fresh, smooth surface of the sample in cross-section for subsequent TOF-SIMS analysis. Due to the friable nature of the paint materials in the historical samples, the TOF-SIMS analysis was performed on the freshly exposed remaining sample surface, and not on the removed thin cross-sections. All paint cross-sections were imbedded in Extec® polyester resin/hardener (mixed at a ratio of approximately 10 mL/0.5 mL). All samples were first hand-trimmed using a Dremel® rotary tool prior to fixing the sample onto an aluminum specimen pin using cyanoacrylate glue. After the resin had cured for at least 24 hours, the sample surface was then prepared by room-temperature microtomy under normal atmospheric conditions. First, the sample was roughly trimmed with a carbon-steel knife (DDK, Inc.) to remove excess resin. A Leica 2035 Jung Biocut (Leica Instruments, GmbH) was used to remove cross-sections less than 1 µm in thickness with a diamond ultramicrotomy knife (DDK, Inc.). Following this, the sample and specimen pin were placed into a sample holder for TOF-SIMS analysis and placed into the TOF-SIMS sample introduction chamber for immediate pump-down.
5.5.4 TOF-SIMS Parameters

TOF-SIMS analysis was performed on a TOF-SIMS IV, upgraded to the capabilities of a TOF-SIMS V (ION-TOF, GmbH) with a bismuth/manganese primary ion source, housed in the Surface Analysis Facility at the University of Delaware. All spectra and images were acquired in the high-current ‘bunched’ mode, utilizing 25-keV Bi$_3^+$ clusters having a pre-bunched pulse width of 640 ps and a target current of ~0.27 pA. A low-energy (75 eV) electron flood gun was utilized to offset any charge accumulation on the sample surface. All images were collected at a pixel density of 128 × 128 pixels, and primary ion dose density less than the static SIMS limit of 1 × 10$^{12}$ ions/cm$^2$. The extraction cone prior to the time-of-flight mass analyzer was pulsed at ± 2 kV depending on the desired secondary-ion polarity, and detection used 10 kV post-acceleration. All sample analysis was performed at an analysis chamber pressure of 5.0 × 10$^{-9}$ mbar or lower.

To estimate the achieved spatial resolution, several ion images of microtomed historical samples were analyzed using the 80%-20% linescan criterion, resulting in an average resolution of 7.5 ± 3.0 µm ($n = 11$). We interpret this to mean that sample-preparation artifacts stemming from microtome-induced smearing were absent or minimal, since similar measurements on a silver edge using the same beam conditions resulted in a similar average 80%-20% linescan edge width of 5.3 ± 0.2 µm ($n = 10$). The small discrepancy in average line width and deviation is explained as the difference between an ideal sample (clean silver edge) and that of a non-ideal sample (microtomed sample containing materials of various hardnesses).
Positive-ion mass-scale calibration was performed with the following ions: H\(^+\), H\(_2\)\(^+\), H\(_3\)\(^+\), C\(^+\), CH\(^+\), CH\(_2\)\(^+\), CH\(_3\)\(^+\), C\(_2\)H\(_2\)\(^+\), C\(_3\)H\(_3\)\(^+\), C\(_4\)H\(_4\)\(^+\), C\(_5\)H\(_5\)\(^+\), C\(_6\)H\(_6\)\(^+\), and C\(_7\)H\(_7\)\(^+\). The negative-ion mass scale was calibrated with the following ions: H\(^-\), H\(_2\)\(^-\), C\(^-\), CH\(^-\), CH\(_2\)\(^-\), CH\(_3\)\(^-\), C\(_2\)H\(^-\), C\(_3\)\(^-\), C\(_4\)\(^-\), C\(_5\)\(^-\), C\(_6\)\(^-\), and C\(_7\)\(^-\). After calibration, instrumental performance metrics were calculated. For negative-mode spectra, 150 peaks were selected from the 10 cross-sectional samples and used for the calculation of some performance metrics. Mass accuracy was calculated to be 4.7 ± 3.9 (n = 150) mAMU, mass precision was calculated to be 103 ± 44 ppm (n = 150), and mass resolving power (m/Δm) was calculated to be 6,000 ± 800 (n = 150; m values ranged from 2526 to 10622). For positive-mode spectra, 130 peaks were selected from the 10 cross-sectional samples and used for the calculation of some performance metrics. Mass accuracy was calculated to be 2.8 ± 2.2 mAMU (n = 130), mass precision was calculated to be 29 ± 26 ppm (n = 130), and mass resolving power (m/Δm) was calculated to be 6,100 ± 1,200 (n = 130; m values ranged from 2105 to 10208). These calculated performance metrics were consistent with previous performance metrics on similar samples, and indicate that TOF-SIMS analysis was able to achieve mass fragment identification based on exact mass assignment, which when used in conjunction with expected isotopic ratios, allowed for unambiguous peak identification. All data processing was completed on ION-TOF Measurement Explorer software, version 6.2. Ion spectra and ion images were normalized to total ion intensity. ImageJ software (version 1.48) was used to produce the positive-mode metal-ion overlay images in Figure 5.4.
5.5.5 Gas-Chromatography Mass Spectrometry (GC-MS) Parameters

A single sample for aggregate analysis was collected from the bottom edge of the painting (near sample S6) and was first analyzed for fatty acids, waxes, and resins. It was then prepared for amino-acid analysis. To reduce the molecular weight and make the components more volatile, one-step treatment of the samples with MethPrep II reagent (Fisher Scientific-Alltech) converted carboxylic acids and esters to their methyl ester derivatives. The sample was placed in a tightly-capped, heavy-walled vial (100-300 µL) and approximately 100 L (or less for smaller samples) of 1:2 MethPrep II reagent in benzene was added to the sample. The vial was warmed at 60°C for one hour on a heating block, removed from heat, and allowed to cool. Analysis was carried out using a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass-selective detector (MSD) and a 7683 automatic liquid injector. Prior to injection the inlet temperature was set to 300°C and the transfer line temperature for the MSD (SCAN mode) was set to 300°C. A sample volume (splitless) of 1 µL was then injected onto a 30-m × 250-µm × 0.25-µm film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 2.3 mL/min). The oven temperature was held at 55°C for two minutes, then programmed to increase at 10°C/min to 325°C where it was held for 10.5 minutes for a total acquisition time of 40 minutes. Methanol was used as the rinse solvent in the syringe preparation.

For subsequent protein analysis the sample was dried down and then heated for 24 hours at 105°C in 5.5-M HCl in a tightly-capped, heavy-walled vial (100-300 µL). The sample was again evaporated to dryness with a gentle stream of pure N2. Approximately 100 µL of MTBSTFA + 1%TBDMCS silylating reagent (Pierce
Chemical Co.) was added to the sample and the vial was capped and heated at 60°C for one hour prior to injection. Analysis was carried out using the RTLMPREP method on the GC-MS. Samples were analyzed using the Hewlett-Packard 6890 gas chromatogram equipped with 5973 mass-selective detector and 7683 automatic liquid injector. Prior to injection the inlet temperature was set to 300°C and the transfer line temperature for the MSD (SCAN mode) was set to 300°C. A sample volume (splitless) of 1µL was injected onto a 30-m × 250-m × 0.25-m film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 1.5 mL/min). The oven temperature was held at 50°C for two minutes, then programmed to increase at 10°C/min to 325°C where it was held for 10.5 minutes for a total acquisition time of 40 minutes. Hexane was used as the rinse solvent in the syringe preparation.

5.6 Results

Because of the complex, multi-composition, and uncontrolled status of the historical samples, a quantitative analysis by TOF-SIMS was not attempted in this study, nor is it typically attempted. Rather, the results presented here were used to infer trends in the data from the spatial positioning and relative intensities (contrast) of the ion emission distributions of the imaged mass fragments, allowing us to form conclusions concerning CdS and binding-medium alteration. It is imperative to identify mass fragments based on exact mass and isotopic ratio to ensure a positive identification. Figure 5.3 is a reference for the process of identification by exact mass and isotopic profile. The top spectrum is of the CdCl\textsuperscript{2−} mass fragment observed in pure standard CdCl\textsubscript{2} powder. Notice the distinct isotopic profile expected from the distribution of
Figure 5.3: Negative-mode ToF-SIMS mass spectra showing isotopic profile of cadmium-containing species. The CdCl\textsuperscript{−} mass fragment that was used to image CdCl\textsubscript{2} impurity in cadmium yellow pigment was selected for representation. The top spectrum resulted from the analysis of the pure reference CdCl\textsubscript{2} powder. Note the minimal hydrocarbon peaks that are right-shifted of nominal mass. The bottom spectrum was obtained from the analysis of Bonheur de vivre sample S115. In contrast to the pure standard powder, the right-shifted hydrocarbon peaks are major components of the spectrum, whereas the left-shifted inorganic peaks are now minor components in the inset spectrum. The arrow in the inset points to the CdCl\textsuperscript{−} mass fragment at $m/z$ 148.873. A comparison of expected isotope ratios and calculated isotope ratios for these spectra is given in Table 5.1. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
Table 5.1: Comparison of expected isotope ratios versus calculated isotope ratios for the CdCl\textsuperscript{−} mass fragment in the pure CdCl\textsubscript{2} reference powder and Bonheur de vivre sample S115, as shown in Figure 5.3. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.

<table>
<thead>
<tr>
<th>Isotopic Mass (m/z)</th>
<th>Expected Isotope Ratio (%)</th>
<th>CdCl\textsubscript{2} Standard</th>
<th>Matisse S115</th>
</tr>
</thead>
<tbody>
<tr>
<td>140.875</td>
<td>0.95</td>
<td>1.09</td>
<td>0.99</td>
</tr>
<tr>
<td>142.872</td>
<td>0.98</td>
<td>1.03</td>
<td>1.11</td>
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<tr>
<td>152.871</td>
<td>1.81</td>
<td>1.87</td>
<td>5.60</td>
</tr>
</tbody>
</table>
both Cd and Cl isotopes found in CdCl₂. The corresponding peak areas as isotope abundance (%) are given in Table 5.1. The bottom spectrum of Figure 5.3 is of the same mass region as the top spectrum, although the spectrum was obtained from the S115 sample taken from Bonheur de vivre. The CdCl⁻ mass fragment peaks are the small peaks that are left-deviated from nominal mass. The larger right-deviated peaks are due to hydrocarbons in the S115 binding medium and/or in the resin cube which holds sample S115, since the spectrum shown here is from the total area of analysis, which we know to include the parts of the resin as well as parts of the S115 sample. The CdCl⁻ isotopic abundance (%) for sample S115 is given in Table 5.1 in comparison to the pure standard CdCl₂ powder. The inset shows a greatly expanded mass axis of the same data, in which it is clear that spectral resolution easily allows for separation and quantification of the CdCl⁻ species from the hydrocarbon species. Comparison of the expected isotope ratio (Table 5.1, column 2) with the observed isotope ratio of the pure CdCl₂ standard (Table 5.1, column 3) shows the expected excellent agreement. On the other hand, comparison of the expected isotope ratio (Table 5.1, column 2) with the observed isotope ratio for the S115 sample (Table 5.1, column 4) shows the presence of larger deviations. These deviations in isotopic ratio can be attributed to overlap of signal from CdS⁻ and its isotope distribution, as expected from a real-world paint sample known to contain both CdS and CdCl₂.

5.6.1 Reference Materials Analyzed Using TOF-SIMS

In previous studies the presence of paint alteration products and residual reagents from the synthesis of CdS pigment have been identified by synchrotron-based analyses.²³⁹,²⁴⁰ To confirm that these materials are indeed leftover synthesis reagents it
is necessary to first analyze the Cd-containing references in pure powder form before analyzing new and aged samples in cross-sectional form (spectra and images of the powders are not shown). From the TOF-SIMS analysis, the pure CdS powder mass fragments were mainly comprised of CdS\(^-\) (145.875 m/z) and CdSO\(_4\)^- (209.855 m/z). The CdSO\(_4\)\(^-\) in the corresponding TOF-SIMS images of the powder film of the standard co-localizes identically to that of the CdS\(^-\), so it is important to distinguish unique fragments by spectral features (exact mass, isotopic profile) and image features (co-localization of mass fragments) to determine identity. Unique mass fragments for the standard CdCl\(_2\) were CdCl\(^-\) (148.872 m/z), CdCl\(_2\)^- (183.841 m/z) and CdCl\(_3\)^- (218.810 m/z). No fragments due to additional cadmium compounds focused on in this study were identified in the CdCl\(_2\) standard material (such as CdS, CdSO\(_4\), and CdCO\(_3\)). Due to the possibility of overlap of responses from CdCl\(_2\)^- and chromate pigment Cr\(_2\)O\(_5\) (183.856 m/z, a difference of 0.015 m/z) signal, TOF-SIMS images shown will be that of the mass fragment CdCl\(^-\).

TOF-SIMS analysis of the standards CdCO\(_3\) and CdSO\(_4\) powder identified several unique mass fragments, however some key beam-induced alteration was noted. The CdCO\(_3\) analysis produced the unique mass fragment CdCO\(_3\)^- (173.888 m/z). In addition, the mass fragments for CdCO\(_2\)^- (157.893 m/z) and CdCO\(^-\) (141.899 m/z) were observed. CdSO\(_4\) produced unique fragments for CdSO\(_2\)^- (177.865 m/z), CdSO\(_4\)^- (209.855 m/z) and CdSO\(^-\) (161.870 m/z). However, critically, the analysis of the CdSO\(_4\) standard also generated mass fragments for CdS\(^-\) (145.875 m/z) and CdSO\(_4\)O\(^-\) (225.850 m/z). This mass is very similar to that of CdS\(_2\)O\(_3\) (225.832 m/z, a difference of 0.018 m/z), which could cause a possible misidentification. When these
fragments were imaged on the standard CdSO$_4$ powder, all the fragments were found to identically co-localize, confirming that they were a result of beam-induced breakdown or rearrangement of the CdSO$_4$ analyte. These results suggest that the identification of CdS$_2$O$_3$ and CdS can be confirmed providing the TOF-SIMS images are not identical to the mass fragment image generated by CdSO$_4$. To identify unique mass fragments associated with CdC$_2$O$_4$, the powdered sample was analyzed, and produced signals for CdC$_2$O$_4^+$ (201.883 m/z) and CdC$_2^-$(137.903 m/z). Due to their chemical similarity, both the CdCO$_3$ and CdC$_2$O$_4$ standards produced the mass fragments CdCO$_2^-$ (157.893 m/z) and CdCO$^-$ (141.899 m/z), so these mass fragments were not used for identification.

Additional reference paint samples (described above) were prepared to mimic the stratigraphy encountered in cross-sectional samples taken from Le Bonheur de vivre, of which only the “pure” cadmium sulfide reference sample is shown herein as an example of freshly prepared, unaltered cadmium sulfide pigment. The TOF-SIMS images relating to positive ion species found in samples S6, S112-2, S115, and S117 are also shown in Figure 5.4 for comparison. All samples in this study were analyzed by SEM-EDX to confirm when CdS from cadmium yellow (and/or other yellow pigments such as chromium) was present (not shown). Sample S115 included in this study had been previously analyzed with SEM-EDS SR-µXRF, µXANES, and SR-FTIR imaging to begin to probe its alteration history, and sample S117 had been analyzed by SEM-EDS and SR-FTIR imaging.$^{239,240}$
Figure 5.4: Optical images and positive-mode overlay of metal ions in the various samples (from left to right: the CdS reference sample, S6, S112-2, S115, S117). The first (top) row is the visual image taken after TOF-SIMS analysis. The second row is the same image, but taken with ultraviolet illumination. The third row is an overlay of positive metal ions identified in the samples. The dotted lines are drawn to highlight the different layers. For all samples, layer “1” is the ground layer (only present on the CdS reference, S6, and S112-2). Layer “2a” is considered the “lower” paint layer, which is usually protected against significant alteration by “2b” the upper paint layer. Lastly, for samples showing significant amounts of alteration the “3” layer closest to atmosphere has formed into an “alteration crust”. The fourth (bottom) row is the optical image from the TOF-SIMS, with the outlined white box being the area of analysis. Note that S117 was large enough to consist of two analysis areas within one image without the risk of oversampling effects, with the two images being processed together in ImageJ. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
5.6.2 Degradation Products Associated with CdS Reagents and Photo-Oxidation

Figures 5.5 – 5.9 shows the mass fragments associated with residual starting materials and photo-induced oxidation products signal for samples S6, S112-2, S115, and S117 (sampling locations shown in Figure 5.2) as well as the photo-aged CdS reference sample. The first (top, left) image corresponds to the emission distribution of CdS$^-$ mass fragment (average 145.870 m/z) that is used to represent unaltered CdS pigment. The second (top, middle) image corresponds to the emission distribution of CdCl$^-$ mass fragment (average 148.873 m/z) that is used to represent residual CdCl$_2$ from the CdS synthesis process. The third (top, right) image corresponds to the emission distribution of CdSO$_4^-$ (average 209.852 m/z) that is used to represent the soluble CdSO$_4$ oxidation product. The fourth (bottom, left) image corresponds to the emission distribution of CdCO$_3^-$ (average 173.892 m/z) that is used to represent the insoluble CdCO$_3$ oxidation product. The fifth (bottom, right) image corresponds to the emission distribution of CdSO$_4$O$^-$ (average 225.850 m/z) that corresponds to either CdSO$_4$ if spatially identical to CdSO$_4^-$ or to CdS$_2$O$_3^-$ if spatially different. Samples S6, S112-2, S115, and S117 all show a fairly uniform distribution of CdCl$^-$ throughout the same CdS$^-$ area, indicating a fairly uniform dispersion of residual CdCl$_2$ contained in the paint layers. This indicates that CdCl$_2$ is an expected impurity in the CdS pigment found throughout Le Bonheur de vivre, as it is located in both intact and altered paint layers (samples S112-2 and S115). It should be noted while CdCl$_2$ mimics CdS behavior, the co-localization is not identical, and certain “hotspots” of either material can be observed. This may be attributed to areas where the CdS and...
the CdCl₂ remain unaltered or may be due to the inhomogeneous nature of the original pigment.

The cross-sectional CdS reference sample (Figure 5.5) revealed the presence of a number of sulfates present in the paint layer as well as the ground due to the presence of barium sulfate used in the ground formulation (not shown). In this case it is not clear whether the strong signal for CdSO₄⁻ in the paint is attributed to the residual cadmium sulfate starting reagent from the pigment synthesis or associated with the photo-oxidation of the CdS due to artificial aging. A low signal for CdCl⁻ was also detected in the reference sample and, as chlorides were not used as reagents for the standard CdS synthesis, it is assumed that this trace amount of atmospheric-based chlorine may have been a residual contaminant from the production of the CdS powder. Of greater interest is the lack of CdCO₃ (as represented by the mass fragment CdCO₃⁻), an insoluble product that has previously been associated with degradation mechanisms involving CdS.²³⁷-²⁴⁰ From this observation we deduce that the protocol and duration used to artificially age the paints may not have been severe enough to drive some of the reactions associated with CdS degradation or that other factors may be involved with these mechanisms (e.g. high humidity/heat, the unexpected presence of chlorides, etc.)

Another important component of CdS alteration is the formation of CdSO₄ · nH₂O, CdCO₃, and CdS₂O₃. These materials may cause fading (as they are all white powders) and eventual instability of the paint layer if present, and are products of photo-induced oxidation of CdS as noted in the literature.²³⁷-²⁴⁰ Figures 5.6 – 5.9 shows the CdSO₄⁻
and CdCO$_3^-$ signals for samples S6, S112-2, S115, S117, in addition to the photo-aged CdS reference sample. As noted, the images of the mass fragment CdSO$_4$O$^-$ that are directly identical to that of CdSO$_4^-$, indicating that CdS$_2$O$_3$ is not present except for sample S115. Image (L) in Figure 5.8 shows discrete particle formation along the paint layer interfaces and the upper “alteration crust” that is significantly different than the image of mass fragment CdSO$_4^-$. Of particular interest is the images related to CdCO$_3$ formation as CdCO$_3$ is not hypothesized as a reagent in the CdS synthesis process for the paints used by Matisse to create *Le Bonheur de vivre*, and its presence would indicate photo-induced oxidation CdS pigment alteration.$^{239,240}$

Although the reference samples were artificially aged as described above, it is possible that a longer exposure time is necessary to observe this particular species as earlier studies have found CdCO$_3$ to be closely linked to CdS photo-oxidation reactions.$^{239,240}$ This further supports the hypothesis that the CdSO$_4$ signal associated with the cross-sectional reference sample (shown in Figure 5.5) is likely due to the large amount of residual soluble sulfides that were used to create the pigment.

In comparing the images in Figures 5.6 – 5.9, the CdSO$_4^-$ and CdS$^-$ signals were not found to co-localize, indicating that they are unique fragments pertaining to the identification of photo-induced oxidation products and/or as residual starting material and are not visible due to beam-induced alteration. Sample S6 (Figure 5.6) has a uniform distribution of both CdSO$_4^-$ and CdCO$_3^-$ signal throughout the paint layer. The paint is fairly thin in this region and lacking a protective surface coating, factors that would influence the production of alteration products that might extend throughout the
Figure 5.5: TOF-SIMS images of the mass fragments associated with residual starting materials and/or photo-induced oxidation of CdS pigment observed in the pure CdS reference sample. Dotted outlines correlate to described layers as detailed in Figure 5.4. The details of each image are as follows; (A) CdS$^-$ emission distribution with maximum intensity per pixel (MC) = 17, and the total ion count per image (TIC) = $9.720 \times 10^3$; (B) CdCl$^-$ emission distribution, MC = 5, TIC = $3.092 \times 10^3$; (C) CdSO$_4^-$ emission distribution, MC = 20, TIC = $2.343 \times 10^4$; (D) CdCO$_3^-$ emission distribution, MC = 2, TIC = $5.380 \times 10^2$; (E) CdSO$_4$O$^-$ emission distribution, MC = 27, TIC = $2.331 \times 10^4$. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
Figure 5.6: TOF-SIMS images of the mass fragments associated with residual starting materials and/or photo-induced oxidation of CdS pigment observed in sample S6 from *Le Bonheur de vivre*. Dotted outlines correlate to described layers as detailed in Figure 5.4. The details of each image are as follows; (F) CdS$^-$ emission distribution, MC = 4, TIC = $8.210 \times 10^2$; (G) CdCl$^-$ emission distribution, MC = 4, TIC = $1.252 \times 10^3$; (H) CdSO$_4^-$ emission distribution, MC = 4, TIC = $1.546 \times 10^3$; (I) CdCO$_3^-$ emission distribution, MC = 5, TIC = $2.289 \times 10^3$; (J) CdSO$_4$O$^-$ emission distribution, MC = 4, TIC = $1.570 \times 10^3$. Reprinted from Voras *et al.*, *Applied Physics A* 2015, 121:1015-1030, with permission of Springer.
Figure 5.7: TOF-SIMS images of the mass fragments associated with residual starting materials and/or photo-induced oxidation of CdS pigment observed in sample S112-2 from Le Bonheur de vivre. Dotted outlines correlate to described layers as detailed in Figure 5.4. The details of each image are as follows; (K) CdS$^-$ emission distribution, MC = 4, TIC = $1.384 \times 10^3$; (L) CdCl$^-$ emission distribution, MC = 8, TIC = $3.515 \times 10^3$; (M) CdSO$_4^-$ emission distribution, MC = 5, TIC = $1.928 \times 10^3$; (N) CdCO$_3^-$ emission distribution, MC = 5, TIC = $1.154 \times 10^3$; (O) CdSO$_4$O$^-$ emission distribution, MC = 7, TIC = $2.267 \times 10^3$. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
Figure 5.8: TOF-SIMS images of the mass fragments associated with residual starting materials and/or photo-induced oxidation of CdS pigment observed in sample S115 from *Le Bonheur de vivre*. Dotted outlines correlate to described layers as detailed in Figure 5.4. The details of each image are as follows; (P) CdS$^-$ emission distribution, MC = 11, TIC = $7.562 \times 10^3$; (Q) CdCl$^-$ emission distribution, MC = 31, TIC = $2.912 \times 10^4$; (R) CdSO$_4^-$ emission distribution, MC = 15, TIC = $1.040 \times 10^4$; (S) CdCO$_3^-$ emission distribution, MC = 11, TIC = $6.301 \times 10^3$; (T) Due to the formation of discrete particles at the layer interfaces and in the alteration crust, CdS$_2$O$_5^-$ emission distribution, MC = 5, TIC = $1.154 \times 10^3$. Reprinted from *Voras et al, Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
Figure 5.9: TOF-SIMS images of the mass fragments associated with residual starting materials and/or photo-induced oxidation of CdS pigment observed in sample S117 from *Le Bonheur de vivre*. Dotted outlines correlate to described layers as detailed in Figure 5.4. The details of each image are as follows: (U) CdS$^-$ emission distribution, MC = 5, TIC = $1.195 \times 10^3$; (V) CdCl$^-$ emission distribution, MC = 6, TIC = $2.218 \times 10^3$; (W) CdSO$_4^-$ emission distribution, MC = 3, TIC = $9.350 \times 10^2$; (X) CdCO$_3^-$ emission distribution, MC = 4, TIC = $2.057 \times 10^3$. (Y) CdSO$_4$O$^-$ emission distribution, MC = 4, TIC = $1.043 \times 10^3$. Reprinted from Voras et al, *Applied Physics A* 2015, 121:1015-1030, with permission of Springer.
entire thickness of the paint layer. In the upper left region of the paint layer in sample S112-2 (Figure 5.7), the CdS\textsuperscript{−}, CdSO\textsubscript{4}\textsuperscript{−}, and CdCO\textsubscript{3}\textsuperscript{−} signals appear to be somewhat uniform, with slight aggregation towards the surface. The lower right region of paint in sample S112-2 showed a more uniform distribution of CdSO\textsubscript{4}\textsuperscript{−} and CdCO\textsubscript{3}\textsuperscript{−}. In the alteration crust of Sample S115 (Figure 5.8, which fragmented during the casting process), the photo-induced oxidation product CdS\textsubscript{2}O\textsubscript{3}\textsuperscript{−} is considered a unique mass fragment as the TOF-SIMS image does not co-localize with CdSO\textsubscript{4}\textsuperscript{−}, and has a discrete particle-like appearance. This discrete behavior of CdS\textsubscript{2}O\textsubscript{3}\textsuperscript{−} continues into the alteration zone where it stops at the interface between the altered and unaltered regions. CdSO\textsubscript{4}\textsuperscript{−} is nearly uniform throughout the alteration crust and the upper paint layers with signal intensity decreasing into the lower paint layer. CdCO\textsubscript{3}\textsuperscript{−} behaves similarly to CdSO\textsubscript{4}\textsuperscript{−} in its uniformity and location. The location of CdS\textsuperscript{−} is nearly the opposite of the photo-induced oxidation products in sample S115 suggesting that in some areas the CdS pigment has become altered through oxidation processes. The CdS\textsuperscript{−} has the strongest signal towards the lower portion of the sample, where the paint layer has been more protected from light damage. Lastly, sample S117 (Figure 5.9) is analogous in the appearance photo-induced oxidation products as the CdS\textsuperscript{−} present in the thin, upper layer appears to have been completely replaced by CdSO\textsubscript{4}\textsuperscript{−} and CdCO\textsubscript{3}\textsuperscript{−}, a definitive marker for the formation of an alteration crust, with the thick, lower paint layers showing minimal photo-induced oxidation product signal.

5.6.3 Hydrolytic breakdown of long-chain fatty acids

A key feature of TOF-SIMS analysis of paint cross-sections is the ability to simultaneously image both inorganic and organic species within a sample. Using this
ability it was possible to observe mass fragments related to hydrolytic breakdown of
the long-chain fatty acids comprising the binding medium component and also their
interaction with CdS pigment. As shown in previous studies long-chain fatty acids
(such as palmitic and stearic) have been imaged in negative-mode in paintings ranging
from the 14th to the 20th centuries and are used here to estimate binding medium
degradation due to pigment oxidation forcing acidification of the binding medium
leading to hydrolytic breakdown of the long-chain fatty acid components of the
binding medium. In addition, the formation of oxalates was observed in several
of the paint samples, a product that is likely due to pigment-binder interactions
resulting from photo-oxidation and/or reactions exacerbated by the application of
unoriginal organic materials during previous restoration campaigns.

Figures 5.10 – 5.14 detail the relevant mass fragments for long-chain fatty acids and
CdC₂O₄ as observed in the cross-sectional samples collected from *Le Bonheur de vivre*
as well as the CdS reference sample. The first (left) image corresponds to the emission
distribution of CdC₂O₄⁻ (average 201.880 m/z) that is used to represent the CdC₂O₄
hydrolysis product. The second (middle) image corresponds to the emission
distribution of C₁₆H₃₁O₂⁻ (average 255.230 m/z) that is used to represent the
remaining long-chain palmitic acid component of the binding medium. The third
(right) image corresponds to the emission distribution of C₁₈H₃₅O₂⁻ (average 283.262 m/z)
that represents the remaining long-chain stearic acid component of the binding
medium. The mass fragment CdC₂O₄ was chosen to represent CdC₂O₄ formation with
palmitic and stearic acid mass fragments shown to represent binding medium
degradation. The CdS reference sample (Figure 5.10) showed expected strong signals
for palmitic and stearic acids throughout the paint and ground layers, but no signal for CdC$_2$O$_4^-$ due to the freshly prepared and minimal aging of the reference sample. Surprisingly, nearly all of the samples collected from the painting show a significant depletion of fatty acid signals in the uppermost paint layers as previously hypothesized by Leone, et al. Sample S6 (Figure 5.11) shows significant loss of long-chain fatty acids as well as a uniform distribution of CdC$_2$O$_4^-$ throughout the paint layer. Although S6 suffered from fragmentation during sample preparation, small areas containing traces of the white ground show relatively strong signals for long-chain fatty acids. A similar trend was observed in Sample S112-2 (Figure 5.12), with the lead-containing ground displaying a strong signal for palmitic and stearic acids. The paint layer in S112-2 is not present as a continuous layer. One section of the paint layer appears to generate strong signals for long-chain fatty acids, suggesting that this particular section of the paint layer may have been protected from light or stabilized during a previous restoration using a consolidant. Conversely, the left (or top) section of the paint layer (an area that was likely exposed to incident light), shows a complete loss of long-chain fatty acid signal while the CdC$_2$O$_4^-$ signal is observed with relative uniformity in all regions containing the CdS pigment.

Samples S115 and S117 do not contain the white ground but do possess examples of an alteration crust that can form atop CdS containing paints. The majority of CdC$_2$O$_4^-$ signal in S115 (Figure 5.13) can be found in the alteration crust and the upper paint layer with a portion of higher intensity signal in the interface between the upper and lower paint layers. In addition, the alteration crust and upper paint layers are nearly void of long-chain fatty acid signal, with the lower paint layer containing the strongest...
Figure 5.10: TOF-SIMS images of the mass fragments associated with hydrolytic breakdown of long-chain fatty acids in the binding medium of the cross-sectional samples taken from the pure CdS reference. Dotted outlines correlate to described layers in Figure 5.4. The details of each image are as follows; (A) $\text{CdC}_2\text{O}_4^-$ emission distribution, $\text{MC} = 3$, $\text{TIC} = 1.341 \times 10^3$; (B) $\text{C}_{16}\text{H}_{31}\text{O}_2^-$ emission distribution, $\text{MC} = 64$, $\text{TIC} = 1.579 \times 10^5$; (C) $\text{C}_{18}\text{H}_{35}\text{O}_2^-$ emission distribution, $\text{MC} = 54$, $\text{TIC} = 1.026 \times 10^5$. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
Figure 5.11: TOF-SIMS images of the mass fragments associated with hydrolytic breakdown of long-chain fatty acids in the binding medium of the cross-sectional sample S6 taken from *Le Bonheur de vivre*. Dotted outlines correlate to described layers in Figure 5.4. The details of each image are as follows; (D) CdC$_2$O$_4^-$ emission distribution, MC = 8, TIC = 2.890 $\times$ 10$^3$; (E) C$_{16}$H$_{31}$O$_2^-$ emission distribution, MC = 7, TIC = 2.448 $\times$ 10$^3$; (F) C$_{18}$H$_{35}$O$_2^-$ emission distribution, MC = 3, TIC = 7.210 $\times$ 10$^2$. Reprinted from *Voras et al, Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
Figure 5.12: TOF-SIMS images of the mass fragments associated with hydrolytic breakdown of long-chain fatty acids in the binding medium of the cross-sectional sample S112-2 taken from *Le Bonheur de vivre*. Dotted outlines correlate to described layers in Figure 5.4. The details of each image are as follows; (G) CdC$_2$O$_4^-$ emission distribution, MC = 5, TIC = $1.955 \times 10^3$; (H) C$_{16}$H$_{31}$O$_2^-$ emission distribution, MC = 68, TIC = $5.524 \times 10^4$; (I) C$_{18}$H$_{35}$O$_2^-$ emission distribution, MC = 16, TIC = $1.776 \times 10^4$. Reprinted from Voras et al, *Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
Figure 5.13: TOF-SIMS images of the mass fragments associated with hydrolytic breakdown of long-chain fatty acids in the binding medium of the cross-sectional sample S115 taken from *Le Bonheur de vivre*. Dotted outlines correlate to described layers in Figure 5.4. The details of each image are as follows; (J) CdC$_2$O$_4^-$ emission distribution, MC = 9, TIC = 4.338 $\times$ 10$^3$; (K) C$_{16}$H$_{31}$O$_2^-$ emission distribution, MC = 12, TIC = 5.469 $\times$ 10$^3$; (L) C$_{18}$H$_{35}$O$_2^-$ emission distribution, MC = 31, TIC = 1.852 $\times$ 10$^4$. Reprinted from *Voras et al, Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
Figure 5.14: TOF-SIMS images of the mass fragments associated with hydrolytic breakdown of long-chain fatty acids in the binding medium of the cross-sectional sample S117 taken from Le Bonheur de vivre. Dotted outlines correlate to described layers in Figure 5.4. The details of each image are as follows; (M) CdC$_2$O$_4^-$ emission distribution, MC = 4, TIC = $3.744 \times 10^3$; (N) C$_{16}$H$_{31}$O$_2^-$ emission distribution, MC = 7, TIC = $1.381 \times 10^4$; (O) C$_{18}$H$_{35}$O$_2^-$ emission distribution, MC = 3, TIC = $2.366 \times 10^3$. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
signal intensity. While sample S117 (Figure 5.14) also shows low-intensity signal for CdC$_2$O$_4$ in the upper paint layer, a mass fragment of an isotope of Cr$_2$O$_6$ overlaps with the signal, giving the false impression that there is larger build up of oxalates in the lower layer (the lower paint layer in this case does contain chromium yellow). As with S115, the fatty-acid component of sample S117 shows a fairly strong, uniform signal throughout the lower paint layer with a decreased intensity signal in the upper paint layer. Long-chain fatty acids have been previously identified using TOF-SIMS analysis in easel paintings containing drying oil and egg tempera (egg yolk) that date to the 15$^{th}$-century thus it is surprising to encounter such a low signal for palmitic and stearic acids in a painting dating to 1905/6. Analysis using gas chromatography-mass spectrometry confirmed the presence of palmitic, stearic, and azelaic acids, the latter confirming the presence of partially un-oxidized drying oil as shown in Figure 5.15. The sample collected for GC-MS analysis, however, was collected from the bottom edge of the painting to reduce visible damage to the painting, and it is likely that these species represent the oil-containing ground that is exposed along the tacking margin.

5.6.4 Detection of Amino Acid Components

Analysis using TOF-SIMS allowed for the co-localization of amino acid fragments in several cross-sections collected from the painting, providing some insight into the complicated stratigraphy and restoration history of Le Bonheur de vivre, an artwork that was created during a crucial yet experimental period of Matisse’s career. Various TOF-SIMS studies have identified unique mass fragments associated with the individual amino acids that are found in large proteins. Additionally, GC-MS
Figure 5.15: Results of the GC-MS analysis performed on a sample taken from the outer edge (near sample S6) of *Le Bonheur de vivre* confirms the identification of long-chain fatty acids and amino acid fragments in the painting. Chromatogram (A) is from the fatty acid derivitization as detailed in section 5.5.5 of this text. Because the GC-MS analysis requires digestion of an entire sample, the spatial positioning of the identified compounds in the chromatograms is unclear. Reprinted from Voras et al, *Applied Physics A* 2015, 121:1015-1030, with permission of Springer.
studies of aged binding media have identified certain amino acids that are expected to be stable during the expected humidity and temperature fluctuations resulting from storage and display of works of art.\textsuperscript{278,279} Building on this foundation, recent studies have demonstrated the ability of TOF-SIMS to distinguish between egg and animal glue (or gelatin) proteins found in paint cross-sections.\textsuperscript{269,270} From these studies it is possible to use the amino acid hydroxyproline to distinguish collagen proteins from egg yolk proteins by univariate methods as the amino acid hydroxyproline is only found in collagen protein and is identified by the unique mass fragment C\textsubscript{4}H\textsubscript{6}NO\textsuperscript{+}. Images in Figures 5.16 and 5.17 show mass fragments for amino acids that were found in the samples collected from \textit{Le Bonheur de vivre}. Shown are mass fragments for glycine (CH\textsubscript{2}N\textsuperscript{+}, 30.034 m/z) and hydroxyproline (C\textsubscript{4}H\textsubscript{6}NO\textsuperscript{+}, 86.061 m/z) while additional amino acid mass fragments (alanine, proline, valine, and isoleucine/leucine) were imaged but not shown here to confirm the presence of proteinaceous material. These amino acid fragments were used to identify animal glue (or gelatin) in samples collected near or along the outer edges of \textit{Le Bonheur de vivre}, as the hydroxyproline fragment was detected in both S6 and S112-2. GC-MS of a sample collected along the edge of the painting (near S6) also confirmed the presence animal glue (or gelatin) protein (Figure 5.18). In both cases, it is difficult to confirm the original source of the collagen, as this material could have possibly been used during the an early restoration lining or may even be residue associated with strips of linen tape that were later adhered to the outer edges (likely containing a glue or gum-glue adhesive). Gel electrophoresis and liquid chromatography mass spectrometry (LC-MS) techniques were used to identify collagen (bovine source) on Matisse’s \textit{Le Luxe II} painted in 1907, however the painting
Figure 5.16: TOF-SIMS images of selected mass fragments associated with amino acid markers observed in the pure CdS reference sample, and cross-sectional sample S6 taken from Le Bonheur de vivre. Dotted outlines correlate to described layers in Figure 5.4. The first (top) row of images corresponds to the emission distribution of $\text{CH}_4\text{N}^+$mass fragment (average 30.033 m/z) that is used to represent the amino acid glycine (GLY), as well as generic amino acid fragment. The second (bottom) row of images corresponds to the emission distribution of $\text{C}_4\text{H}_8\text{NO}^+$mass fragment (average 86.065 m/z) that is used to represent the amino acid hydroxyproline (HYP) that is used as a univariate identifier for the presence of collagen protein. The first column is the CdS reference showing (A) $\text{CH}_4\text{N}^+$emission distribution, MC = 6, TIC = $3.306 \times 10^3$; (B) $\text{C}_4\text{H}_8\text{NO}^+$emission distribution, MC = 3, TIC = $1.527 \times 10^3$. The second column is sample S6 showing (C) $\text{CH}_4\text{N}^+$emission distribution, MC = 16, TIC = $6.415 \times 10^3$; (D) $\text{C}_4\text{H}_8\text{NO}^+$emission distribution, MC = 9, TIC = $1.428 \times 10^3$. Reprinted from Voras et al, Applied Physics A 2015, 121:1015-1030, with permission of Springer.
Figure 5.17: TOF-SIMS images of selected mass fragments associated with amino acid markers observed in the cross-sectional samples S112-2, S115, and S117 taken from *Le Bonheur de vivre*. Dotted outlines correlate to described layers in Figure 5.4. The first (top) row of images corresponds to the emission distribution of CH$_4$N$^+$ mass fragment (average 30.033 m/z) that is used to represent the amino acid glycine (GLY), as well as generic amino acid fragment. The second (bottom) row of images corresponds to the emission distribution of C$_4$H$_8$NO$^+$ mass fragment (average 86.065 m/z) that is used to represent the amino acid hydroxyproline (HYP) that is used as a univariate identifier for the presence of collagen protein. The first column is sample S112-2 showing (E) CH$_4$N$^+$ emission distribution, MC = 27, TIC = $6.429 \times 10^3$; (F) C$_4$H$_8$NO$^+$ emission distribution, MC = 6, TIC = $5.380 \times 10^2$. The second column is sample S115 showing (G) CH$_4$N$^+$ emission distribution, MC = 35, TIC = $1.084 \times 10^3$; (H) C$_4$H$_8$NO$^+$ emission distribution, MC = 2, TIC = $7.560 \times 10^2$. The third column is sample S117 showing (I) CH$_4$N$^+$ emission distribution, MC = 5, TIC = $2.057 \times 10^3$; (J) C$_4$H$_8$NO$^+$ emission distribution, MC = 2, TIC = $2.820 \times 10^2$. Reprinted from Voras et al, *Applied Physics A* 2015, 121:1015-1030, with permission of Springer.
Figure 5.18: Results of the GC-MS analysis performed on a sample taken from the outer edge (near sample S6) of *Le Bonheur de vivre* confirming the identification of long-chain fatty acids and amino acid fragments in the painting. Chromatogram (B) is from the amino acid derivitization as detailed in section 5.5.5 of the text. Because the GC-MS analysis requires digestion of an entire sample, the spatial positioning of the identified compounds in the chromatograms is unclear. Reprinted from Voras et al, *Applied Physics A 2015, 121:1015-1030*, with permission of Springer.
was both lined and consolidated with gelatin (source unidentified) making it difficult to confirm whether Matisse was in fact experimenting with a “distemper” medium.\textsuperscript{245}

Samples collected from the center of the painting (S115, S117) also showed inconsistent results relating to signals corresponding with amino acid fragments as shown in Figure 5.16. Sample S117 showed extremely low signals for amino acids, while S115 showed moderate signals for glycine, alanine, and proline, but no signal for hydroxyproline. Unexpectedly, the protein signals co-localize with the upper paint layer(s) in S115 further indicating that the protein source is most likely not from a collagen-based lining adhesive applied to the back of the canvas (especially as no amino acids were detected in the ground layer seen in S112-2). Further analysis is needed to confirm the protein source observed in S115 although it appears that collagen is unlikely due to the poor signal for hydroxyproline. Although recent studies attribute Matisse’s purported use of “distemper” to animal glue, archival sources also suggest the use of casein paint, a protein source that has not been extensively studied using TOF-SIMS. As Matisse appears to have used an oil-containing ground for \textit{Le Bonheur de vivre}, applications of an aqueous medium would likely have given rise to a reticulating pattern, a visual effect caused by surface tension between the aqueous medium and the slick oil ground.\textsuperscript{276} This effect is not observed in the paint layers used to create \textit{Le Bonheur de vivre}, although one cannot exclude the possibility that Matisse may have manipulated his paints using additives or other methods to promote better adhesion to his oil-primed canvas. Additional research is necessary to confirm whether the amino acid fragments found in S115 are associated with restoration materials (e.g. collagen-based adhesive) or reflect Matisse’s exploratory painting technique.
5.7 Conclusion

TOF-SIMS analysis was performed on multiple samples taken across the Henri Matisse painting *Le Bonheur de vivre* (1905/6). The results shown relating to CdS pigment alteration are consistent with those measured by various synchrotron-based techniques.\textsuperscript{239,240} While the inorganic species were not quantified by TOF-SIMS they were spatially imaged with resolution down to 4.5 \(\mu\)m. CdS pigment was identified throughout the four analyzed samples, with the residual CdCl\(_2\) co-localized throughout the paint layers. The products CdSO\(_4\) and CdCO\(_3\) identified the photo-oxidation mechanism of alteration for CdS pigment as a possible source of fading/chalking of the once-bright yellows in *Le Bonheur de vivre*. Additionally, organic analysis by TOF-SIMS confirmed the hydrolytic breakdown of the binding medium, leading to the production of CdC\(_2\)O\(_4\) and depletion of long-chain fatty acids as a possible mechanism that leads to the friability of the upper paint layers of *Le Bonheur de vivre*.

Furthermore, previous studies conducted by Leone et al. suggest that high humidity promotes the formation of sulfuric acid in CdS paints, contributing to acid hydrolysis of the oil medium.\textsuperscript{236} While the painting may have been exposed to high levels of humidity prior to its arrival at the Barnes Foundation, significant amounts of heat and water were undoubtedly used during the glue/paste lining process early in the paintings history. While the complicated restoration history of the picture may relate to the low yield of fatty acid fragments, this observation may also relate to various techniques employed by the artist. By this point in his career, Matisse had become enamored with the dry and colorful surfaces he encountered on wall paintings during his excursions throughout France and Italy.\textsuperscript{233-235} Consequently several paintings
created during this period exhibit a dry, matte-like quality, a characteristic that is also associated with *Le Bonheur de vivre*.\(^{233,245}\) While Matisse may have been experimenting with aqueous media to achieve this effect it is also possible that the artist sought alternative methods such as draining the excess oil from his tube paints and/or excessively diluting the colors using a solvent such as turpentine.\(^{245}\) Either method would have created paint layers containing extremely low concentrations of drying oil, possibly explaining why certain passages of the composition appear underbound and have occasionally suffered from flaking. A non-CdS containing sample, collected from the green foliage also showed a complete lack of fatty acids when analyzed using TOF-SIMS (not discussed), further suggesting that this phenomenon may not be solely attributed to interaction with CdS pigments.

As this study was primarily focused on the analysis of chemical alteration due to CdS pigment, further analysis is required to understand the role of pigment-binder interactions to fully assess the chemical alteration present in *Le Bonheur de vivre*. Further analysis is necessary to confirm the exact nature of Matisse’s ground(s) present in *Le Bonheur de vivre*, but TOF-SIMS did confirm the use of a lower lead-white/barium sulfate containing ground and revealed that it was bound in a drying oil, a layer that is present across the entire canvas. According to visual examination of the painting, two grounds are present on the composition, with the second being less continuous and applied to local areas of the composition. Moreover, the interactions between original paint material and applied conservation treatments must also be investigated to determine if these previous campaigns had (if any) significant contributions to chemical alteration of the paintings by Matisse and his
contemporaries. The non-conclusive ability to identify original versus restoration material in this study provides the need for future analysis into the possible restoration materials and their co-localization in extant cross-sections taken from *Le Bonheur de vivre*.

### 5.8 Acknowledgements

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### 5.9 Concluding Remarks

As seen in this chapter, the relative abundance of binding medium degradation will be highly affected by both reactivity of the pigment and potential treatments and storage conditions of the painting. For *Le Bonheur de vivre*, the combination of a highly fugitive pigment (CdS), possible artistic choice of a distemper style, and potentially harsh treatments (involving high heat and humidity) may have all played a role in the alteration of both pigment and binding medium. From previous results seen in binding medium degradation of Renaissance-era painting relating to depletion of fatty acid components of a paint film, the next chapter of this thesis will cover the use of weathering chambers to degrade thin films of egg tempera to identify the surface interactions of those films with their immediate environment.
REFERENCES


Chapter 6

SURFACE INTERACTIONS OF EGG TEMPERA AND ENVIRONMENTAL WEATHERING CONDITIONS

6.1 Introductory Remarks

Over the past few chapters, a distinction has been made to identify molecular alteration as it pertains to binding media degradation. The depletion of intact free fatty acid signal from Renaissance-era artwork and complete loss of fatty acid signal from *Le Bonheur de vivre* gave reason for further investigate the degradation of fatty acids in paint layers. This chapter covers the results from the experiments pertaining to artificial weathering of egg tempera thin films to investigate any surface interactions caused by environmental conditions and an unpigmented egg tempera paint layer.

6.2 Introduction

A large body of work has been established in the field of pigment alteration, covering several artistic eras.\textsuperscript{280-282} While these studies are fundamental to the understanding of physical and chemical properties pertaining to color as seen in paintings, they do not cover the important facet of molecular alteration due to degradation of the binding medium of these paintings. By using surface analytical techniques proven in the study of cultural heritage materials, it is possible to elucidate the effects of degradation inherent to binding media and also to add to the knowledge of pigment-binder
interactions. Previous research into chemical alteration seen in binding media has been studied using techniques focused on bulk material analysis, such as gas chromatography-mass spectrometry (GC-MS).\textsuperscript{283-287} While these studies provide a framework for understanding binding media alteration, they do not provide detail about the initial surface interactions of the paint layers with their immediate environment. To establish the efficacy of current and novel painting treatments, it is imperative to understand the chemical processes that occur at the paint-environment interface.

Of interest is the study of Renaissance-era painting, as transition from egg tempera to drying oil binding media provided entirely new stylistic choices for the artist. One goal of modern scientific analysis is to provide organic analysis of paint layers found in Renaissance paintings to reinforce the understanding of painting technique and to provide art conservators with complete knowledge of the materials found in these paintings to aid in treatment. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) can image historical paint cross-sections from Renaissance-era artwork and provide identification of various proteinaceous and oil-based paint layers.\textsuperscript{288,289} It is through this work that we have found that proteinaceous binders have shown considerable susceptibility to degradation by either treatment or environmental conditions, with egg tempera showing significant depletion of intact fatty acids in upper paint layers.\textsuperscript{290}

One important aspect of TOF-SIMS is the ability of the technique to identify changes in molecular species such as amino acids, free fatty acids and triglycerides.\textsuperscript{291-298} Since
the chemical pathways of binding medium degradation involve changes in large molecular structures, observation of the upper chemical surface (and therefore the first point of interaction with its immediate surroundings) of degraded binding media provide a valuable insight into the pathways of degradation. Previous research has shown that the changes in mechanical properties of a paint film due to binding medium alteration can be attributed to specific changes in chemical composition of the binding medium in question.299,300

X-ray photoelectron spectroscopy (XPS) is a surface analytical technique used for quantitation elemental and oxidative state information present on a sample surface.301 Previously, XPS has mostly been used to study corrosion products of metal and stone materials in cultural heritage research, although the technique is suited for the investigation of oxidation state of binding media during degradation.302-304 With this technique, it is possible to monitor any localized surface changes in oxidation state due to environmental degradation.

The advancement of gas cluster ion beam (GCIB) technology into a commercial-grade sputter source has allowed for the routine analysis of sub-surface chemical information of soft materials.305,306 There have been rigorous studies for the ability of GCIB to depth profile through soft materials without leaving any traces of beam-induced degradation.307,308 By controlling gas cluster size and acceleration, it is possible to optimize sputter rate for the intended soft material while still maintaining no beam-induced degradation.309 Combining GCIB with XPS, elucidating any changes in chemical oxidation and reduction as a function of depth is possible for a given
material with its exposure to its surroundings. For this study, chemical information gathered by both TOF-SIMS and XPS, a complete characterization of both short-range (XPS) and long-range (TOF-SIMS) molecular alteration egg tempera degradation is presented.

6.3 Methods

Thin films of egg tempera were prepared by spin casting. Eggs (USDA certified organic) were cracked and the egg white was separated and discarded. Next, the yolk sac was pierced and the egg yolk was collected while the yolk sac was discarded. After collection, the egg yolk was diluted with a similar (1:1 w/w) mass of DI water and mixed. The egg tempera mixture was then cast onto 1 × 1 inch silicon wafers that were previously sonicated in isopropanol for 15 minutes and placed into a spin coater. The wafers were spun at 3000 rpm for three minutes to produce a uniform thin film of egg tempera. Samples were then placed as a set inside of a weathering chamber to simulate environmental degradation effects.

The thin film weathering was completed inside of a laboratory-built weathering chamber. Detailed in Figure 6.1, the chamber consists of an N₂ purge, heat source, UV light source, and a humidity source. The chamber contains sensors to measure sample temperature and chamber humidity, as well as gas flow meters for in- and out-flows to ensure no leaks are present during the weathering experiment. The heat within the chamber is controlled by heating the sidewalls of the chamber and measuring the internal temperature using a type-K thermocouple. Humidity is controlled by separately heating the bottom plate of the weathering chamber that will heat a dish of
Figure 6.1: Weathering chamber used for control of sample heat, relative humidity, and UV exposure for the degradation of thin films of binding media. By controlling the chamber temperature, N\textsubscript{2} purge rate, and UV source various environmental conditions can be controlled and monitored over a given time range.
DI water that is constantly stirred. By changing the gas flow of the N$_2$ purge gas and the temperature of the DI water, a specific humidity can be held constant and measured by a humidity sensor. UV exposure is done with a 254-nm Hg-lamp (BHK, Inc.) with a peak intensity of 30 mW/cm at 20 cm. By controlling the heat, humidity and UV exposure on the thin films the individual effects of these environmental factors and their associated chemical pathways of initial interaction leading to degradation can be studied.

6.4 Experimental

Figure 6.2 outlines the use of a single sample to provide multiple analysis spots. Using this scheme, variability in sample chemical composition will be taken into account during analysis. For GCIB-XPS analysis, three spots were taken per sample maintaining space between each depth profile to not allow for re-deposition of sputtered material between spots. For TOF-SIMS, each sample was analyzed six times per ion mode for adequate sample sites for multivariate analysis.

6.4.1 XPS and GCIB

XPS and GCIB depth profiling were conducted with a K-Alpha+ with MAGCIS (Thermo-Scientific, Inc.) located in the Surface Analysis Facility at the University of Delaware. Monochromated Al K$_\alpha$ x-rays (1486.6 eV) with a spot size of 100 µm was used for all analyses. All high-resolution scans were run with a pass energy of 20
Figure 6.2: Analysis layout for GCIB-XPS and TOF-SIMS measurement of degraded thin films of spin-cast egg tempera. Shown in gray are the areas used for GCIB depth profiling and XPS analysis. The large areas are 1 mm by 2 mm depth profile craters, with a XPS spot size of 100 µm centered in the craters. Shown in green is the area reserved for TOF-SIMS analysis. Analysis areas of 250 µm² were maintained to minimize any effects of oversampling. The red area is where the XPS sample holder clip is placed, an area avoided for XPS analysis and not used for TOF-SIMS analysis.
eV and the scan numbers were adjusted for optimal signal-to-noise ratios. By running all samples with three analysis spots for XPS, all atomic percentages were averaged across the same sample to account for any inhomogeneity across the same thin film surface. GCIS profiling was done with a 4 kV Ar\textsubscript{2000} cluster for 60 s each level of sputtering, where the three X-ray spots were profiled for 5, 15, and 30 levels respectively. All curve-fitting was done in CasaXPS software using Shirley-type background correction. The sputter rate of the egg tempera was measured using atomic force microscopy and found to be 4.5\times10^{-3} \text{ nm/Ar atom}.

6.4.2 TOF-SIMS

TOF-SIMS was conducted with a TOF-SIMS IV (ION-TOF GmbH), upgraded to TOF-SIMS V capabilities, located in the Surface Analysis Facility at the University of Delaware. 25-kV Bi\textsubscript{3}\textsuperscript{+} primary ions were directed towards the sample surface in “high-current bunched mode” and secondary ions were extracted with ±2 kV into the time-of-flight mass analyzer and given a 10 kV post-acceleration. All spectra were collected in triplicate per sample in both positive- and negative-mode, where each spectrum was collected over an area of 250 \textmu m\textsuperscript{2} with primary ion beam dosage taken to the static SIMS limit of 1\times10^{12} \text{ ion/cm}^2. All spectral processing was completed in Measurement Explorer software. Positive-ion mass-scale calibration was performed with the following ions: H\textsuperscript{+}, H\textsubscript{2}\textsuperscript{+}, H\textsubscript{3}\textsuperscript{+}, C\textsuperscript{+}, CH\textsuperscript{+}, CH\textsubscript{2}\textsuperscript{+}, CH\textsubscript{3}\textsuperscript{+}, C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}, C\textsubscript{3}H\textsubscript{5}\textsuperscript{+}, C\textsubscript{4}H\textsubscript{7}\textsuperscript{+}, C\textsubscript{5}H\textsubscript{9}\textsuperscript{+}, C\textsubscript{6}H\textsubscript{13}\textsuperscript{+}, and C\textsubscript{7}H\textsubscript{15}\textsuperscript{+}. The negative-ion mass scale was calibrated with the following ions: H\textsuperscript{−}, H\textsubscript{2}\textsuperscript{−}, C\textsuperscript{−}, CH\textsuperscript{−}, CH\textsubscript{2}\textsuperscript{−}, CH\textsubscript{3}\textsuperscript{−}, C\textsubscript{2}H\textsuperscript{−}, C\textsubscript{3}H\textsuperscript{−}, C\textsubscript{4}H\textsuperscript{−}, C\textsubscript{5}H\textsuperscript{−}, C\textsubscript{6}H\textsuperscript{−}, and C\textsubscript{7}H\textsuperscript{−}.
6.4.3 Multivariate Analysis

All data processing was completed in Matlab, using the correlated optimized warping (COW) package and the PLSToolbox. After COW alignment of the TOF-SIMS data to remove sample variance due to mis-calibration, the data were preprocessed with mean centering and then analyzed with principal components analysis (PCA).

6.5 Results and Discussion

From previous literature, the degradation process was determined to come from two sources: heat/humidity exposure and UV exposure.\textsuperscript{282-287} The three trials set forth in the experiment were to expose the egg tempera thin films to the following conditions: i) 60 °C, >80% RH, and a dark chamber; ii) 20 °C, 0% RH, and UV exposure; and iii) 60 °C, >80% RH, and UV exposure. XPS and GCIB depth profiling were used to identify any changes made to the oxidation state of the egg tempera film due to weathering, mainly pertaining to changes in triglycerides to free fatty acids. TOF-SIMS was used to identify any changes in molecular composition changes of the fatty acid portion of the egg tempera films as previous research has indicated that alteration of the fatty acid composition is observed in historic egg tempera paint layers.

6.5.1 High Heat/Humidity/Dark XPS and GCIB Results

Table 6.1 summarizes the upper surface (no depth profiling) XPS results from the first scenario: 60 °C, >80% RH, dark chamber. These exposure conditions were used to study the surface interactions of relatively high heat and humidity on an egg tempera-based binding medium layer. As is shown in Table 6.1a, the relative atomic ratios do
not change drastically over the course of the weathering experiment. Instead, to highlight changes in the individual atomic species, the fitted components are used, with the carbon 1s region being highlighted as the functionalities present in egg yolk are shown in the carbon 1s region. Table 6.1b highlights the alteration of the carbon 1s region as a result of the weathering experiment. Table 6.1b has the most reduced form of carbon (C-C) on the far right, and the highest oxidation states (COOH) on the far left. As egg yolk is a biological material, the exact chemical concentration of the carbon functionalities is not known, and as such the nitrogen-containing components will have overlap with the carbon-oxygen components. Instead, the approach of chemical speciation is used to highlight any changes in oxidation due to weathering. As is shown in Table 6.1, the sample is clearly becoming more oxidized as a result of weathering due to the loss of C-C components and increase in the left-shifted oxidation components. Most significant is the drastic increase of the C-O/C-N component in comparison to the loss of the C-C component.

Figure 6.3 is the result of the GCIB-XPS experiment to monitor the penetration of degradation products as a function of depth. Shown in Figure 6.3a are the fitted components of the C 1s region of the final day (Day 5, 120 hours) of weathering for the upper surface. Shown in Figure 6.3b is the GCIB depth profile that follows the degradation from the surface down to the bulk of the thin film. By comparison to the lowest bulk level, there is insignificant change after 7-10 levels of sputtering to return to unaltered egg yolk.
Table 6.1: (a) Elemental and (b) C 1s relative atomic percentages after weathering in 60 °C, >80% RH, and a dark chamber for 5 days. Day zero is a non-weathered control used for normalization in Figure 6.6. The elemental atomic percentages in (a) were determined by comparison of high-resolution scans of the selected elements (C 1s, O 1s, N 1s, and P 2p, respectively). The fitted components in (b) were minimally constrained to have FWHM of <1.8 and a center BE position within ± 0.2 eV.

(a)

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<th>N</th>
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(b)

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<th>CO/CN</th>
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Figure 6.3: Results of GCIB-XPS analysis of weathered egg tempera under conditions of 60 °C, >80% RH, and a dark chamber for 5 days focused on the C 1s region. The fitted components of the C 1s upper surface are shown in (a) with the depth profile shown in (b). GCIB was performed using 4 kV Ar$_{2000}^+$ ions with a sputter yield of $4.5 \times 10^{-3}$ nm$^3$/Ar atom.
6.5.2 Ambient Heat/Dry/UV Exposure XPS and GCIB Results

Table 6.2 summarizes the results of the only UV exposure weathering experiment. Table 6.2a is the result of analyzing the upper surface of the thin films and shows any changes in relative atomic percentage of the thin film as a result of weathering. Table 6.2a shows that after UV exposure, the relative amount of oxygen increases as carbon decreases, with nitrogen and phosphorous staying unchanged. The C 1s region in Table 6.2b shows that the conversion into COOH-type carbon is seen after 5 day (120 hours) of UV exposure, given no added heat and a dry N2 purged chamber. Additionally, the removal of the COO/CON component agrees with the presumed conversion by oxidation and hydrolysis of aldehyde and amide components into carboxylic components under UV exposure.

Figure 6.4 shows the results of GCIB-XPS depth profiling on a thin film of egg tempera that has been under UV exposure for 5 days (120 hours). Shown in Figure 6.4a are the fitted components of the C 1s region from the upper surface of Day 5 (120 hours) showing the loss of the COO/CON species. While it is more difficult to ascertain the interface between the altered surface and unaltered bulk, the depth profile shown in Figure 6.4b appears to become unaltered bulk around level 7-10, similar to the above data in Figure 6.3b.

6.5.3 High Heat/High Humidity/UV Exposure XPS and GCIB Results

Table 6.3 summarizes the XPS results from the weathering conditions that simulate exposure to 60 °C, >80% relative humidity, and UV exposure. Table 6.3a is for all of the atomic species present, showing a small increase in oxygen
Table 6.2: (a) Elemental and (b) C 1s relative atomic percentages after weathering in 25 °C, 0% RH, and 254-nm UV exposure for 5 days. Day zero is a non-weathered control used for normalization in Figure 6.6. The elemental atomic percentages in (a) were determined by comparison of high-resolution scans of the selected elements (C 1s, O 1s, N 1s, and P 2p, respectively). The fitted components in (b) were minimally constrained to have FWHM of <1.8 and a center BE position within ±0.2 eV.

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<th>COO/CON</th>
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<td>72.7 ± 1.7</td>
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Figure 6.4: Results of GCIB-XPS analysis of weathered egg tempera under conditions of 25 °C, 0% RH, and 254-nm UV exposure for 5 days focused on the C 1s region. The fitted components of the C 1s upper surface are shown in (a) with the depth profile shown in (b). GCIB was performed using 4 kV Ar$_{2000}$ ions with a sputter yield of $4.5 \times 10^{-3}$ nm$^3$/Ar atom.
relative abundance in comparison to a drop in both carbon and nitrogen relative abundances. As shown in Table 6.3b, the C 1s region is a combination of both the above two weathering scenarios, with increases in the CO/CN and COOH components, as well as removal of the COO/CON component.

Figure 6.5 is the results of the GCIB-XPS depth profile of the Day 5 (120 hours) weathered sample showing the C 1s region. Shown in Figure 6.5a are the fitted components of the top surface before depth profiling, and Figure 6.5b are the results from the depth profile showing the change from degraded surface to unaltered bulk of the egg tempera film. Similar to Figures 6.3 and 6.4, the interface between degradation and unaltered bulk is estimated to be between levels 7 and 10.

6.5.4 Relative Atomic Ratios During Weathering

To summarize the results of XPS analysis after weathering, Figure 6.6 highlights the relative atomic percentages over the 5 days (120 hours) normalized to the control sample. Given the unique differences in oxidation as shown above, the plots in Figure 6.6 highlight general trends in atomic ratios for all weathering parameters. The plots in Figure 6.6 are from each atomic region, and show changes in relative atomic percentage vs. day of all three weathering scenarios. The y-axis of each plot is normalized to the control sample atomic percentage, which each sample containing three analysis spots for any inhomogeneity of the egg tempera film surface. As is shown in Figure 6.6a, UV exposure (blue) generally lowers the overall carbon species present on the sample, where heat and humidity (red) exposures generally maintains the same carbon content. Figure 6.6b tracks the oxygen content, where UV exposure
Table 6.3:  (a) Elemental and (b) C 1s relative atomic percentages after weathering in 60 °C, > 80% RH, and 254-nm UV exposure for 5 days. Day zero is a non-weathered control used for normalization in Figure 6.6. The elemental atomic percentages in (a) were determined by comparison of high-resolution scans of the selected elements (C 1s, O 1s, N 1s, and P 2p, respectively). The fitted components in (b) were minimally constrained to have FWHM of <1.8 and a center BE position within ± 0.2 eV.
Figure 6.5: Results of GCIB-XPS analysis of weathered egg tempera under conditions of 60 °C, > 80% RH, and 254-nm UV exposure for 5 days focused on the C 1s region. The fitted components of the C 1s upper surface are shown in (a) with the depth profile shown in (b). GCIB was performed using 4 kV Ar$_{2000}$ ions with a sputter yield of 4.5x10$^{-3}$ nm$^3$/Ar atom.
(blue) will increase the relative atomic percentage of oxygen, and again heat and humidity (red) will remain constant. As the last weathering scenario combines heat, humidity, and UV exposure (green), the weathering falls within the UV (blue) and heat and humidity (red) exposures, showing that all three condition have a noticeable trend on surface weathering. Figure 6.6c shows the relative nitrogen atomic percentage that correlates with the carbon plot (A) with a general loss of material, and Figure 6.6d shows a slight increase in the relative phosphorous atomic percentage.

6.5.5 TOF-SIMS and Multivariate Analysis Results

For the TOF-SIMS data, PCA was performed to identify any multivariate changes in glyceride structure relevant to chemical alteration due to weathering. While the data were mass calibrated using the Measurement Explorer (ION-TOF, GmbH) software, the data were aligned using correlated optimized warping (COW) prior to PCA. COW was used to ensure that no bias due to mis-calibration of the mass spectra was observed in the PCA results. Both positive- and negative-ion data were collected over the mass range of 0 – 800 amu which is shown below. In positive mode, mass fragments at 572 – 582 amu were used to monitor changes to triglycerides found in egg yolk and any changes to either the glycerol backbone or substitutions on the alkyl chains. For negative mode, masses 279 – 287 amu were used to monitor changes made to free/mono- stearic acid in relation to substitutions in the alkyl chain.
Figure 6.6: Tracking changes in elemental ratio as a function of weathering for the egg tempera thin films for the data shown in Tables 6.1a – 6.3a. The relative atomic ratios have been normalized to the non-weathered “Day 0” control sample.
6.5.6 Positive-Ion Mode Multivariate Results

Figure 6.7 and 6.8 highlight the results of COW followed by PCA of all samples in the weathering study as analyzed in TOF-SIMS positive-ion mode. The data shown in Figure 6.8 are the scores plot comparing both principal component (PC) 1 and PC 2 resulting from a PCA of the full mass range of 0 – 800 amu, and is sorted by weathering parameter and day. The control sample (no weathering) is shown in black. “HH” stands for 60 °C, >80% relative humidity, and a dark chamber and is shown in red. “UV” stands for UV exposure only and is shown in blue. “HHUV” is the combination of 60 °C, >80% relative humidity, and UV exposure and is shown in green. While no distinct grouping is formed in the plot, it appears as though the weathered samples have a slight difference due to specific parameter, with the “UV” trending towards a negative value for PC 2, and “HHUV” trending positive in PC 2.

For a more detailed look into the positive-ion mode data, the mass range of 572 – 582 amu was selected from the data to highlight any changes in the triglycerides found within that mass range. Figure 6.8 is the resulting PCA from that analysis, with (a) showing the scores plot comparing PC 1 and PC 2 and (b) the loadings plots for both PC 1 and 2. The mass fragment of C_{34}H_{73}O_{6}^+ at 577.50 amu is highlighted as a point of reference. As shown in the scores plot, the groupings for the three weathering conditions are much more distinct than in Figure 6.7, with the “HH” samples being distinct from the “UV” and “HHUV”, showing that the UV exposure may have a significant effect on the alteration of triglycerides than heat and humidity. By comparing the loadings plots under (b), PC 1 variance is effected positively by having increased saturation of the alkyl chains, and negatively by removal of the saturated
Figure 6.7: Positive-ion TOF-SIMS data after COW alignment and PCA for the mass interval of 0 – 800 amu to identify any molecular changes in positive-ion mass fragments. While distinct groupings are not observed, the “HHUV” samples do fall between both the “HH” and “UV”, showing that molecular effects due to weathering may undergo a synergistic process.
Figure 6.8: Positive-ion TOF-SIMS data after COW alignment and PCA for the mass interval of 572 – 582 amu to identify any molecular changes in di- and triglyceride after weathering. Shown on the left (a) is the scores plot. Shown on the right (b) are the individual loadings plots as expressed after PCA.
hydrogen’s. The loadings plot for PC 2 is less obvious in the chemical identification for the variance. From the loading plots, it is more obvious that grouping based on PC 1 indicate that UV exposure plays a significant role in the hydrolysis process by which free fatty acids are produced from intact triglycerides.

6.5.7 Negative-Ion Mode Multivariate Results

Figures 6.9 and 6.10 summarize the results of COW followed by PCA of all negative-ion mode TOF-SIMS data for all samples after weathering. Figure 6.9 is the PCA scores plot comparing PC 1 and PC 2 across the full mass range (0 – 800 amu). As no discernible grouping is present, it is necessary to look only at a subset of relevant mass fragments of interest. Figure 6.10 is the result of PCA of only masses 279 – 287 amu that are directly measuring stearic acid, either as a free fatty acid or as a fragment of a larger triglyceride. Figure 6.10a is the scores plot comparing PC 1 and PC 2 showing obvious grouping between the three weathering parameters and the control sample. Of note, the distribution between the UV exposure and the combination of 60 °C, >80% relative humidity, and UV exposure have some overlap in their distribution in the scores plot, as well as the distinction of the 60 °C, >80% relative humidity grouping. By looking at the loadings plots in Figure 6.10b, the reason for variance can be explained as the addition of double bonds (unsaturation) in the alkyl chain in comparison to the saturated stearic acid molecular weight as identified with the arrow at 283.3 amu. As UV exposure is known to stimulate both hydrolysis and cross-linking of fatty acids, this molecular alteration is expected.
Figure 6.9: Negative-ion TOF-SIMS data after COW alignment and PCA for the mass interval of 0 – 800 amu to identify any molecular changes in negative-ion mass fragments. While distinct groupings are not observed, the “HHUV” samples do fall between both the “HH” and “UV”, showing that molecular effects due to weathering may undergo a synergistic process.
Figure 6.10: Negative-ion TOF-SIMS data after COW alignment and PCA for the mass interval of 279 – 287 amu to identify any molecular changes in stearic acid molecular ion. Shown on the left (a) is the scores plot comparing. Shown on the right (b) are the individual loadings plots as expressed after PCA.
6.6 Conclusions

This study provides an initial look into the chemical pathways of surface molecular alteration in relation to degradation of fatty acid-containing binding media relating to environmental factors. The selective removal of intact free fatty acids as observed in various historic artworks has been linked to the hydrolysis of di- and triglyceride into free fatty acids which can diffuse through a paint layer towards the upper surface. By subjecting thin films of egg tempera to various parameters relating to ambient heat, relative humidity, and UV exposure, the identification of glyceride breakdown has been observed by XPS and TOF-SIMS analysis. For the first time in cultural heritage research, depth profile analysis using GCIB on the egg tempera films was used in conjunction with XPS to observe any changes in oxidation as a function of depth after weathering.

XPS analysis showed the oxidation of egg tempera into higher abundance of ester and amide functionality after head and humidity exposure, as well as a shift towards carboxylic functionality after UV exposure. This confirms the process of hydrolysis and breakdown of glyceride (and amino acid backbone) components of egg tempera. While not discretely observed, the humidity aspect of the weathering will incorporate water into the thin film that is aqueous soluble. The UV exposure will then begin the hydrolysis reaction, leading to breakdown of both the glyceride and amino acid backbone.

TOF-SIMS analysis provided a framework of molecular alteration pertaining to glyceride breakdown. By observing both molecular glyceride (in positive-ion mode)
and stearic acid (in negative-ion mode) molecular fragments it was possible to observe trends in alteration due to environmental weathering. By using PCA the observation of greater unsaturation after weathering of stearic acid shows the great volatility of the free fatty acid components. In comparison, the positive-ion mode results indicate an increase in saturation of alkyl chains in molecular glyceride, leading to decreased cross-linking and increase in hydrolysis of the glyceride backbone. While contradictory, this explanation describes the process of alteration going from intact, cross-linked glyceride to mobile, unsaturated fatty acids.

6.7 Acknowledgments

I thank Mark Schrader for machining related to the weathering chamber and XPS sample holders. I acknowledge the NSF (94-13498; 97-24307) and the NIH NIGMS COBRE program (P30-GM110758) for partial support of activities in the University of Delaware Surface Analysis Facility.
REFERENCES


Chapter 7

CONCLUSIONS

7.1 Introductory Remarks

In this dissertation, the study of soft material degradation in the context of cultural heritage research has provided many avenues of research across multiple projects. While not the main focus of this dissertation, the Appendices cover three additional projects that highlight the use of surface analysis for the study of soft material degradation, two of which are for cross-sectional sample from artwork, and the third is the study of polymer degradation for artistic bronze protection.

7.2 Combining Surface Analysis and Cultural Heritage Research

Collaboration between the fields of art conservation and surface science plays a new and important role in the identification of chemical degradation processes in works of art. Through improvements in sample preparation and careful experimentation, the chemical basis behind paint-layer fracture, flaking, discoloration, and other assorted degradation processes have been identified, discussed at various national and international conferences, and published in the literature. The major goal of these projects is to provide art conservators with detailed chemical information pertaining to the objects that they conserve, to better aid their conservation efforts. The instrumentation involved has provided the detailed long- and short-range chemical
information that is present on a sample surface. The primary analytical techniques involved in my studies are time-of-flight secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS). TOF-SIMS is used to obtain images and spectra that provide long-range chemical information (atomic and molecular mass fragments), while XPS is used to obtain short-range chemical information, such as elemental oxidation state and functional groups. While many projects have been completed over the past five years, a major theme has been in the identification of the degradation process of the binding medium found in paintings of various eras.

7.3 Renaissance-Era Artwork

The first set of studies evaluated the ability of ToF-SIMS to identify the various organic components of typical Renaissance-era paintings (Chapters 3 and 4). This was a collaboration with Winterthur Museum (Kristin deGhetaldi, Brian Baade, and Jennifer Mass), the Walters Art Museum (Glenn Gates, Eric Gordon), and North Dakota State University (Stuart Croll). These studies were beneficial in two ways: the design of a new sample preparation method for cross-sectional paint sample analysis that minimized or eliminated the chemical alteration prior to analysis, and the identification of various pigments and binding media found in Renaissance-Era artwork. This set of experiments included the identification of both original materials as well as degradation products. Historic samples were loaned from the Walters Art Museum (Baltimore, MD) and included samples taken from Raphael’s Madonna of the Candelabra (1513, bound in oil) and Matteo di Giovanni’s Pentecost (1480-89, bound in egg tempera). Analysis of these samples provided two major conclusions:
First, the mass fragments observed in “fresh” samples are also able to be observed in samples that are >500 years old, and second, that there was an observable depletion of molecular fatty acid signal near the upper surface of the paint layers. This critical observation had never been made prior in the literature. The depletion was more prominent in the egg tempera-bound painting than in the oil-bound painting. This depletion pattern is a novel first-time observation, and subsequently has been identified in multiple samples taken from various museums, confirming its occurrence.

7.4 Fauvist-Era Artwork

The second major study was to link together the degradation mechanisms of binding media to the color-change associated with cadmium yellow (cadmium sulfide) pigment. Using TOF-SIMS, analysis was completed on various paint cross-sections taken from The Joy of Life (Le Bonheur de vivre, 1905-06) by Henri Matisse. This study was in collaboration with Winterthur Museum (collaborators listed above) and the Barnes Foundation and head conservator Barbara Buckley. Using comparison observations obtained from various synchrotron-based spectroscopy techniques, compounds related to cadmium sulfide degradation (and discoloration) were imaged within each of the cross-sectional samples. The chemical species identified were associated with degradation of the residual starting material and/or chemical change induced through contact with binding medium/atmospheric conditions. A major finding that was identified only through TOF-SIMS analysis was the significant loss of intact long-chain fatty acids from the oil-based binding medium. This observation of fatty acid depletion was in direct inverse to the formation of cadmium oxalate, a
proposed (but until now never observed) component in the cadmium sulfide degradation process.

7.5 Environmental Weathering of Egg Tempera

The third (and final) study aimed to mimic the observed fatty-acid depletion in binding media based on artificial weathering of environmental conditions. Using a custom designed degradation chamber, the effects of humidity, temperature, and UV illumination were observed to study their effect on fatty-acid depletion. This set of experiments involved several analytical challenges: producing uniform thin films of binding medium materials (usually complex biological systems); having complete control over each variable in the degradation chamber; using a cluster sputter source to profile through the thin film with high depth resolution; and analyzing the data to identify any differences in the pathways of degradation due to the defined environmental conditions. The ability to sputter through a soft material without beam-induced degradation is a new technology that has yet to be used in the study of cultural heritage materials. It uses the technology of argon-cluster sputter sources, where large clusters (500-2000 atoms per cluster) of argon are singly ionized and directed towards the sample surface. By coupling the capabilities of “gentle” depth profiling to the complementary data sets provided by XPS and TOF-SIMS, a comprehensive “top-down” analysis of egg tempera degradation has been shown using both univariate and multivariate analysis (Principal Components Analysis). This study provided evidence that heat/humidity and UV exposure provide synergistic effects on the hydrolysis of fatty acids to increase their mobility and volatility, as well as removing the cross-linking provided by oxidation of glyceride networks in drying oils.
7.6 Conclusions

This work has provided a fundamental understanding required to characterize soft materials and their interactions (surface and bulk) with their environment fully, starting from their initial application to canvas and ending in their failure and degradation components. These studies have furthered the knowledge of binding medium degradation from which art conservators can use to better detail treatment processes. This work will further aid in establishing the complex chemistry found in soft materials related to cultural heritage research, with a special focus on binding media degradation and pigment-binder interactions.
Appendix A

THE TRIUMPH OF DAVID BY PIETRO DA CORTONA

A.1 Introductory Remarks

This Appendix covers research that was a part of the conservation and treatment of the painting *The Triumph of David* attributed to Pietro da Cortona. TOF-SIMS analysis was performed as initial solvent testing on the varnish and paint layer were not provided useful results as to the identity of the binding medium present on the painting. The results of this work are to be published in an upcoming book chapter “Resurrecting a Giant: Using Solvent Gels and Aqueous Systems to Restore Villanova University’s *Triumph of David,*” chapter in *Gels in Conservation* (London: Archetype Publications, Ltd.; expected publication date 2018). The author list for the chapter is Kristin deGhetaldi, Emily Wroczynski (Colonial Williamsburg/Paintings Conservator), Zachary Voras, and Thomas J. Beebe, Jr.

A.2 Introduction

Beginning in the Fall of 2013, a conservation and treatment effort of *The Triumph of David* attributed Pietro da Cortona was headed by Kristin deGhetaldi and performed by a team of interns, scientists, and graduate students. The large (4 m tall and 6 m wide) painting is housed in the Old Falvey Library at Villanova University, and efforts to conserve the painting came after questions pertaining to provenance and original
intentions. Scrutiny of the painting technique revealed a varied approach in both style and technique, hinting at possible attribution issues, as well as X-ray radiography and infrared reflectography uncovering a kneeling figure in the painting. While the focus of the project was on the conservation using aqueous gels for cleaning prior to treatment, the role of TOF-SIMS to identify unexpected materials was overall beneficial for the conservators and provided an interesting scientific inquiry.

A.3 Methods

The analysis was performed on the IONTOF, GmbH TOF-SIMS IV upgraded to capabilities of the TOF-SIMS V that is housed in the Surface Analysis Facility in the Department of Chemistry and Biochemistry at the University of Delaware. Previous chapters of this thesis outline the various instrumental parameters and calibration data useful for the analysis of paint cross-sections.

A.4 Results

During cleaning tests, it was noted that a single cleaning approach would not be sufficient for the entirety of the painting. While not unheard of, due to the size and relative unknown history of the painting additional binding medium analysis was required. Initial testing via GC-MS indicated amounts of fatty acids and amino acids in the blanched coating that was particularly thick. For spatial analysis, TOF-SIMS of the same area (blue dress of crouching woman) provided insight into the interesting layer structure due to prior conservation treatments as shown in Figure A.1
Figure A.1: TOF-SIMS images of a cross-sectional sample taken from *The Triumph of David* (crouching woman in blue dress). In order, the images show: (A) optical image under UV illumination; (B) positive-ion total ion image; (C) overlay of lead, aluminum, and calcium mass fragments showing pigmentation; (D) hydroxyproline mass fragment image; (E) proline mass fragment image; (F) alanine mass fragment image, (G) stearic acid mass fragment image; and (H) stearic acid mass fragment image. Reprinted with permission from Kristin DeGhetaldi and Villanova University.
As shown in Figure A.1 the unpigmented surface coating was found to contain a number of amino acids including hydroxyproline, corroborating the results obtained with GC-MS, while fatty acids (palmitic and stearic) were only found in the lower paint and ground layers. The results suggested the presence of an animal glue in the blanched surface coating, a material that was likely used to coat the surface in an attempt to consolidate the paint and ground layer(s) during a previous restoration campaign. Further supporting this supposition, this coating could also be seen filling a large crack that extends through both the paint and ground layers, and the signals corresponding to the amino acid fragments were seen both along the surface of the paint cross section and within the interstices of the crack, co-localizing with the blanched, unpigmented surface coating. These findings attest to the difficulty the conservation team encountered when attempting initial cleaning tests using free solvents and solvent gels.

A.5 Conclusions

Through the use of TOF-SIMS analysis, the identity of a thick, unpigmented glue layer was observed on The Triumph of David attributed to Pietro da Cortona that is housed at Villanova University. The identification of this unexpected layer aided the conservation team in initial removal of outer dirt and grime from the painting surface. Additionally, TOF-SIMS analysis helped in establishing previous conservation treatments as the historical record of the painting was incomplete.
Appendix B

COMPLEX STRATIGRAPHY OF THE FISHERMAN’S RETURN BY HENRY OSSAWA TANNER

B.1 Introductory Remarks

After initial successes identifying the binding media of Renaissance-era artwork (Chapter 4), a foray into highly complex multi-layered paint structure was undertaken in collaboration with Amber Kerr-Allison of the Smithsonian American Art Museum. This work pushed the ability of TOF-SIMS to identify remarkably thin individual layers of binding media as painted by Henry Ossawa Tanner on The Fisherman’s Return. The results of this study were presented and published as part of the International Council of Museums – Committee for Conservation (ICOM-CC) 17th Triennial Conference with an author list of Amber Kerr-Allison, Kristin deGhetaldi, Brian Baade, Zachary Voras, Thomas P. Beebe, Jr., and W. Christian Peterson.310

B.2 Introduction

Henry Ossawa Tanner is arguably the first African-American artist to receive formal training in the United States, beginning with training at the Pennsylvania Academy of the Fine Arts in Philadelphia, Pennsylvania. He went on the travel the world becoming a renowned artist for his style and mastery of technique.311 During his studies, he pursued experimental painting techniques which would provide his work with highly
detailed and complex layered structures to achieve a final effect unique to his work. By combining new painting methodologies with previous proven techniques, Tanner’s works provide a demanding challenge in their analysis and conservation.

TOF-SIMS analysis was sought to understand the complex stratigraphy found in cross-sectional samples taken from *The Fisherman’s Return* by Tanner. Previous GC-MS analysis had shown that the paint layers may contain a variety of materials, ranging from flaxseed mucilage and resins in addition to the common fatty acids and amino acids. The use of TOF-SIMS was primarily for qualitatively understanding the layered structure of the painting and not for quantitative identification of individual layers.

### B.3 Methods

The analysis was performed on the IONTOF, GmbH TOF-SIMS IV upgraded to capabilities of the TOF-SIMS V that is housed in the Surface Analysis Facility in the Department of Chemistry and Biochemistry at the University of Delaware. Previous chapters of this thesis outline the various instrumental parameters and calibration data useful for the analysis of paint cross-sections.

### B.4 Results

As shown in Figure B.1, the complex stratigraphy associated with Tanner is imaged in a cross-sectional sample taken from *The Fisherman’s Return*. Figure B.1a and B.1b
Figure B.1: Detail of cross section collected from The Fisherman’s Return shown at 100Å~ magnification under visible light (A) and ultraviolet light (B). Images C–E were collected using the TOF-SIMS in negative-ion mode and show the total ion count image (C) and maps demonstrating the presence of organic (D) and inorganic materials (E). Image D shows the distribution of protein (CN⁻; blue) in layers 1 and 3, while region 2 is rich in palmitic and stearic fatty acids (C₁₆H₃₁O₂; red/C₁₈H₃₅O₂; green). Image E shows the distribution of inorganic species associated with pigments; layer 1 contains barium sulphate (blue) with trace amounts of zinc-related compounds (green), region 2 is rich in zinc, while the top layer contains primarily lead compounds (possibly both as a pigment and a drier). The protein-oil-protein sequence in image D corresponds with Tanner’s writing on the back of the painting’s stretcher bar. Reprinted with permission from ICOM-CC.
show optical images taken under visible and UV illumination, respectively, highlighting the thin, multi-layered structure of the cross-sectional sample. Figure B.1c is the total ion image taken in negative-ion mode showing all mass fragments observed in the cross-sectional sample. Figure B.1d is an overlay of palmitic acid (red), stearic acid (green) and cyanide ion (blue) to observe fatty acids and proteinaceous content of the layers. Figure B.1e is an overlay of pigments found throughout the cross-sectional sample, showing lead (red), zinc (green), and barium (blue).

**B.5 Conclusions**

TOF-SIMS analysis was able to identify a multi-layered system as observed in *The Fisherman’s Return* by Henry Ossawa Tanner. TOF-SIMS analysis supported the previous the GC-MS results as well as SEM results for pigment identification. Additionally, the observed stratigraphy of protein/oil/protein was noted by Tanner himself, and so the identification of original materials helped to further establish provenance of the painting.

While not performed in this study, TOF-SIMS analysis of additional organic materials will be beneficial in the analysis of complex stratigraphy as used by Tanner and other artists. Expected materials such as dyes, resins, and lacquers, as well as unexpected materials such as beeswax and mucilage should be investigated by TOF-SIMS for positive identification in layered paint cross-sections.
REFERENCES


Appendix C

DEGRADATION OF INCRALAC POLYMER ON ARTISTIC BRONZE

C.1 Introductory Remarks

For this Appendix, the work was completed in collaboration with Postdoctoral Fellow Rosie Grayburn from the Getty Conservation Institute in the Spring of 2016, which included a three-day visit to the Surface Analysis Facility. The TOF-SIMS results of this visit (and subsequent analysis) have been presented at conferences as well as being published in the literature in the journal *Progress in Organic Coatings* with the title “Ion Probe Techniques to Measure the Distribution of Substrate Elements in Coatings for Copper Alloys”. The GCIB-XPS results are currently in preparation for submission. Co-authors on the *Progress in Organic Coatings* include Christopher Goodwin, Ming-Chang Liu, Thomas P. Beebe, Jr., and Alan Phenix.

C.2 Introduction

For the protection of outdoor artistic bronze (statues), the polymer Incralac has been used for its optical and protective qualities. Incralac is a blend of Paraloid™ B44 (a mixture of poly-methyl methacrylate (PMMA), poly-ethyl acrylate (PEA), and epoxidized soybean oil) and benzotriazole (BTA) corrosion inhibitor. The exact method of action for BTA is unknown in the Incralac films given a wide variety of factors, including environmental pH, oxidation state of the copper substrate, and UV
exposure of the films. For this study, analysis with TOF-SIMS imaging and GCIB-XPS depth profiling was used to identify the localization of BTA within the Incralac film after artificial and natural aging to determine the method by which BTA inhibits corrosion of artistic bronze.

C.3 Methods

The samples came prepared as thin films of Incralac as either spin-cast or spray-coated on small circular copper coupons. Both unaged and aged samples were brought. The samples were artificially aged in an Atlas Ci4000 Weather-O-Meter under ISO4892-2:2013 parameters. An attempt was made to prepare the samples for TOF-SIMS analysis using ultramicrotomy to cut a 2° angle off of the surface (exposing the copper substrate below), although the susceptibility of the Incralac coating to peel off the coupon did not allow for a reproducible successful cut. In addition to the microtome cuts, analysis on the depth profile crater edges were used for TOF-SIMS images as shown in Figure C.1. Figure C.1a is a side-profile view of an Incralac thin film showing (1) a small void on the copper substrate surface where polymer was able to settle into. Figure C.1b shows the top-down view after a sputter crater has formed, showing area (2) and (3) where TOF-SIMS analysis was performed. Area (3) is of the same void as (1).

The instrumental parameters and calibration information pertaining to TOF-SIMS analysis was performed as detailed in earlier chapters of this dissertation. Images were collected with an analysis area of 500 µm × 500 µm. For XPS analysis, A Thermo-Scientific K-Alpha+ with MAGCIS (housed in the Surface Analysis Facility) was
Figure C.1: Schematic of using a sputter crater left behind after a depth profile analysis for TOF-SIMS imaging for BTA localization. Shown in ‘a’ is the side-profile view of the Incralac films on the copper substrate showing a void (1) where polymer was able to lay below the macro surface. Shown in ‘b’ is the top-down view of the sputter crater where TOF-SIMS images were taken of the sidewalls (2) and the remaining polymer in the void (3) in order to identify BTA localization.
used, where monochromated Al Kα X-rays with a spot size of 100 µm and a low-energy flood gun used for sample surface charge compensation. For depth profiling, the MAGCIS (Monoatomic Gas-Cluster Ionization Source) was used with 6 keV Ar$_{1000}^+$ clusters for 30 s of sputter time per level with no sample rotation.

C.4 GCIB-XPS Results

GCIB-XPS was used to compare the results between a sample of aged Incralac polymer (which contains BTA inhibitor) and aged Paraloid™ B44 polymer (which does not contain BTA inhibitor) to see if any differences in polymer and/or copper oxidation are present at the buried interface between the polymer-copper substrate. As BTA is less than 1% w/w of the total Incralac composition, conclusions regarding BTA position in the film are insignificant as there is not enough nitrogen present for detection with XPS. Figure C.2 is the results of a depth profile through the aged B44 sample showing: Figure C.2a elemental atomic percentages; Figure C.2b fitted components of C 1s, O 1s, and Cu 2p region; and Figure C.2c an explanation of the C 1s fitted components. Figure C.2a shows an expected depth profile trace for a polymer over the copper substrate. At the copper/B44 interface no remarkable features are present in the profile except a smooth transition from polymer signal to metal signal. Figure C.2b provides the details that the polymer may be degraded at the interface of the copper/B44 interface as is shown with highlight ‘1’, showing a temporary increase in the C-O component of the polymer and ‘2’ a much larger increase in βC-O component.
Figure C.2: Results of GCIB-XPS analysis on an aged spray-coated B44 polymer film on a copper substrate. Shown in ‘a’ is the elemental signal as a function of sputter time; ‘b’ is the same profile with individually fit components; ‘c’ is the identification of the C 1s components as traced in ‘b’.
showing a reduction in the polymer sidegroups and possible hydrolysis/cleavage of the sidegroups entirely. Lastly, as shown with highlight ‘2’, the βC-O component stays at a relative steady-state throughout the polymer layer in comparison to a decrease in the higher-oxidation components reinforces the conclusion that the B44 polymer is becoming altered in approach to the B44/copper interface.

Figure C.3 is the results from a GCIB-XPS analysis of an aged spin-cast Incralac film on a copper substrate. Figure C.3a is the trace of elemental C 1s, O 1s, and Cu 2p atomic percentages as a function of sputter time, Figure C.3b is the trace of all fitted components for the above elements, and Figure C.3c is again the identification of the C 1s fitted components for PMMA and PEA. As shown in Figure C.3a, a remarkable feature (1) is seen in the elemental atomic percentage oxygen trace, a non-smooth transition into the copper metal indicates that an unexpected feature is present at the Incralac-copper interface. This behavior is explained in Figure C.3b as the fitted components for carbon behave significantly different than in Figure C.2b, as the higher oxidized carbon species do not abruptly increase in signal at the Incralac-copper interface, showing that the polymer molecular structure in unaltered up to the interface. In contrast to Figure C.2b, a change is seen in the fitted oxygen components where (2) an increase of highly oxidized species and (3) a completely new oxygen species (which is right shifted) which would be related to a copper oxide species. This behavior indicates that the complete Incralac formulation (which includes the BTA inhibitor) will maintain any corrosion products at the polymer-copper interface, and does not result in premature degradation of the bulk polymer.
Figure C.3: Results of GCIB-XPS analysis on an aged spin-cast Incralac polymer film on a copper substrate. Shown in ‘a’ is the elemental atomic percentage signal as a function of sputter time; ‘b’ is the same profile with individually fit components; ‘c’ is the identification of the C 1s components as traced in ‘b’.
Lastly, to compare the observation of copper oxides present at the polymer-copper interface, Cu \( LMM \) Auger regions were collected during the depth profile analysis to prepare difference spectra, as the Cu \( LMM \) satellite peak positions are highly sensitive to copper oxidation state. Figure C.4 is the comparison of the aged B44 (a, c) and the aged Incralac (b,d). Figure C.4a is the autoscaled data from before/after the interface (this explains the change from no signal to observable signal) for the aged B44 sample, with the difference spectra shown in Figure C.4c. Figure C.4b is the autoscaled data from before/after the interface for the aged Incralac sample, with the difference spectra shown in Figure C.4d. If any oxides are present at the interface, then the difference spectra would show a significant peak, which is not present for the aged B44 sample (c), and possibly present for the aged Incralac sample (d). This supports the depth profile data that any copper corrosion products are held at the interface for the BTA-containing Incralac and not for the B44 film.

C.5 TOF-SIMS Results

TOF-SIMS analysis was performed on the sputter craters following GCIB-XPS analysis to identify any inhomogeneity of the BTA within the polymer layer. This was accomplished by imaging the crater walls that would show the entire polymer layer from upper surface to the copper substrate. Figure C.5 summarizes the results of TOF-SIMS analysis of the sputter crater for the aged Incralac sample. Images ‘a’ through ‘e’ were imaged at the location denoted “2” in Figure C.1b, and images ‘f’ through ‘j’ were imaged at the location denoted ‘3’ in Figure C.1b. Figure C.5a and C.5b are signals coming from the copper substrate, Figure C.5c is signal relating to
Figure C.4: GCIB-XPS spectra overlay to compare the formation of copper oxides at the polymer-copper interface. C.4a and C.4b show the Cu LMM Auger region (autoscaled immediately before and after the interface. C.4c and C.4d are the resulting difference spectra of the Cu LMM Auger region, any indication of peak formation would be due to the presence of copper oxides.
Figure C.5: ToF-SIMS images of aged Spin-cast Incralac film on copper-bronze coupon. The SIMS image was taken on the edge of a crater sputtered using a 4 kV Ar$_{2000}^+$ gas cluster ion beam (GCIB). (A) is the copper image as an addition of Cu$^+$ and $^{65}$Cu$^+$ mass fragment images. (B) is the zinc image as an addition of Zn$^+$ and $^{66}$Zn$^+$ mass fragment images. (C) is the PMMA/PEA image as an addition of C$_2$H$_3$O$_2^+$, C$_2$H$_5$O$^+$, and C$_3$H$_5$O$_2^+$ mass fragment images. (D) is the BTA image as an addition of NH$_4^+$ N$_3^+$, C$_6$H$_5$N$_2^+$, and C$_6$H$_4$N$_3^+$ mass fragment images. (E) is an overlay of images (A) through (D) with the following color channels: (A) blue, (B) cyan, (C) red, (D) green. (F) is the copper image as an addition of Cu$^+$ and $^{65}$Cu$^+$ mass fragment images. (G) is the zinc image as an addition of Zn$^+$ and $^{66}$Zn$^+$ mass fragment images. (H) is the PMMA/PEA image as an addition of C$_2$H$_3$O$_2^+$, C$_2$H$_5$O$^+$, and C$_3$H$_5$O$_2^+$ mass fragment images. (I) is the BTA image as an addition of NH$_4^+$ N$_3^+$, C$_6$H$_5$N$_2^+$, and C$_6$H$_4$N$_3^+$ mass fragment images. (J) is an overlay of images (F) through (I) with the following color channels: (F) blue, (G) cyan, (H) red, (I) green. An observed drop in Incralac molecular signal is present at the Incralac-copper interface, although no definitive copper-BTA fragments were observed at the interface as theorized.
PMMA/PEA mass fragments, Figure C.5d is signal relating to BTA mass fragments, and Figure C.5e is an overlay of copper (blue), zinc (cyan), PMMA/PEA (red) and BTA (green). Figure C.5f is signal coming from copper in the metal substrate, Figure C.5g is signal coming form zinc in the metal substrate, Figure C.5h is signal coming from mass fragments related to PMMA/PEA, Figure C.5i is signal coming from mass fragments related to BTA, and Figure C.5j is an overlay with copper (blue), zinc (cyan), PMMA/PEA (red), and BTA (green). From the images, no discernable increase of BTA is observed at the copper-polymer interface. In addition, no mass fragments for a Cu-BTA complex were observed with TOF-SIMS analysis.

C.6 Conclusions

The results of this study were useful in identifying differences in degradation mechanisms related to Incralac polymer for artistic bronze. GCIB-XPS was able to identify differences in molecular degradation between a sample of aged Paraloid™ B44 polymer (which does not contain the BTA corrosion inhibitor) and that of aged Incralac (which does contain the BTA corrosion inhibitor. The observation of oxidation occurring throughout the B44 film in contrast to oxidation only occurring at the polymer-metal interface of Incralac provides evidence of BTA as a stabilizer and corrosion inhibitor. TOF-SIMS results were not as conclusive as no Cu-BTA complex was identified, however the observation of BTA throughout the entire film provides evidence that BTA is not as mobile as theorized.
REFERENCES


Appendix D

LIST OF PERMISSION FOR TABLES AND FIGURES

For this dissertation, several figures were shown that were pulled from the literature, as well as articles published by the author. The following permissions will have a note for which table/figure they permit. For Figures 1.7 and 1.22, the original publications were published under open-access guidelines, and as such permissions are not required for educational and non-profit use.
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I am Zachary Voras, a graduate student working at the University of Delaware. For my PhD thesis, I am wishing to reprint figures in my dissertation from two articles in Journal of Cultural Heritage. The citations and requested figures for the articles are as follows:


from which I would like to use Figure 18,


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Thank You,

Zachary Voras

Issy-Les-Moulineaux, 22-Jun-2016

To the attention of Mr Zachary Voras

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Good morning!
I have a question and a comment:

1) I would like to use one of the figures from the *Triumph of David* chapter in my intro/review of surface science/cultural heritage materials. How close is this to publication? I would need permission from the publishing house of the book to reprint the images. Who should I contact?

Zach

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Kd

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Joan Marie Reifsnyder,

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Thank You,
Zachary Voras

Dear Zachary,

I am the one. And Yes, you may use the figure 6 from the paper you cited. Please include citation as you sent it to me in your notes.

Best,
Joan

Joan Marie Reifsnyder
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