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Discoloration of a Green Pigment in Tintoretto's Allegorical Figure of Spring and Analysis of the Chemical Properties and Stability of Copper Resinate

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DISCOLORATION OF A GREEN PIGMENT IN TINTORETTO'S *ALLEGORICAL*

FIGURE OF SPRING AND ANALYSIS OF THE CHEMICAL PROPERTIES AND

STABILITY OF COPPER RESINATE

by

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ABSTRACT

DISCOLORATION OF A GREEN PIGMENT IN TINTORETTO'S *ALLEGORICAL FIGURE OF SPRING* AND ANALYSIS OF THE CHEMICAL PROPERTIES AND STABILITY OF COPPER RESINATE

Sarah Wells Connor Horn
Old Dominion University, 2016
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The focus of this thesis is the discoloration of a common historical green pigment, copper resinate. In this research the discoloration was investigated in Jacopo Tintoretto's painting, *Allegorical Figure of Spring*, painted c. 1555. This painting is believed to have been painted with copper resinate which has discolored to brown over the centuries. The state of repair of the painting was determined using visual analysis under visible and UV light and the use of copper green pigments was confirmed using energy-dispersive X-ray fluorescence, including copper resinate based upon supplementary historical evidence. Substantial evidence was found from visual inspection and XRF determination of pigments that the painting had originally been lozenge-shaped and had been given its current rectangular shape only after the addition of supplementary canvas to its corners and top and bottom. Inspection of the painting under UV light highlighted areas of damage and repair, and the appearance of modern pigments such as titanium white and zinc white indicated that repairs and overpainting had been conducted as recently as the twentieth century.

I also conducted an investigation of copper resinate in the laboratory to determine its chemical composition, stability and possible modes of degradation. For my study of copper resinate, I used pigments synthesized by historic and modern recipes to determine its composition using mass spectrometry and FTIR. I determined that in either case copper resinate

is a mixture of copper compounds containing acetate and abietate ligands in varying ratios including $[Cu_2Ab_4]$, $[Cu_2Ab_3Ac]$, and $[Cu_2Ab_2Ac_2]$. I investigated its chemical properties and stability by extraction, UV absorption, subjection to various solvents and environments. I found that the green color of copper resinate is a result of a combination of blue copper carboxylate compounds and free abietic acid, which is yellow in color. I also found that the drying process of copper resinate is light- and water-dependent and that both verdigris and copper resinate quickly discolor to brown upon the addition of a dilute basic solution. From this evidence, I hypothesize that the discoloration of copper resinate results from exposure to water in the environment and traditional treatments leading to the slow degradation of the pigment to brown copper oxide.

DEDICATION

As in all areas of my life, I owe a great debt of gratitude to my parents, Michael and Linda, who first encouraged me to study science, who supported my education and who were my first and most enthusiastic supporters. I am also grateful to my husband, Charlie, who began this process with me in a long distance relationship and will end it as my husband and co-parent. His unfailing support and encouragement has kept me going on a daily basis and I am incredibly grateful for his unselfish ability to pick up the slack I've left when work and school were especially time-consuming. And, finally, I would like to acknowledge our little girl whose fast-approaching due date has kept me motivated to finish this thesis better than any other deadline!

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

The early sixteenth century was a golden age of Venetian art, marking a time of an explosion of artistic experimentation and genius [1]. Venice's positioning as a port city made it a nexus for artisans from a variety of trades, which led to the development of a great variety of pigments including ground glass [2] and ceramics, organic dyes from textiles [1] new pigment binders, drying oils, and varnish treatments [3]. Combined with new techniques of layering and mixing colors to increase their depth and vibrancy [1, 3, 4], every easel painting from this time period is unique. Unfortunately, as paintings age they often undergo changes such as cracking or losses in the various layers, discoloration of pigments, structural damages such as weakening canvases and accidental damages and purposeful editing [5, 6]. Conservators today employ a variety of analytical techniques to study paintings and determine what changes they may have undergone, if any of the changes can or should be reversed, and how to protect the painting from the effects of aging going forward [3, 6]. These techniques include X-ray radiography (XRR); X-ray fluorescence spectrometry (XRF); infrared (IR); Raman and UV/Visible spectroscopy; mass spectrometry; and microscopy, among others [6, 7, 8].

Early Venetian masters like Giorgione and Jacopo Bellini paved the way for the Venetian School of painters in the sixteenth century like Titian, Jacopo Tintoretto, Paolo Veronese and Jacopo Bassano. The Venetian School was known for their treatment of colors and light to overcome the darker light of Northern Italy and the use of lead and wax in their oil medium to create a matte-like finish [1, 4]. Jacopo Bellini's son, Giovanni Bellini instructed both Giorgione

and Titian and was perhaps the first great Venetian painter of the Renaissance, but he is overshadowed in history by his pupils.

Slightly after Titian, another Venetian painter, Jacopo Robusti, nicknamed "Tintoretto" ("the little dyer") for his family trade of textile dyeing [9], gained renown. He was placed under Titian's tutelage at a young age, but as legend has it, he was sent away when the master saw talent that might overshadow his own [9]. By his own admission, Tintoretto greatly admired Titian's use of color, and indeed, sought to combine Titian's colors with Michelangelo's design [9] to achieve what he considered the height of artistic perfection. What he succeeded in, however, was developing a style all his own, with bright colors combined with heavily-contrasted light and shadow, and muscular, active, twisting figures [10] that begin to suggest the Mannerist that was beginning in the early sixteeth century. With his family trade and location in a port city, Tintoretto had access to a diverse array of pigments and dyes. The early Italian Renaissance was a time of expansion for artists' palettes with the introduction of lead-tin yellow, ultramarine and copper resinate to the colors already in use since ancient times [3, 11] (Table 1). Additionally, although ground glass pigments such as smalt (cobalt blue glass, ground and suspended in oil) did not become widely popular until the sixteenth century, its extensive use by Venetian artists including Tintoretto was observed earlier, due most likely to Venice's proximity to the island of Murano, known for its glass blowing [2, 10].

Table 1
The most common pigments available to artists during the Italian Renaissance.

Pigment Name	Color	Chemical Name	Chemical Formula
Ancient Pigments			
Azurite	Blue	Basic copper carbonate	$2CuCO_3 \cdot Cu(OH)_2$
Indigo	Blue	Indigotin	$C_{16}H_{10}N_2O_2$
Ultramarine	Blue	Natural *lapis lazuli*	$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$
Red ochre	Red	Anhydrous iron(III) oxide	Fe_2O^3
Red Lakes	Red	Kermes, lac and madder	Mix of organic compounds
Red Lead	Red	Lead(II,IV) oxide	Pb_3O_4
Vermillion (cinnabar)	Red	Mercury(II) sulfide	HgS
Yellow Ochre	Yellow	Iron oxyhydroxide	$FeO(OH)$
Orpiment	Yellow	Arsenic trisulfide	As_2S_3
Malachite	Green	Basic copper carbonate	$CuCO_3 \cdot Cu(OH)_2$
Verdigris	Green	Copper(II) acetate	$Cu_2(C_2H_3O_2)_4(OH)_2$
Terre Verte	Green	Aluminosilicate minerals	1
Charcoal	Black	Carbon	C
Lamp Black	Black	Carbon	C
Chalk	White	Calcium carbonate	$CaCO_3$
Gypsum	White	Hydrous calcium sulfate	$CaSO_4 \cdot 2H_2O$
Lead White	White	Basic Lead(II) carbonate	$2PbCO_3 \cdot Pb(OH)_2$
New Pigments available during the Renaissance			
Smalt	Blue	Potassium glass with cobalt	SiO_2, K_2O, Al_2O_3, CoO
Lead-tin yellow	Yellow	Lead stannate or Lead tin oxide silicate	Pb_2SnO_4 or $Pb(Sn,Si)O_3$
Copper Resinate	Green	Copper(II) abietate	Mixture of verdigris and Venice turpentine

Tintoretto differed from the other Venetian artists, combining more wax with his paints for a more deep and fluffy effect. Moreover, he worked with great speed, allowing mistakes to go unfixed and colors to overlap each other, as long as they did not interfere with the overall effect of the painting [4]. Tintoretto often worked on a large scale on high, dimly lit ceilings where he could concern himself more with the overall impression his paintings made, than with

the minutia of the production [12]. His hurried workmanship and vast array of available painting materials make Tintoretto's painting often a confusing conglomeration of layers and pigments.

Around 1555, Tintoretto was commissioned to paint the ceiling of the Casa Barbo, a private residence in San Pantaleone, Venice. He painted the central panel, *The Dreams of Men* (Fig. 1)*,* described by Carlo Ridolfi in his 1684 manuscript, *The Life of Tintoretto* [9], as "a dream sequence with some goddesses in the sky and various images of the things produced in the minds of mortals in their sleep" [9]. He went on to describe surrounding paintings of the Four Seasons, which are believed to be *Allegorical Figure of Spring* (Fig. 1), currently housed at the Chrysler Museum of Art in Norfolk, VA, *Allegorical Figure of Summer* (Fig. 1) currently at the National Gallery in Washington, DC, *Allegorical Figure of Autumn*, in a private collection in Italy, and a fourth of winter whose location is unknown [13].
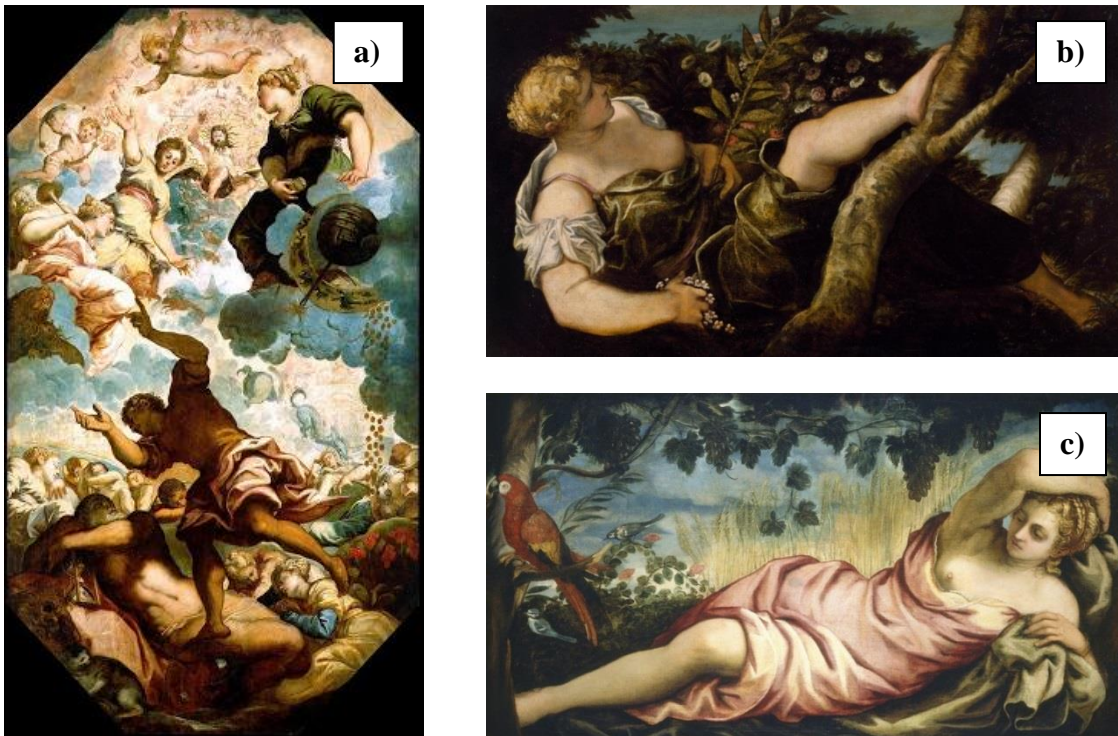
Figure 1. (a) Tintoretto's *Dreams of Men* and two of the four paintings that originally surrounded it in Casa Barbo; (b) *Allegorical Figure of Spring* and (c) *Allegorical Figure of Summer.*

In this thesis, I will closely examine Tintoretto's easel painting, *Allegorical Figure of Spring*, which appears to have changed in color from a spring-like green to dark brown over time. The works of art we now appreciate are in our stewardship for a brief time and it is our responsibility to pass them onto the next generation. This charge, along with a desire to elucidate the artistic process, is behind my investigation of Tintoretto's work and its apparent discoloration. Copper resinate, a popular Renaissance pigment, has a well-documented record of discoloration from green to brown [14], but its presence must be confirmed. Possible pigments used in the original painting will be identified, as well as any changes or additions that appear to have been made over time. I hope to confirm what pigment is responsible for the discoloration and elucidate its mechanism of degradation. To study the painting, microscopy, visible and UV light, as well as X-ray fluorescence spectroscopy for be utilized. For the chemical analysis of the discolored pigment, mass spectrometry, UV spectroscopy and IR spectroscopy will be utilized. This research will yield insight into the pigments used in *Allegorical Figure of Spring* and a better understanding of the chemical makeup and stability of the green pigment which has deteriorated over time.

The Typical Stratigraphy of Renaissance Oil Paintings

Before any physical or chemical examination of the painting, it is first necessary to understand the complex layers that comprise the painting [3, 6, 15]. The typical stratigraphy of a painting from this time period begins with the support layer, usually canvas and wood, which is then covered by a layer of animal-based glue called size, followed by one or more layers of ground (a priming layer of chalk or plaster), several paint layers, possible layers of glaze and the varnish layer (Fig. 2). Despite the diversity of techniques encountered in the Italian Renaissance,

easel paintings of this time period still remain fairly consistent in the general stratigraphy of their layers.

The most common supports are canvas and wood, although glass, copper plates, stone and even obsidian can be found [6]. In the case of canvas, the surface is usually impregnated with a layer of animal-based glue (size) [5] for protection, to prevent the subsequent ground layer from becoming absorbed, and to create a bond between the support and ground layer [3, 6]. Metal and stone supports might be rubbed with garlic to improve paint adhesion and copper plates might include a layer of lead white in oil [3]. Canvases are subject to weakening over time and are often relined or impregnated with glue multiple times throughout a painting's
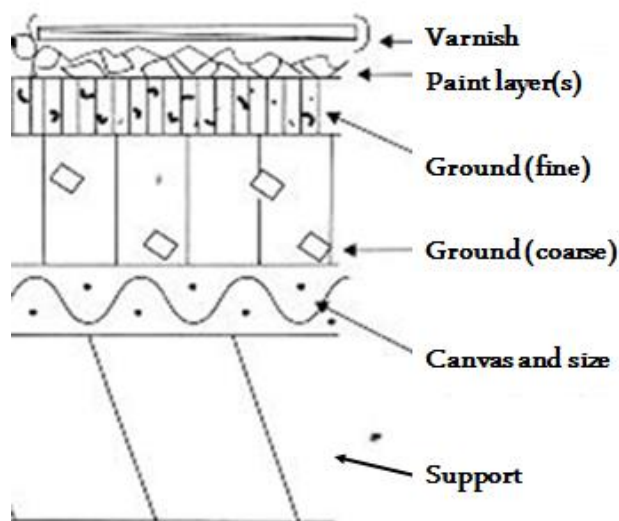
Figure 2. Common stratigraphy for early Italian Renaissance paintings. [5]

history. From the late 1800s through the 1900s wax was used to adhere new lining to the old canvas and resulted in the darkening of the painting when the wax seeped through to the paint and ground layers. Lining a canvas also involves heat and pressure to adhere the new canvas, a

process which flattens the three-dimensionality of the paint (called impasto) resulting in cracking, moating, and canvas weave showing through [3].

The ground layer serves as a priming layer and effects the tone and texture of the subsequent paint layers. It consists of inert solids such as chalk, gypsum, or whiting suspended in glue or oil [3]. White ground layers are traditional but colored ground ranging from pale gray to brown, red and black may be used throughout a painting or selectively to give depth to certain areas. Tintoretto was known to mix his leftover palette scrapings with his ground, meaning his grounds were typically colored [16]. The ground layer is usually actually comprised of multiple layers beginning with the size (animal-based glue) to seal the canvas and followed by one or more ground layers of decreasing granularity [3]. A final priming layer may consist of clay, shellac or drying oil [3]. The sketch, or underdrawing, for the painting is applied on the dried ground layer, followed by a possible under layer of egg or oil [5].

The subsequent paint layers are characterized by pigments obtained from animal, plant and mineral sources, suspended in organic binding medium such as egg, oil, or wax. Most ancient pigments came from readily available materials such as iron oxide reds (Fe_2O_3) or other ochres, lead white ($2PbCO_3 \cdot Pb(OH)_2$), charred bones or lamp black (C), green verdigris ($Cu_2(C_2H_3O_2)_4(OH)_2$) from copper and vinegar, or ground minerals like malachite ($CuCO_3 \cdot Cu(OH)_2$), cinnabar (vermilion, HgS) and azurite ($2CuCO_3 \cdot Cu(OH)_2$) (Table 1) [3]. Dyes were also used since ancient times including indigo, madder, lac and saffron (all organic compounds), all of which could be processed into function as pigments known as lake pigments [3] by precipitating the dye onto an inert binder such as chalk or alumina. In the Renaissance many new pigments were added to artists' palettes including copper resinate (made from verdigris), ultramarine ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$), lead-tin yellow ($Pb_2SnO_4$ or $Pb(Sn,Si)O_3$), Naples

yellow ($Pb(SbO_3)_2$ or $Pb(SbO_4)_2$) and smalt (SiO_2, K_2O, Al_2O_3, CoO), made from ground cobalt blue glass [3]. The pigments in the Renaissance color palette had varying stability, with color distortions appearing even within the artists' own lifetime. Copper resinate, azurite, smalt and vermilion are all known to darken to brown or black, while lake pigments are notoriously fugitive and prone to fading [3]. From the late eighteenth century to the present, new synthesized pigments have been developed, including Prussian blue ($Fe[Fe3+Fe2+(CN)6]3$), zinc white (ZnO) and titanium white (TiO_2), which were cheaper, safer and chemically and physically stable [3]. Around the fifteenth century, Italian artists transitioned from water-based binders such as egg or animal glue, to oil-based binders (although water-based binders were still used for certain pigments as necessary). Some oils, such as olive oil, do not dry, but certain oils, such as walnut oil, linseed oil and poppy oil, known as "drying oils," will slowly polymerize in contact with light and oxygen in the air to form a hard film. In this process, photo-induced fatty acid radicals may polymerize with other fatty acid radicals. Oxidation adjacent to double bonds results in hydroperoxides, which then cross-link with neighboring fatty acids. Thus, a stable network of cross-linked fatty acids is formed and the oil hardens [17] (Fig. 3). The slow drying time allowed for more blending of colors [3] as well as a new addition to the strata of the painting: the glaze layers. Glazes are very thin applications of paint, such that the pigment particles are spaced much further apart, yielding subtle effects to the painting such as shadow and color depth [5].

The final layer, the varnish, is usually a late addition to the painting, applied at least a year after the painting was complete in order to ensure the oils had dried completely [3]. Typically of spirit or oil during the Italian Renaissance, the varnish layer serves to protect the paint layers, but also alters the appearance of a painting. Because the varnish layer was added so

long after the artist had completed the work, and because older varnish has usually been removed and replaced due to discoloration, it is often difficult to discern whether the varnish was included in the artist's original vision or if it detracts from its intended aesthetic.
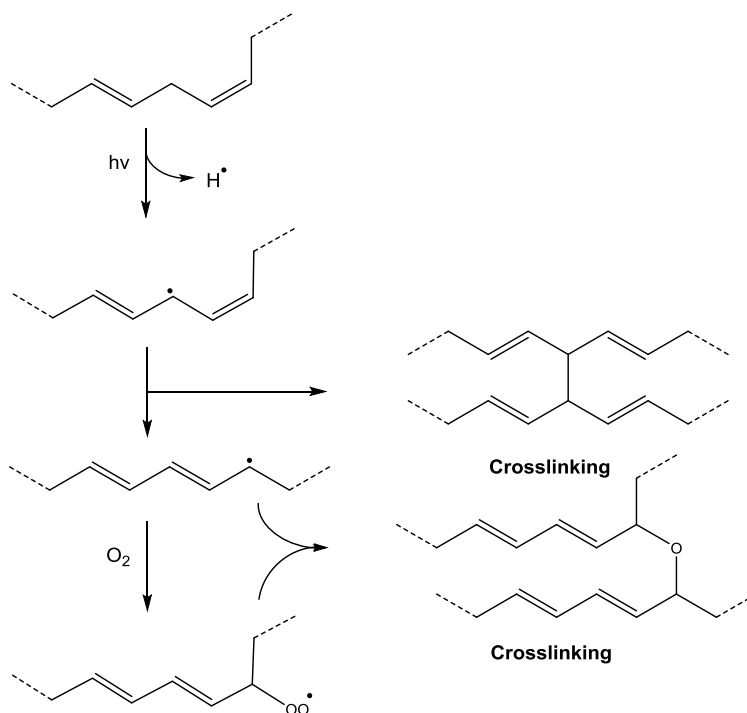
Figure 3. The general mechanistic scheme for the hardening of oil media through the formation of cross-links between fatty acids.

Chemical Analysis Methods Used

Modern analytical chemistry has developed an array of techniques for examining paintings and other cultural artifacts [3, 6, 7, 8]. Each of these techniques serves to examine a different part of the painting, and can all be classified as either destructive or non-destructive. Non-destructive methods involve no alteration to the painting or samples from the painting. The support of the painting is often analyzed using non-destructive X-ray radiography (XRR). Examining the stratigraphy of the ground and paint layers often requires the use of destructive

analysis through the removal of paint flakes or cross-sections to view the layers using microscopy visible light, UV light, using scanning electron microscopy or IR spectroscopy. Sample sizes are small, which restrict the destruction of the painting's appearance. Cross sections can also be pulverized for analysis of pigment and binder molecules through mass spectrometry. Non-destructive methods for examining the paint layers can range from simple observation under various light sources such as visible or UV or different light angles such as raking light to irradiation with different wavelengths of light.   UV light may be applied non-destructively to assess damage in the paint or varnish layer.   X-ray fluorescence (XRF) can be used to assess what elements are present in the painting. Raman and IR spectroscopy can either be applied destructively to cross-sections or non-destructively to the surface of the painting to identify the pigments present. The underdrawing may be visualized non-destructively using IR reflectography (IRR). IR light (1100-1700 nm) passes easily through pigments in the paint layer to reach the underdrawing where it is reflected by the ground but absorbed by charcoal with which the drawing is usually articulated. Thus, a camera detecting reflected IR light can generate a picture of the underdrawing [18].

In this thesis, I am focusing on determining areas that may have been altered or retouched over time and determining the pigments present in the original painting. To that end, I will analyze *Allegorical Figure of Spring* non-destructively under visible and UV light as well as use XRF spectroscopy, and I will examine the painting destructively by removing cross-sections and examining them with visible light microscopy.

Raking Light

Analysis of a painting with raking light involves the use of visible light at an oblique angle to bring the surface texture of the painting into more relief [3]. This technique will reveal any anomalies in the paint layers such as cracking or peeling, and any changes in the reflectivity of the surface which might indicate damage or retouching. But this method will also highlight the texture of the ground and canvas as well as seams or joints in the support. In this research I will be using raking light to more closely examine areas of cracking in the paint layer, as well as the weave of the canvas.

Ultraviolet Light

Ultraviolet (UV) light is usually used to assess damage to a painting and indicate areas of retouching, but it can also provide some insight into the types of materials in a painting [3]. Analysis by UV light generally focuses on the varnish layer, which will fluoresce differently based on the age and type of varnish. Aged damar (vegetable resin) will fluoresce greenish-yellow, shellac (varnish from insect secretions) will fluoresce orange, and synthetic varnish will fluoresce clear or lavender. Old varnish will fluoresce much more than new varnish, thus making spots of varnish touch ups easily visible [3]. Older pigments will sometimes also fluoresce more than newer pigments, but the fluorescence from the paint layer is often covered by that of the varnish layer.

Problems arise with this method of analysis when a newer varnish coat containing UV inhibitors is present. The purpose of the UV inhibitors is to slow the aging and discoloration process of the varnish, but it also masks any information that might be obtained from UV analysis [3]. Furthermore, older paintings may contain contaminants that also fluoresce,

resulting in unreliable information on the state of the painting [19]. In this research, I will be using UV light on the surface of the painting to identify any areas of damage or retouching.

X-Ray Fluorescence

X-ray fluorescence spectrometry (XRF) can be used to identify pigments and is frequently applied to analysis of paintings [6, 20, 21]. XRF can be applied to the surface of a painting or to a cross-section sample and is, therefore, both a destructive and a non-destructive analytical technique. This method is capable of determining the elements present at a certain location on the painting or in a cross-section, and when applied to the surface of a painting, it can also determine the thickness of paint or glaze layers. The elemental spectra of certain pigments have been catalogued to aid in using the spectrum to identify the pigments present [22].

When atoms are irradiated with X-rays, they emit fluorescent radiation characteristic of their particular electron configuration. Electrons in lower energy levels (the inner shell electrons closer to the nucleus) are photoionized by the high-energy X-rays leaving an inner orbital of atom empty [23]. Electrons in higher energy levels (the valence electrons farther from the nucleus) fill the inner orbitals left empty by the excited electrons and release energy in the form of photons. Each element has a different arrangement of electrons in its energy levels, therefore elements can be identified by their unique energy and fluorescence pattern. An electron may drop to the first, second or third energy level, and the resulting fluorescence will be given the designation K, L, or M, respectively. The fluorescence is also designated α, β, γ, δ etc. based on the energy level from which the electron originated. If the electron falls just one energy level, its fluorescence is given the designation α. If it falls two energy levels it is given the designation β etc. Therefore an electron transitioning from the third to the first energy level will be given the

designation K_β. Depending upon the energy of the transition, either the K or L lines are typically detected within XRF. For example, the fluorescence spectrum of Cu results from the 2s, 2p, 3s, 3p or 3d electrons falling to fill the 1s orbital and therefore its K_α (2s,2p→1s) and K_β (3s,3p,3d→1s) fluorescences are observed at 8.04 and 8.90 eV. In contrast, the strongest fluorescence for Pb will be for its L_α and L_β lines in which electrons fall from the 3s, 3p, 3d, 4s, 4p or 4d orbitals to the 2s or 2p orbitals (10.55 and 12.60 eV). The K lines of Pb are such low energy that they do not appear on the spectrum. For any individual element, α fluorescence counts will always exceed β, which will always exceed γ etc. But the strength of the fluorescence signal compared with that of other elements depends both on the amount of the element present and if the element is on the surface of the painting or buried beneath other layers.

There are two main types of XRF which differ in their method of fluorescence measurement. Wavelength Dispersive XRF (WD-XRF) uses an analyzing crystal which diffracts the X-ray fluorescence waves with different energy waves being diffracted at different angles. The fluorescence intensity at each wavelength is then detected by either a single mobile detector or multiple detectors at various angles to determine the total count of each type of fluorescence. Energy Dispersive (ED-XRF) collects all of the fluorescence waves in the same silicon lattice detector but differentiates between them by how many electrons they knock free in the detector. A higher energy wave will knock more electrons free in the detector than a lower energy wave and each x-ray is measured individually to determine its energy [24]. XRF methods are capable of detecting elements from Mg to U in concentrations as low as ppm. However, it is extremely difficult to detect some of the lighter elements even within this range [25]. Sensitivity in the range of lighter elements can be improved using filters as well as vacuum to reduce interference from background radiation [24].

The use of XRF is common in art conservation because it is a non-destructive technique that imparts a lot of information about the pigments present. False identification of elements is unlikely with this method, but pigments composed of the same elements are indistinguishable, such as red lead (Pb_3O_4) versus lead white ($2PbCO_3 \bullet Pb(OH)_2$) with red lake dye (a mix of organic compounds) [6]. Organic pigments are generally undetectable because they are composed of elements below the XRF detection limit. ED-XRF was employed successfully to expose a forgery called "Violeiro" allegedly attributed to Emiliano di Cavalcanti by comparing the pigments used in the fake to his usual palette. In other paintings by di Cavalcanti, high fluorescence of lead and mercury are observed in his red oil pigments. In the "Violero", the red appeared to be an organic lake pigment based on the absence of higher Z elements in the XRF spectrum [26].

Variations on XRF include micro-XRF, macro-XRF, confocal XRF and handheld XRF. Micro-XRF can be used to accurately identify pigments in small areas but the dwell time (the time required for the instrument to remain in one place to obtain a reading) is very long [6]. Micro XRF can probe a much smaller area than macro-XRF, which is available as a mobile instrument. Confocal XRF uses two mirrors instead of one in order to limit the amount of fluorescence that reaches the detector to a smaller volume of the sample than in standard XRF. Therefore, the individual layers of the painting may be analyzed by moving the selected volume of sample deeper into the subject. Handheld XRF is advantageous due to its mobility, which is especially beneficial as the artwork need not be exposed to the risks of transportation. I will be using a handheld ED-XRF device loaned from Bruker to analyze the elements present at various points in *Allegorical Figure of Spring*.

CHAPTER II

EXAMINATION OF TINTORETTO'S *ALLEGORICAL FIGURE OF SPRING*

For the examination of *Allegorical Figure of Spring,* I will employ selected non-destructive and destructive methods outlined above, including surface analysis under raking and UV light, XRF spectroscopy, and microscopic examination of cross-sections under visible light. These methods will allow us to assess the physical condition of the painting, observe any major areas of damage or alteration, and develop an elemental profile of the painting to aid in assignment of the pigments used by the artist.

Physical Examination

Tintoretto's *Allegorical Figure of Spring,* painted c. 1555, is one of a four-part series depicting the four seasons. Of the other three paintings, *Allegorical Figure of Summer* is currently at the National Gallery in Washington, D.C., *Allegorical Figure of Autumn* is in a private collection in Italy and the whereabouts of *Allegorical Figure of Winter* is unknown [12]. The four-part series was originally painted for the ceiling of Casa Barbo, a private residence in San Pantaleone, Venice, where it surrounded another of Tintoretto's paintings, *The Dreams of Men,* currently at the Detroit Institute of Arts. In 1957 *Allegorical Figure of Spring* showed up in a private collection in France and the following year appeared in the Newhouse Galleries in New York City. In 1971, it was obtained by Walter P. Chrysler, Jr. and became part of the Gift of Walter P. Chrysler, Jr. to the Chrysler Museum of Art in Norfolk, VA, where it resides today.

The painting is in oil medium on canvas. The physical examination of this painting took place in the conservation lab of the Chrysler Museum of Art in Norfolk, VA under a combination of natural and artificial light as well as under ultraviolet light. The overall repair of the painting was examined, the canvas weave was inspected and measured, and detail photographs were taken.

The original canvas is supplemented by at least one additional glued lining canvas. The last additional canvas is a plain weave with yarns of uneven diameter and 28 warp and 28 weft threads per square inch. The glued lining is in good condition. The original canvas is a twill weave canvas, estimated to be linen. The weave of the canvas runs horizontal and vertical in the main body of the painting but can be seen in the corners to run at a slightly different angle (Fig. 4).

At each of these corners there are cracks running at least as deep as the paint layer, if not deeper, at 45 degree angles to the corners, as well as horizontal cracks about $1 \, ^{1}/_{8}$" from the top and bottom (Fig. 4). The cracking is especially pronounced in the upper left corner of the painting where lifting of the crack is apparent. There is smoothness around all of the cracks where the weave of the canvas is lost indicating that the cracking or seams were once filled. There are patches of imprinted canvas weave on the diagonal cracks, where this smoothness was intentionally disrupted in order to blend them with the rest of the painting, but these patches are not visible on the horizontal cracks (Fig. 5). This painting, along with *Allegorical Figure of Summer* at the National Gallery in Washington, D. C., was originally fitted with a lozenge-shaped frame [13] but it is unknown whether the canvas was originally lozenge-shaped or rectangular. It is speculated that these cracks indicate later additions to the canvas and that the canvas itself was originally lozenge-shaped.
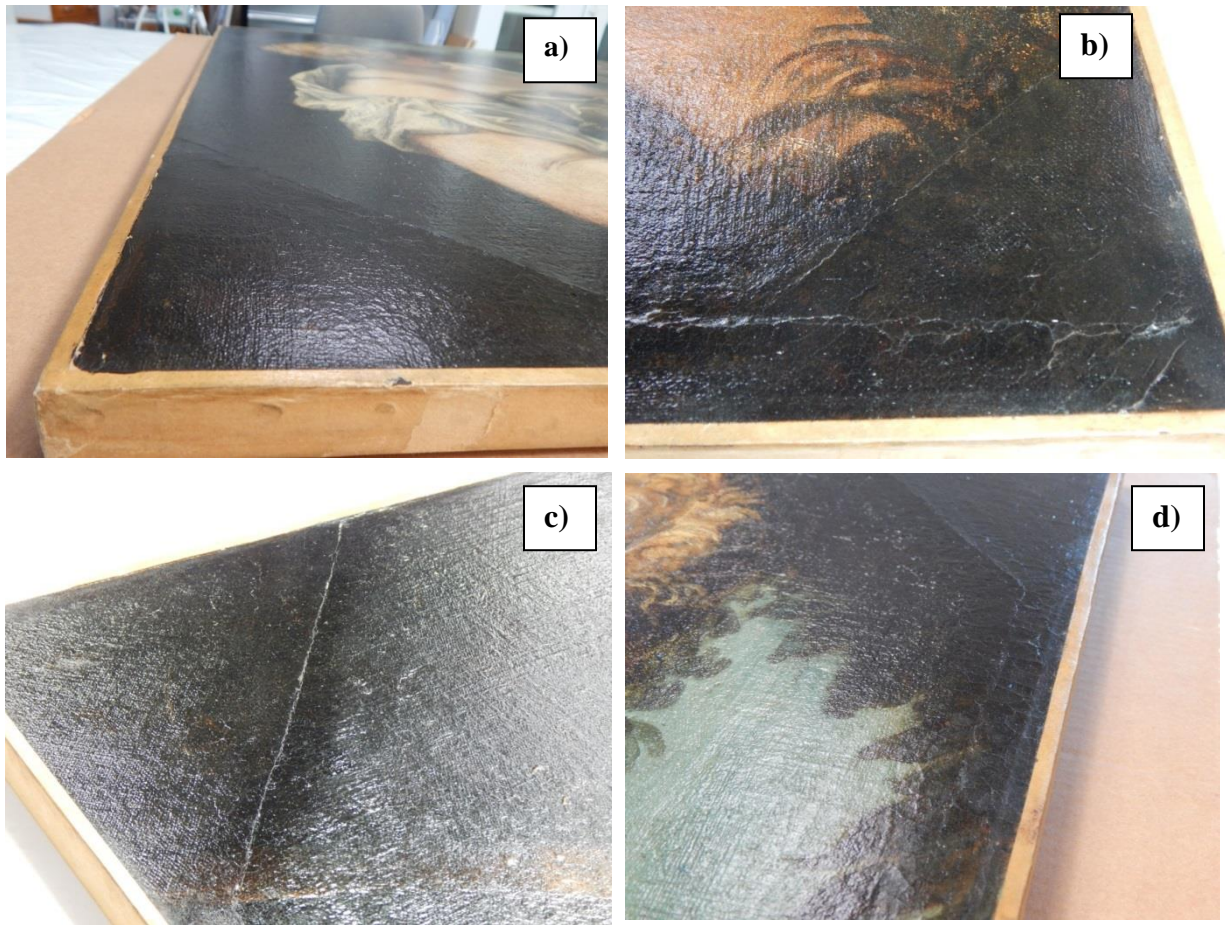
Figure 4. Detail of the 45° crack in the corners and the horizontal cracks on the top and bottom of the painting. Cracks are shown in the (a) lower left corner of the painting, (b) lower right corner of the painting, (c) upper right corner of the painting, and (d) upper left corner of the painting. The difference in the weave between the corner and the rest of the painting is also visible.
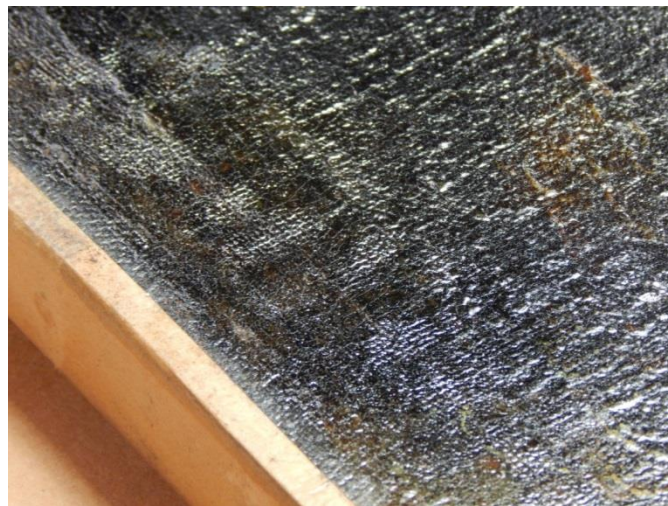
Figure 5. Detail of imprinted weave pattern along the length of a crack. The pattern appears to have been intentionally added to disrupt the smoothness where the cracks were blended.

The original impasto, characteristic of Tintoretto's imprecise and exuberant method of paint application, has been largely lost due to the heat and pressure applied during relining of the canvas. Moating (brought about from the flattening of a previously raised paint profile) and visible brushstrokes indicate that the paint was applied loosely, and thickly in highlighted areas. This flattening of the impasto is especially visible in the flowers.

Some areas of *pentimenti* (evidence that changes were made prior to the final design) can be seen suggesting previous designs that were covered over. Most noticeable are two horizontal lines extending upwards along the woman's thigh (Fig. 6), and two similar lines extending upwards out of her right hand (Fig. 7). These lines may indicate where branches had originally been intended. Also visible on the woman's left foot is a series of curved paint strokes, where foliage may have originally covered her feet (Fig. 8). Perhaps a last minute change in the design of her foot explains why it appears now to be at an awkward angle to the rest of her body.

Old retouches are visible under ultraviolet light, most especially in the flesh areas. One large area of retouching appears on the woman's right forearm. Also somewhat visible in visible light, but more visible in UV light, are several areas of retouched damage in the fabric covering the woman's right thigh. The surface coating is a varnish, estimated to be older natural resin as it autofluoresces under ultraviolet light. The weave of the canvas has significant dirt buildup and there is an overall brown cast in many places, which may be due to discolored varnish. Small areas that do not auto-fluoresce under ultraviolet light indicate areas of touchup, especially in the flesh areas.

Figure 6. *Pentimento* on woman's thigh. Two vertical lines visible of the woman's thigh may indicate a previous design that was painted over.

Figure 7. *Pentimento* extending from woman's hand. Lines extending upwards out of the woman's right hand may indicate a previous design such as a branch that was covered over
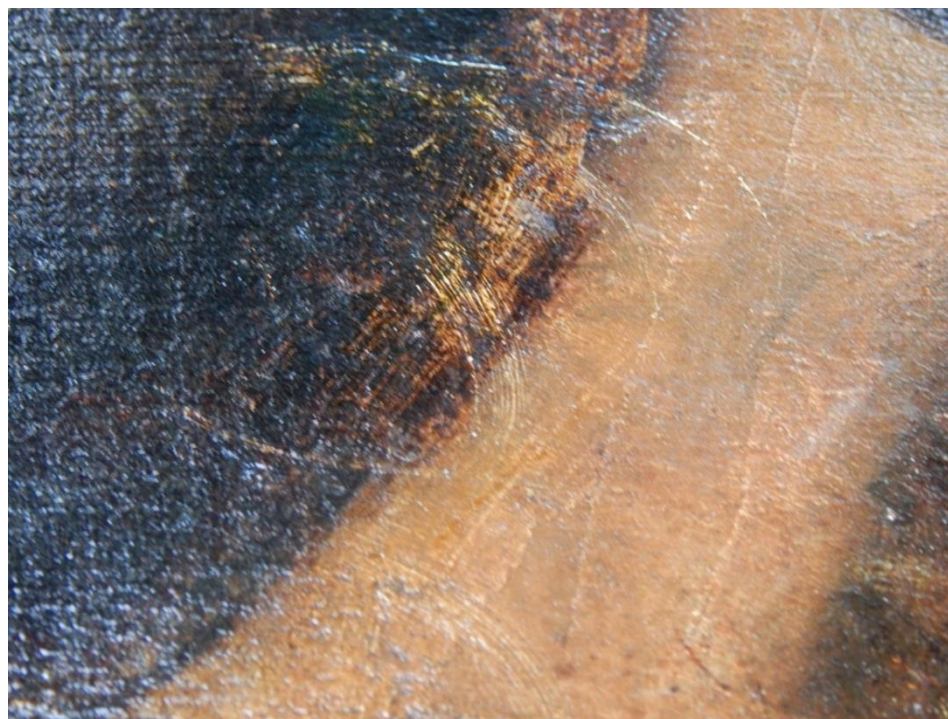
Figure 8. *Pentimento* on woman's foot. Here, a detail of the woman's foot is shown with brush strokes that may indicate where foliage originally covered her foot.

XRF Analysis

The elements present in the painting were analyzed at 41 points by ED-XRF (Fig. 9, Table 2). The main purposes of this analysis were to identify the pigments that may have been used in the original painting, but also to determine if differences in elemental composition throughout the painting indicated non-original or altered areas. I therefore scanned various areas in the painting, making sure to include the area of flesh damage already determined by UV light, as well as the corners and strips on the top and bottom separated from main area of the painting by large cracks that may indicate later additions.

The XRF used was a handheld Bruker Tracer III-SD pXRF, fitted with a tripod for biaxial movement, stability and delicate adjustment near the painting. The XRF was operated in
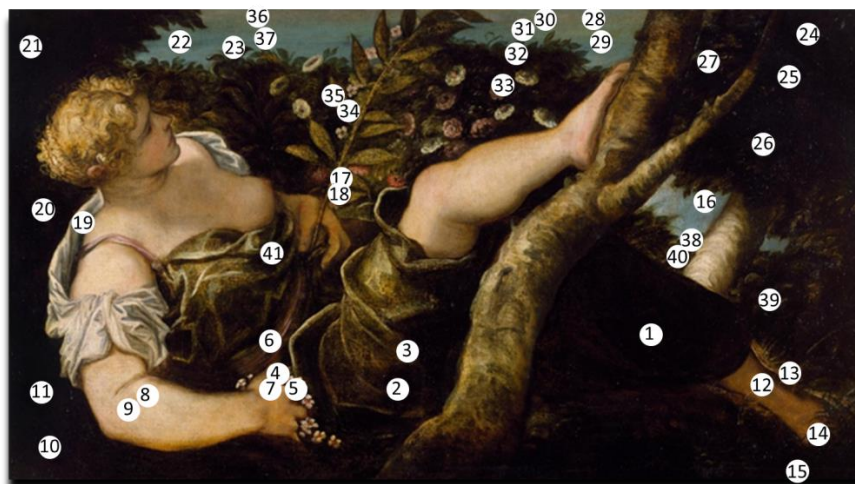
Figure 9. Locations of sample points taken by ED-XRF.

Table 2
Elements found at each sample point taken by ED-XRF and assignment of pigments present.

Painting Area	Sample Points	Elements Present	Estimated Pigments Present
Main Area			
Dark green	1, 2, 3, 11, 20, 23, 25, 26, 27, 32, 38, 39, 40	Pb, Cu, Ca, Fe, Mn,	Copper-based green pigment, possibly mixed with lead white, umber
Light green	13, 18, 34, 35	Pb, Cu, Fe, Ca,	Copper-based green pigment and lead white
Pink flower	5, 17, 33	Pb, Cu, Hg, Ni, Ca, Fe	Vermilion over lead white and copper-based green pigment
White flower	4	Pb, Cu, Ca, Fe,	Lead white over copper-based green pigment
Sky	16, 22, 29, 31, 37	Pb, Cu, Fe, Ca,	Lead white, azurite
Belt	6	Pb, Cu, Fe, Hg, Mn, Ca	Vermilion over copper-based green pigment and umber
Flesh damage	9	Pb, Zn, Fe, Ti, Ca, Ni, Hg	Lead white, zinc white, titanium white, vermilion
Flesh	7, 8, 14, 12	Pb, Fe, Hg, Ca, Mn	Lead white, umber, vermilion
Shadow of white mantle	19	Pb, Fe, Ca	Lead white, Prussian blue (later addition)
Areas Outside of Cracks			
Sky top strip	28, 30, 36	Pb, Fe, Ca, Ti, Cr, Zn, Cu	Prussian blue, titanium white, zinc white
Lower left corner	10	Fe, Cu, Pb, Ca, Mn, Hg, Zn	Umber, copper-based green pigment, vermilion, zinc white
Lower right corner	15	Fe, Ca, Pb, Mn, Cu, K, Zn, Ti	Green earth, umber, zinc white, titanium white
Upper left corner	21	Fe, Cu, Pb, Ca, Mn, Hg, Zn, Ti	Umber, copper-based green pigment, vermilion, zinc white, titanium white
Upper right corner	24	Fe, Pb, Ca, Mn, Cu, Zn, Sr, K	Green earth, umber, zinc white

air with no filter at a voltage of 40 keV and a current of 30 µA for collection periods of 20-40 seconds. The data was taken during the museum open hours with the painting in its normal place so that visitors to the museum could observe the process and ask questions. The elemental analysis at each point was used to propose the pigments used in each area of the painting.

Main Area of Painting

Ground and Medium

Throughout the painting, excluding the corners and strips outside of the cracked lines previously mentioned, the elements most consistently present in the XRF data points are calcium, lead, and iron (Table 2). The calcium is most likely a result of a chalk ground layer. Tintoretto was known to paint with a tinted ground, sometimes very dark [4, 16]. Calcium sulfate has been identified in his grounds, along with charcoal black, and sometimes an array of other elements from palette scrapings as Tintoretto was known to combine his ground with the pigments left over from other works [16]. The lead might be a combination of many sources. Lead white has been identified in Tintoretto's underdrawings on tinted ground [16] but the uniform presence of lead indicates another source as well. Whiting materials like lead were often used as part of the ground layers. Additionally, as early as the Middle Ages it was understood that lead enhanced the siccative property of oil mediums, but resulted in a thick, viscous oil that was difficult to apply [4]. In the fifteenth century, the Italian painter, Antonello da Messina, developed a method of using lead as a drying agent while maintaining the workability of the oil [4]. This method may have been introduced to Tintoretto and the rest of the Venetian school by Giovanni Bellini [4]. In this method, one or two parts basic lead

carbonate or lead(II,IV) oxide was combined with 20 parts raw oil and heated to achieve proper viscosity [4]. Thus, lead may be part of the oil binder throughout the painting, the ground layer, and the under drawing, which would explain its uniform presence in the XRF results. Iron shows less fluorescence than lead and calcium, but also has a constant presence throughout the painting and may therefore also be part of the ground layer. Red ochre or some other iron-based pigment may have been used to tint the ground or priming layer. The priming layer is typically much thinner than the other ground layers, which may explain the lower fluorescence.

Green Pigments

In the dark and light green areas of the painting, besides calcium and lead already discussed, copper and iron appear to dominate the elements present (Fig. 10). Based on the appearance of the paint layer and the likely browning that has occurred over time, it is possible that the presence of copper is due to a copper resinate glaze to create the green foliage. The green could also be attributed to malachite $(CuCO_3 \cdot Cu(OH)_2)$, or terre verte $(K[AlFe^{III}),(Fe^{II},Mg](AlSi_3,Si_4)O_{10}(OH)_2)$, but neither of these pigments has been associated with browning over time. Copper resinate was a new and popular green pigment in the Renaissance, created from the ancient green pigment, verdigris [4, 14, 27]. The copper resinate may also have been mixed with lead white as an initial layer and then covered with copper resinate glaze, which was a method sometimes used to give depth to green foliage.

The points sampled on the dress show a pattern of fluorescence very similar to that of the green foliage, suggesting that the dress was likely originally painted green with copper resinate. As the figure was intended to represent the figure of Spring, a more verdant color palette is more plausible than the somber brown currently observed. Furthermore, the jubilant colors of the

parrot and woman's pink dress in this painting's summer counterpart, *Allegorical Figure of Summer,* suggests that Tintoretto did not intend for the paintings to be dark and morose.
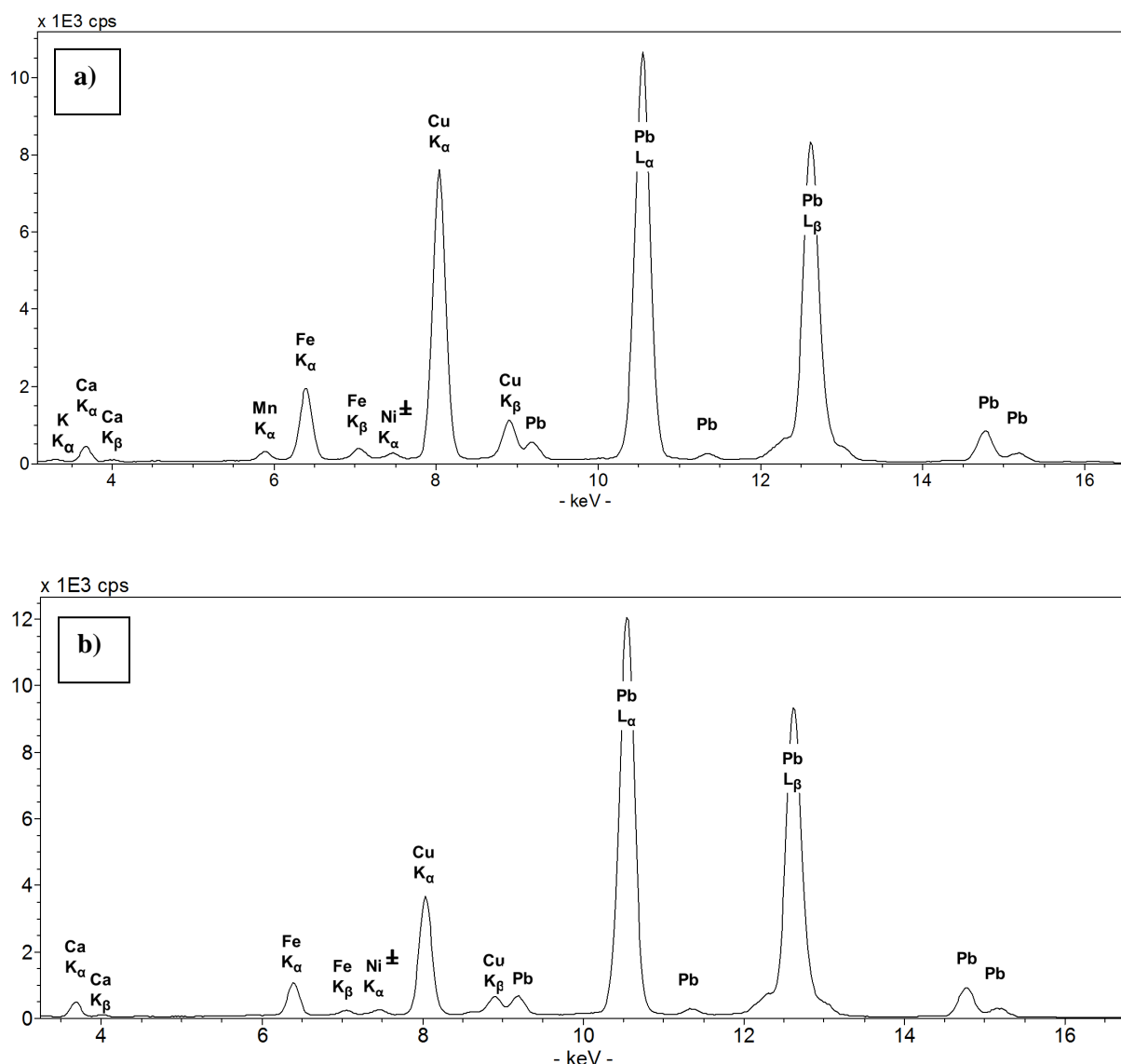
Figure 10. XRF spectra of green or discolored areas of painting. (a) shows the spectrum of sample point 1, representative of the dark areas of foliage and (b) shows the spectrum of sample point 18, representative of all light areas of foliage in the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.

Red Pigments

Mercury, indicating vermilion red (HgS), appears in the pink flowers (Fig. 11), the skin

tones (Fig. 12), and the purplish belt on the woman's dress (Fig. 13). Along with vermillion red,

copper, iron and manganese appear in the pink flowers, indicating that the flowers were painted

over the green foliage with the umber under painting.
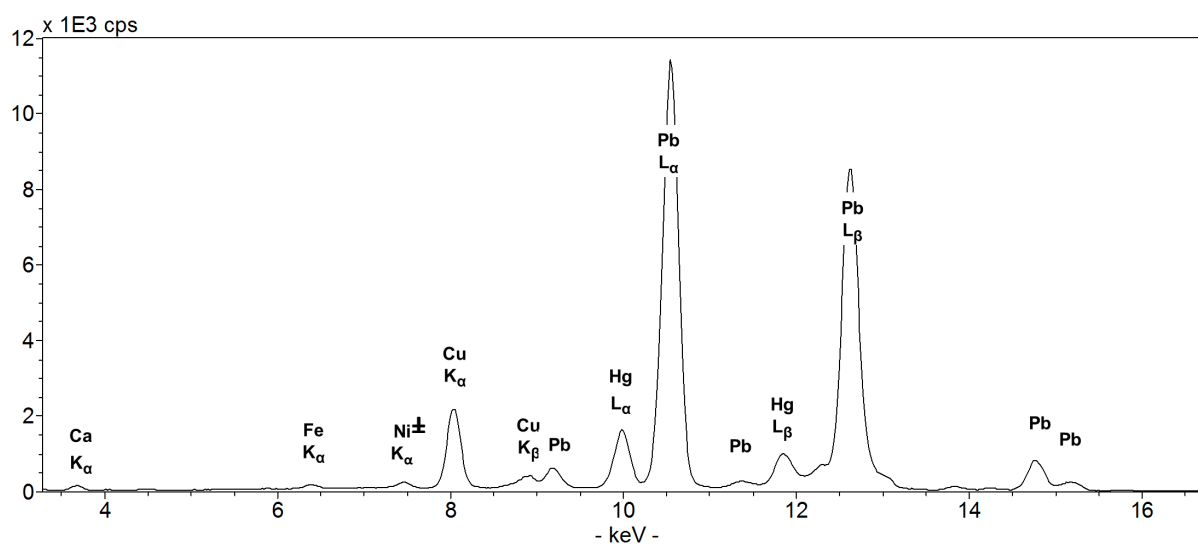
Figure 11. XRF spectrum of sample point 5, representative of pink flowers in the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
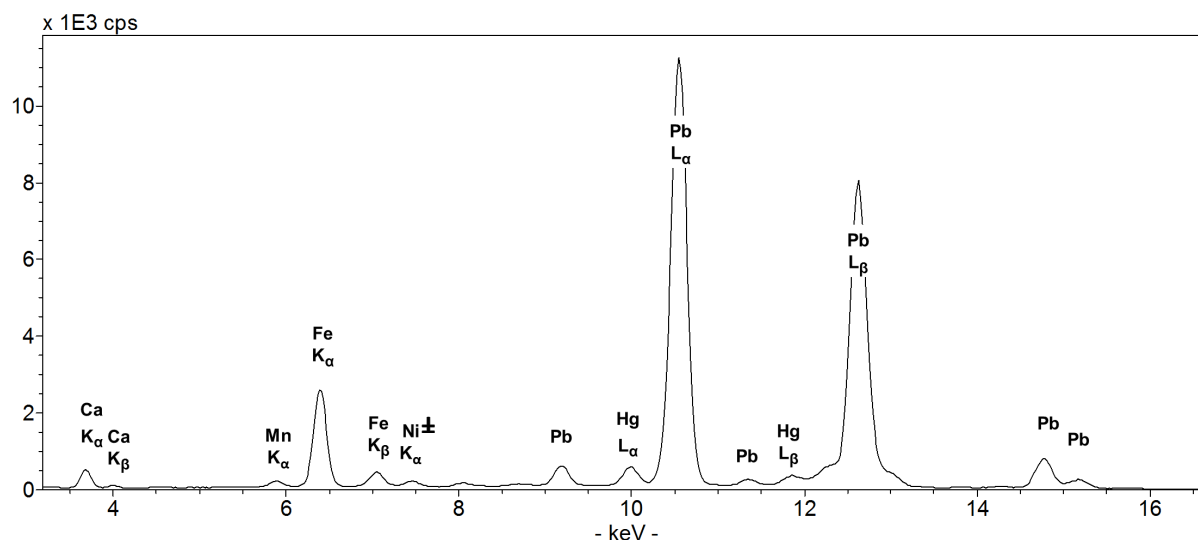
Figure 12. XRF spectrum of sample point 12, representative of the undamaged areas of flesh in the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
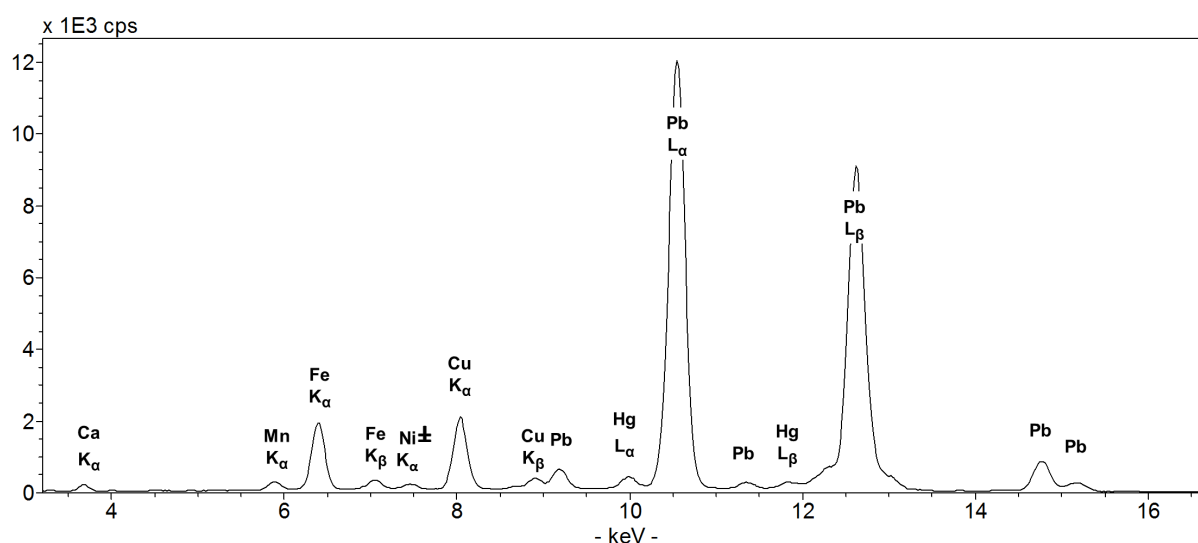
Figure 13. XRF spectrum of sample point 6, from the woman's belt. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.

The use of purple in art was new to European painters in the Renaissance, and its use was

pioneered primarily by Tintoretto's teacher, Bellini. Artists often employ complementary colors

within a painting as they are satisfying to the eye and enhance one another's brilliance. Bellini's

use of darkened yellows, (the complement of violet), allowed for much greater exploration in the violet range. Venice was known for its high-quality red lake pigments in particular, which Venetian artists often mixed with other non-lake pigments to create new colors [28]. The woman's violet belt in *Allegorical Figure of Spring* may contain an organic dye, which is a material Tintoretto would have had easy access to, given his family's business. Tintoretto is known to have used red lakes, identified by thin-layer chromatography, mixed with blue pigments to create a purple color in other paintings [16]. In *Allegorical Figure of Spring*, organic dyes would not be detected by XRF analysis as the elements are too light for detection. Thus, the purple could be a combination of vermillion, as evidenced by the presence of mercury, and a blue lake such as indigo.

Another use of complementary colors is as an under-layer to give the surface paint layer more depth. This technique was known to Tintoretto's contemporaries [29, 30] and Tintoretto may have used this concept in the foliage area of the painting where red, the complement of green, might enhance the green. In this case, red umber may be used as a layer underneath the green to enhance the depth of the foliage. Although iron appears elsewhere throughout the painting, its fluorescence in the green foliage areas is closely related with the fluorescence of manganese (Fig. 14). Red umber ($Fe_2O_3 \cdot H_2O$, $MnO_2 \cdot nH_2O$, Al_2O_3) is a clay-based pigment which contains both iron and manganese in ratios that differ depending on the source of the clay and affect the shade of the red umber. Because the ratio between iron and manganese remains consistent throughout the green foliage, it suggests the use of one source and shade of red umber. The same ratio also appears in the flesh tones of the woman's arm and leg (Fig. 15). The ratio of iron to manganese increased slightly in the shadow area of the foot at point 14, possibly

suggesting that a different umber pigment was used in this area or another iron pigment was added.
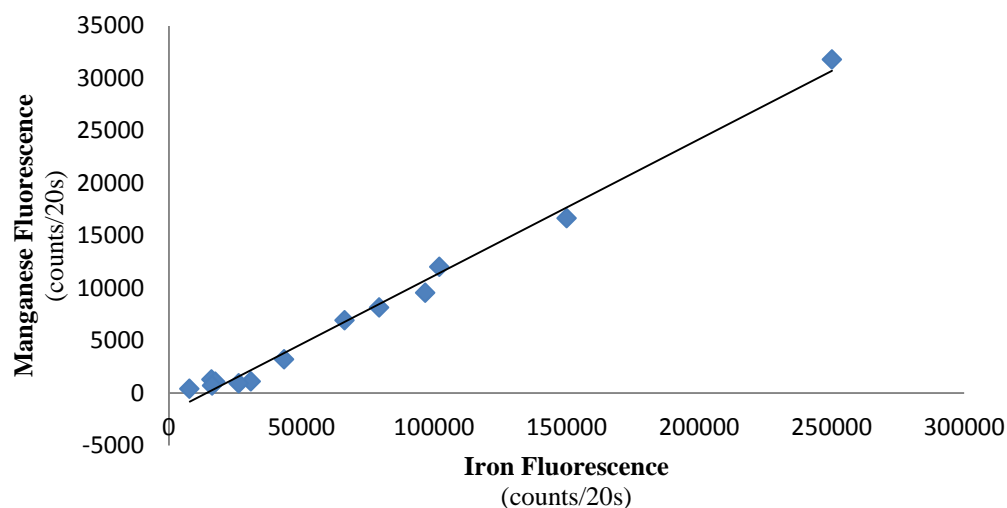
Figure 14. Correlation between manganese and iron fluorescence indicating the presence of umber in the dark green areas of foliage and dress. Sample points include 1, 2, 3, 11, 20, 23, 25, 26, 27, 32, 38, 39, and 40. $R^2 = 0.99$.
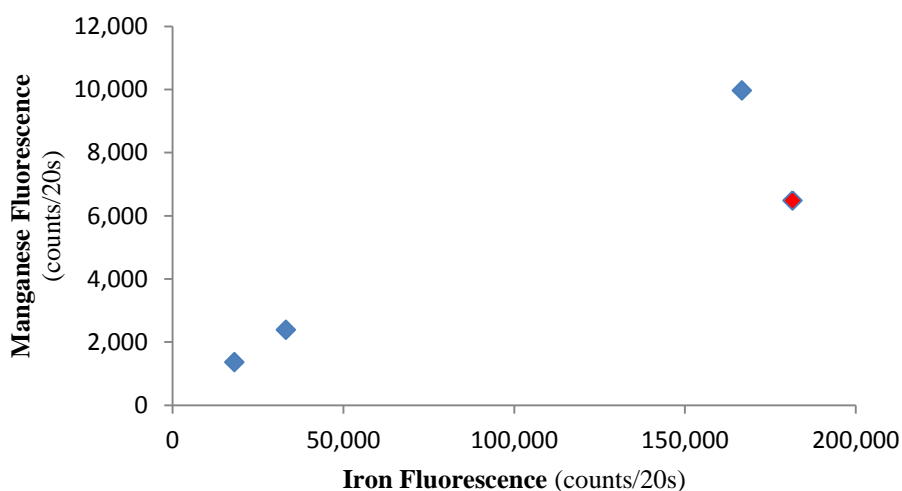
Figure 15. Correlation between manganese and iron fluorescence indicating the presence of umber in flesh areas. Sample points include 7, 8, 12 and 14. Sample point 14 is in red showing the increased ratio of iron to manganese in the darker shadow area of flesh.

Blue Pigments

In the main portion of the sky (Fig. 16) copper and iron were observed. Copper is most likely indicative of azurite ($2CuCO_3 \cdot Cu(OH)_2$), which was in use since ancient times. A greater fluorescence of lead indicates that lead white was mixed to lighten the blue color. There is no correlation between iron and manganese, so the iron may just be part of the ground layer. Alternatively, it is possible that iron may be assigned as Prussian Blue ($Fe[Fe^{3+}Fe^{2+}(CN)_6]_3$), which was not used until the eighteenth century, and would therefore indicate a later touchup of color. The blue color in the shadow of the woman's mantle (Fig. 17) fluoresces only for elements already assigned to the ground layer and may therefore be attributed to an organic blue such as indigo.
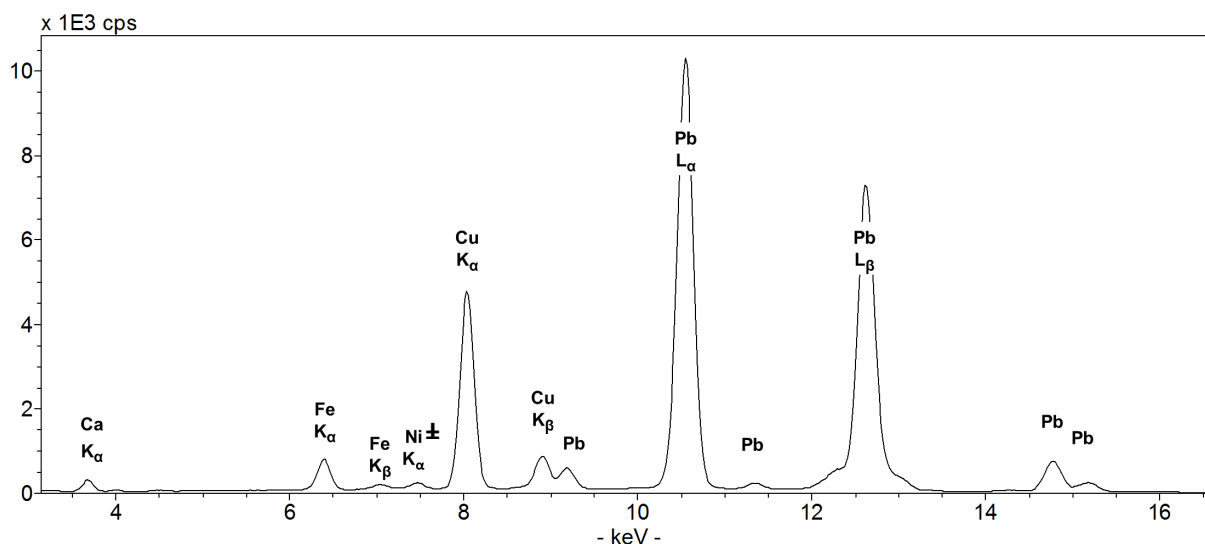
Figure 16. XRF spectrum of sample point 37, representative of the sky in all the main areas of the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
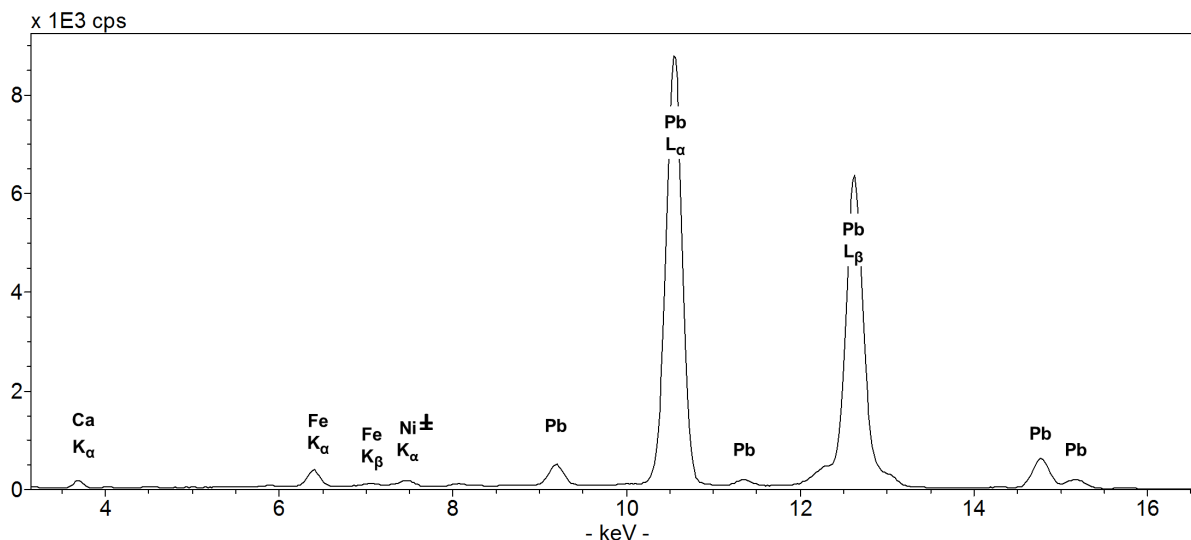
Figure 17. XRF spectrum of sample point 19, on shadow of the woman's white mantle. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.

White pigments

In the lighter green areas of foliage (Fig. 10), the presence of lead increases significantly compared with the darker foliage, indicating that lead white must have been mixed in in these areas to create a lighter green shade. Lead white was probably also mixed with other pigments to obtain the pink of the flower petals (Fig. 11), the flesh tones (Fig. 12), as well as the blue of the sky (Fig. 16), all of which show a prominent lead fluorescence. The white flowers (Fig. 18) were clearly painted with lead white, but also show fluorescence from copper, iron and manganese, indicating that these flowers, like the pink ones, were painted over the green foliage with the umber under painting.

Several areas in the painting indicate touchups done in the twentieth century, based on the pigments used and when they were first made available for artists. One obvious area of repair is point 9 (Fig. 19), where examination under UV light had revealed damage and repair.

In this area, zinc and titanium appear, indicating the use of zinc white (ZnO) and titanium white (TiO$_2$). However, zinc white was not used until the nineteenth century, and titanium white not until the twentieth, dating the latest repair work to the twentieth century.
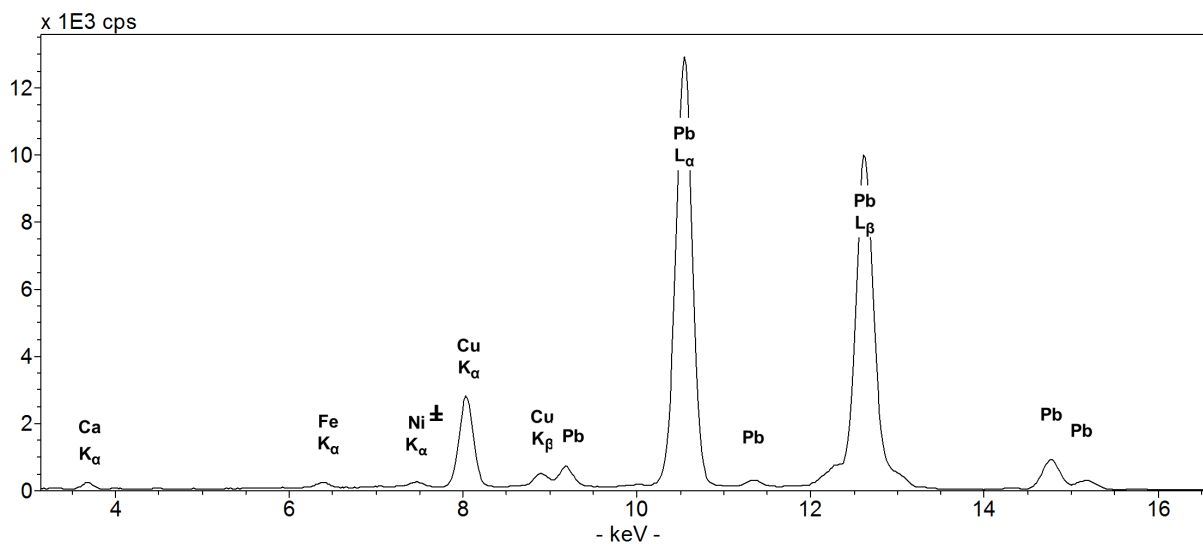
Figure 18. XRF spectrum of sample point 4, representative of all white flowers in the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
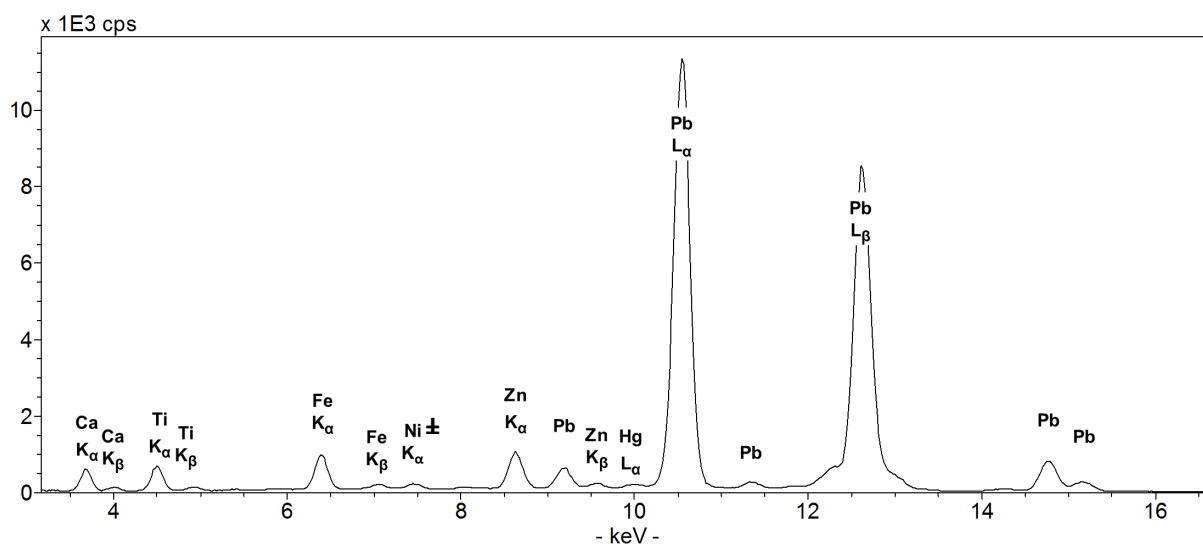
Figure 19. XRF spectrum of sample point 9, an area of damage and repair on the woman's arm. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.

Areas Outside of Cracks on Painting

On the areas outside of the cracks on the painting (Fig. 20), very different elemental profiles emerge from that observed on the main portion of the sky, supporting the hypothesis that they were later additions to the painting. On the main portion of sky, fluorescence due to copper is generally strong but is very weak on the strip of sky above the crack (Fig. 21). Instead, iron fluoresces most strongly after lead. The most likely blue pigment that contains iron is Prussian blue, which did not come into use until the eighteenth century. Similarly, the appearance of chromium in the top strip of the sky may indicate the use of chrome yellow ($PbCrO_4$) to warm the hue of the blue pigment, which was not in use until the nineteenth century. Therefore, the strong presence of iron and the appearance of chromium are both clues that the top strip of sky may have been added to the painting later. Alternatively, it is possible that the top edge of the painting sustained more damage than the main part of the painting and therefore was subject to more extensive touchups in recent centuries.

Zinc and titanium also appear in the top strip above the crack in the sky and on the area of damage on the woman's arm. Their appearances indicate the use of titanium white and zinc white in a few distinct areas of the painting. Zinc and titanium white did not appear in artists' color palettes until the nineteenth and twentieth centuries, respectively.

One point in the sky that particularly stands out is 30, which shows an increase in fluorescence of calcium, iron, titanium and chromium, and a decrease in lead compared with other points in the top strip of sky. Point 30 may therefore be a damaged area that underwent a more extensive restoration than the rest of the top strip.
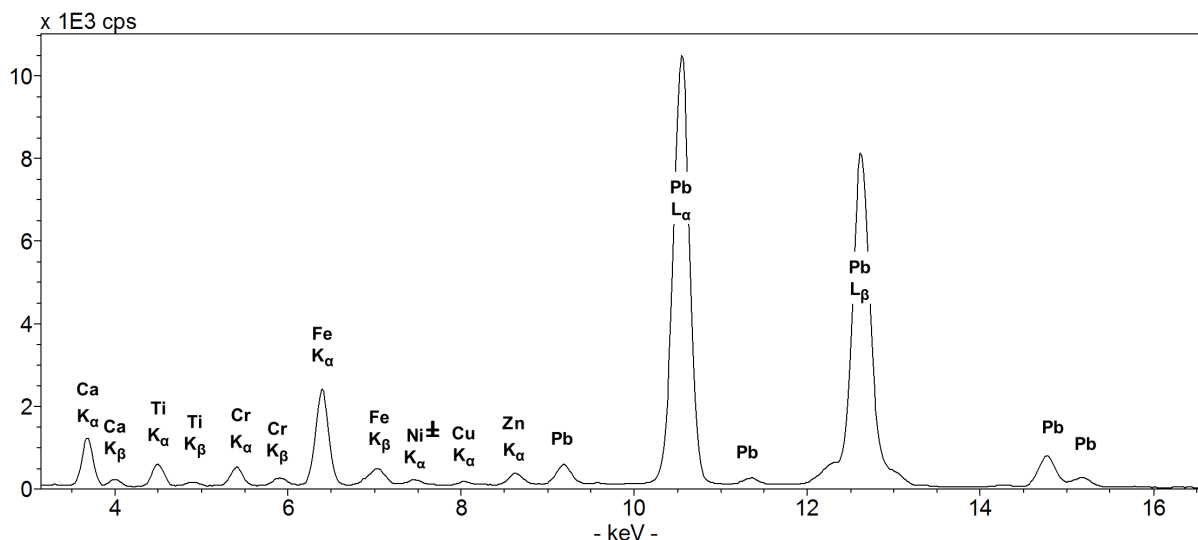
Figure 20. XRF spectrum of sample point 36, representative of the top strip of sky above the horizontal crack in the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
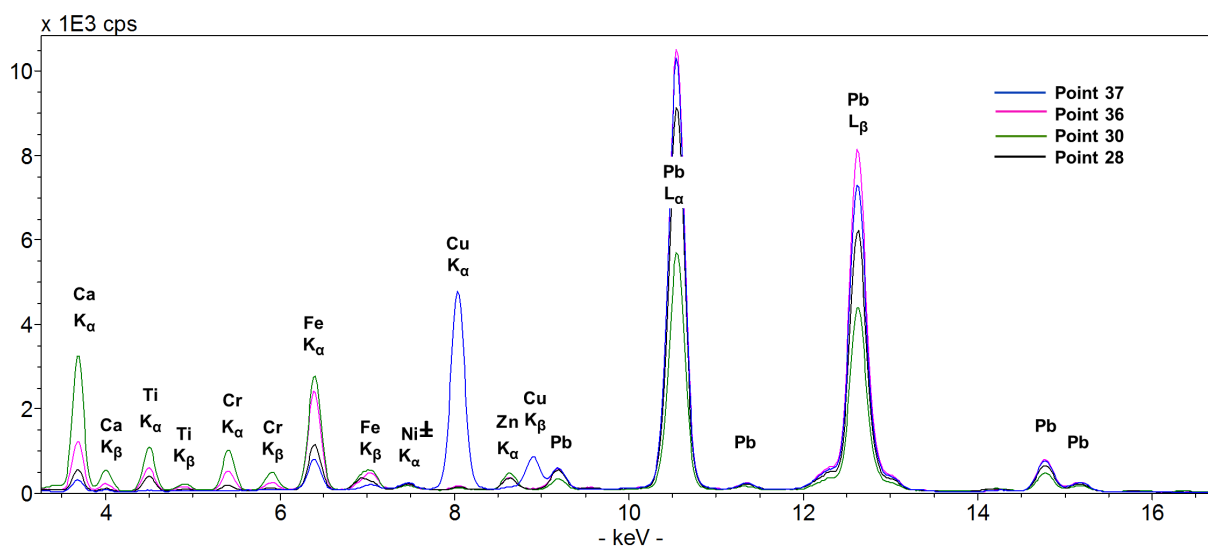
Figure 21. Comparison of XRF spectra for sample 37 (blue), representing the sky in the main area of the painting, and sample points 28 (red), 30 (green), and 36 (pink), from the sky above the top horizontal crack. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.

The elemental profiles in the corners of the painting (Fig. 22-25) also differ significantly from areas of foliage in the main portion of the painting (Fig. 26). On the main portion of the

painting, copper fluoresces more strongly than iron. Within the corners this ratio is reversed, indicating that a different pigment may have been used to produce green. Terre verte, for example, which has been in use since before the Renaissance, contains iron and potassium, both of which appear in points 15 (Fig. 23) and 24 (Fig. 25). In points 10 (Fig. 22) and 21 (Fig. 24) potassium does not appear but copper fluoresces more strongly, indicating that a copper-based green may have been used. At point 24, strontium appears for the first time, probably as an impurity in the calcium carbonate used in the ground layer, indicating that this ground differs from other areas of the painting. Thus, not only are the corners different from the main portion of the painting, but they are also different from each other. While the foliage in the main area of the painting remains fairly consistent (Fig. 27) the corners differ from one another significantly. It is possible that they are from four different paintings that were patched onto the original lozenge-shaped painting in order to make it square.

The presence of lead also decreases in relation to the iron in the corners, while a weak fluorescence due to zinc appears for the first time in the foliage. The decrease in lead suggests that it was not used as a siccative agent in the corners or a different ground was used in these areas, thereby marking them as of a different origin than the rest of the painting. The zinc is undoubtedly from the presence of zinc white, which was not used until the nineteenth century, indicating that the corners were either retouched in that century, or were not added on until that time. It is conceivable that the corners may have been retouched in the 1800s and the rest of the foliage not given the same treatment, as areas of addition and areas near the edge tend to be more susceptible to damage and in need of repair. The ratio of iron to manganese in the corner samples is not consistent with the main portion of the painting (Fig. 28), suggesting that either

umber was not used, or that a different source of umber with a different composition was used

for the additions to the painting.
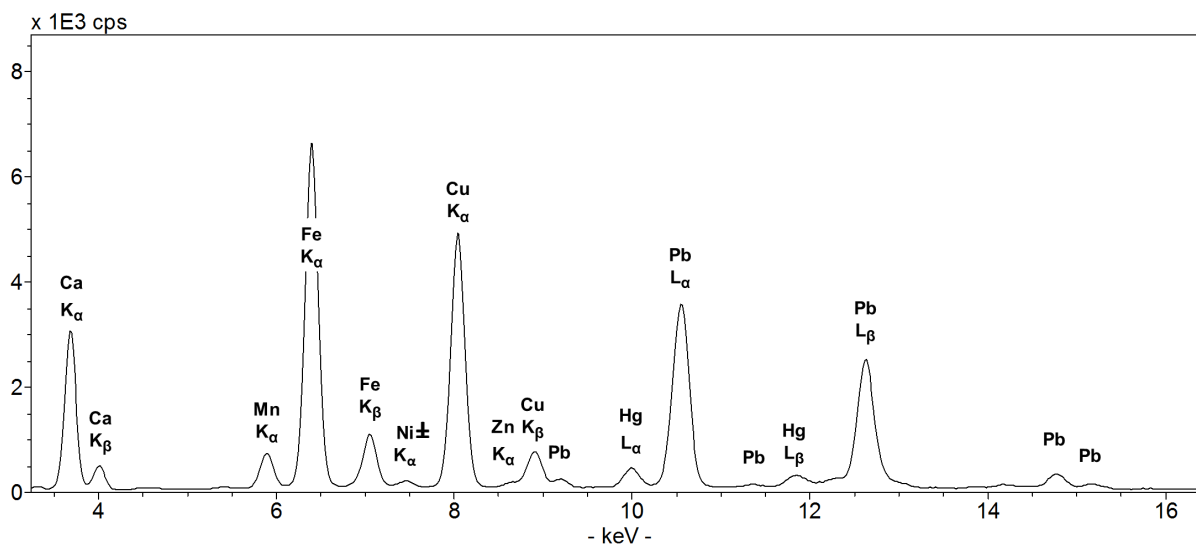
Figure 22. XRF spectrum of sample point 10, the lower left corner of the painting, outside of the diagonal cracks. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
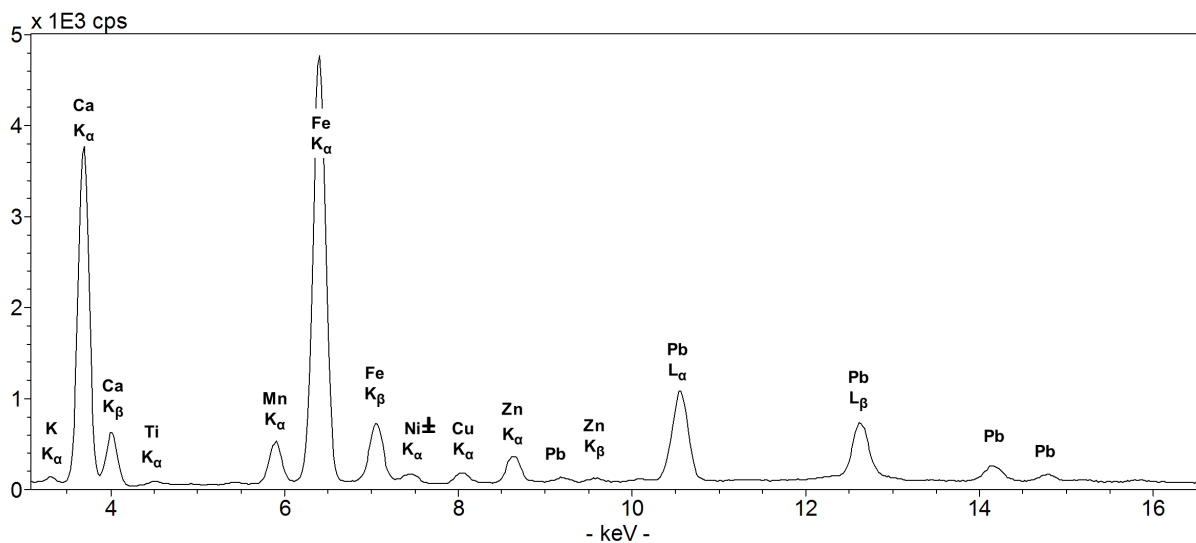
Figure 23. XRF spectrum of sample point 15, the lower right corner of the painting, outside of the diagonal cracks. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
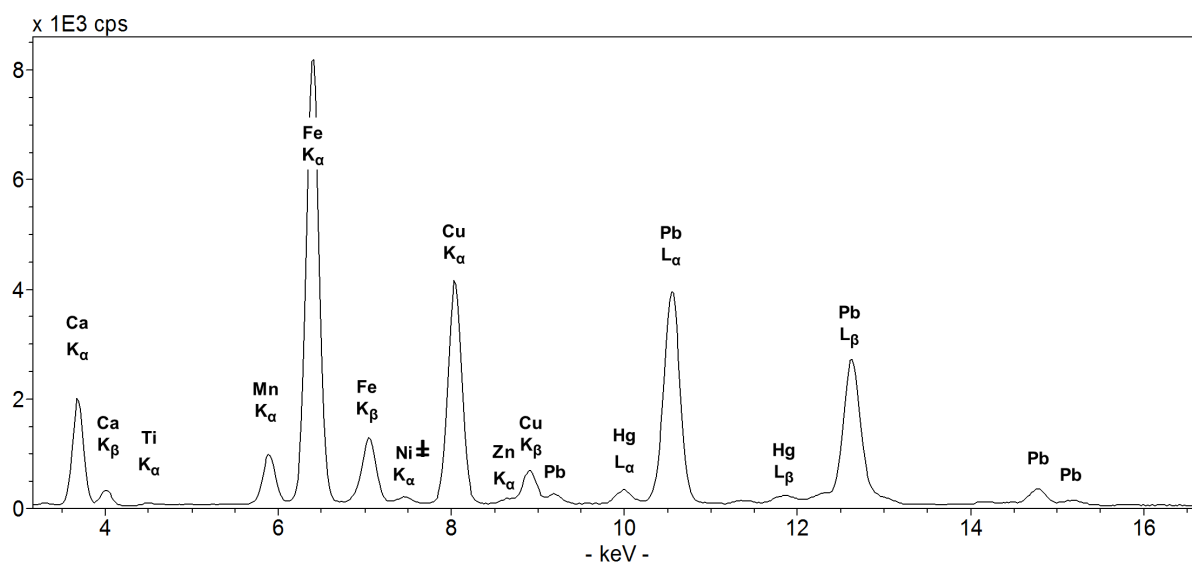
Figure 24. XRF spectrum of sample point 21, the upper left corner of the painting, outside of the diagonal cracks. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
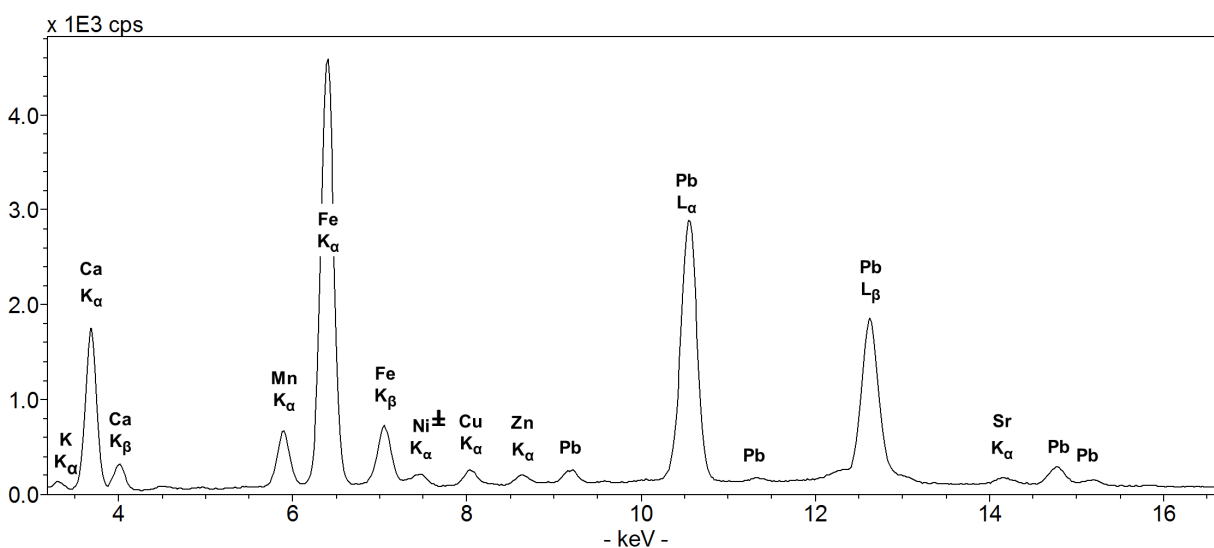
Figure 25. XRF spectrum of sample point 24, the upper right corner of the painting, outside of the diagonal cracks. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
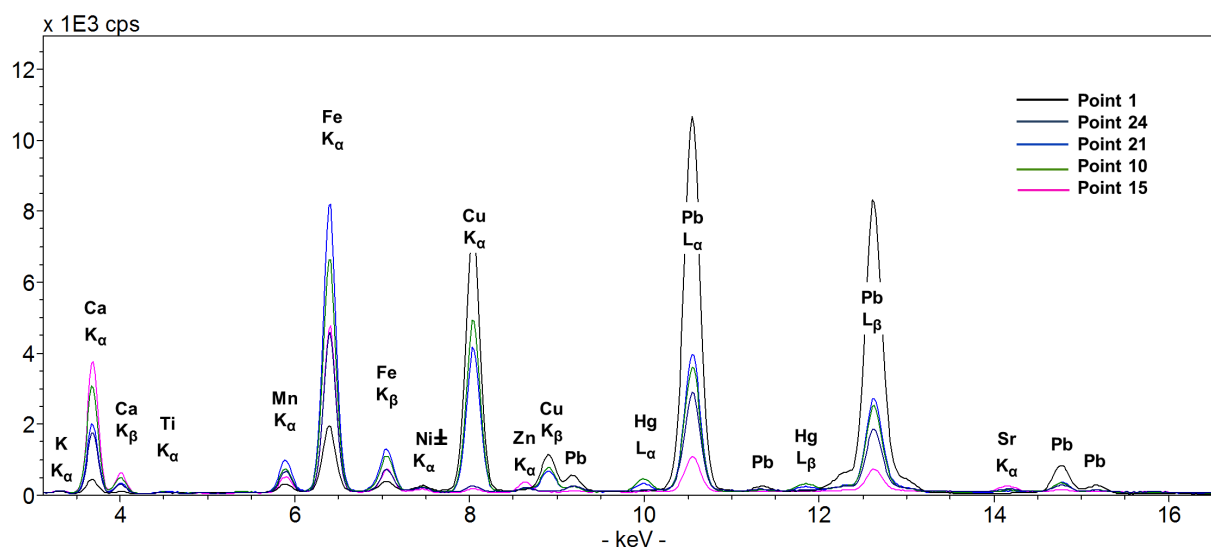
Figure 26. Comparison of XRF spectra for corners and main area of foliage. Sample points 1 (black), represents the main areas of foliage in the corners of the painting, and sample points 10, 15, 21 and 24 are from the corners of the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
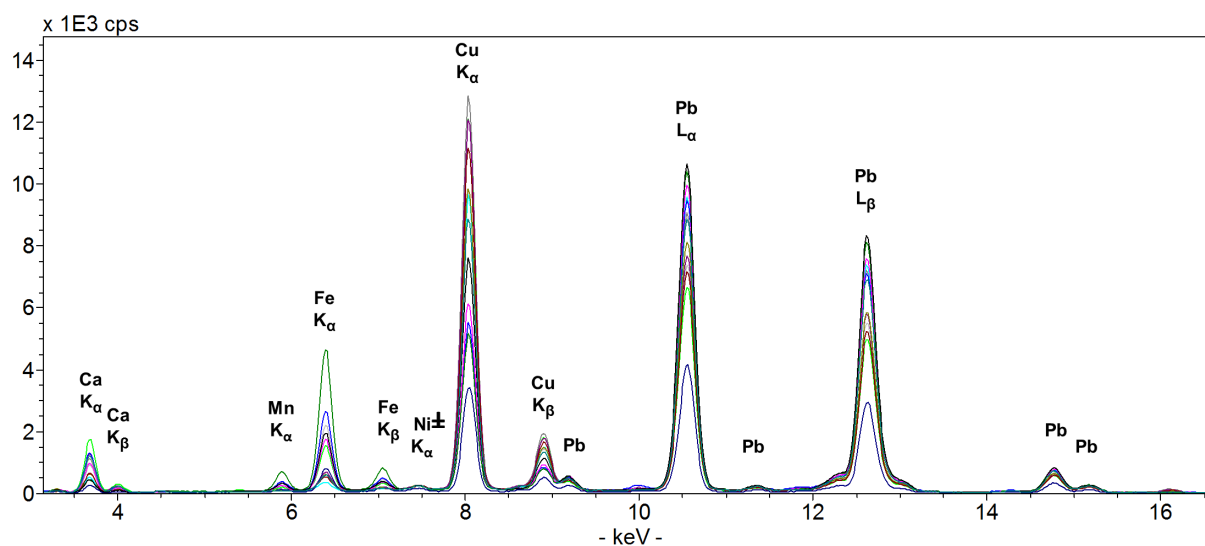
Figure 27. Comparison of XRF spectra for all points of dark green in the main area of the painting. ‡ Nickel appears as an artifact from the XRF target which is housed in a nickel tube.
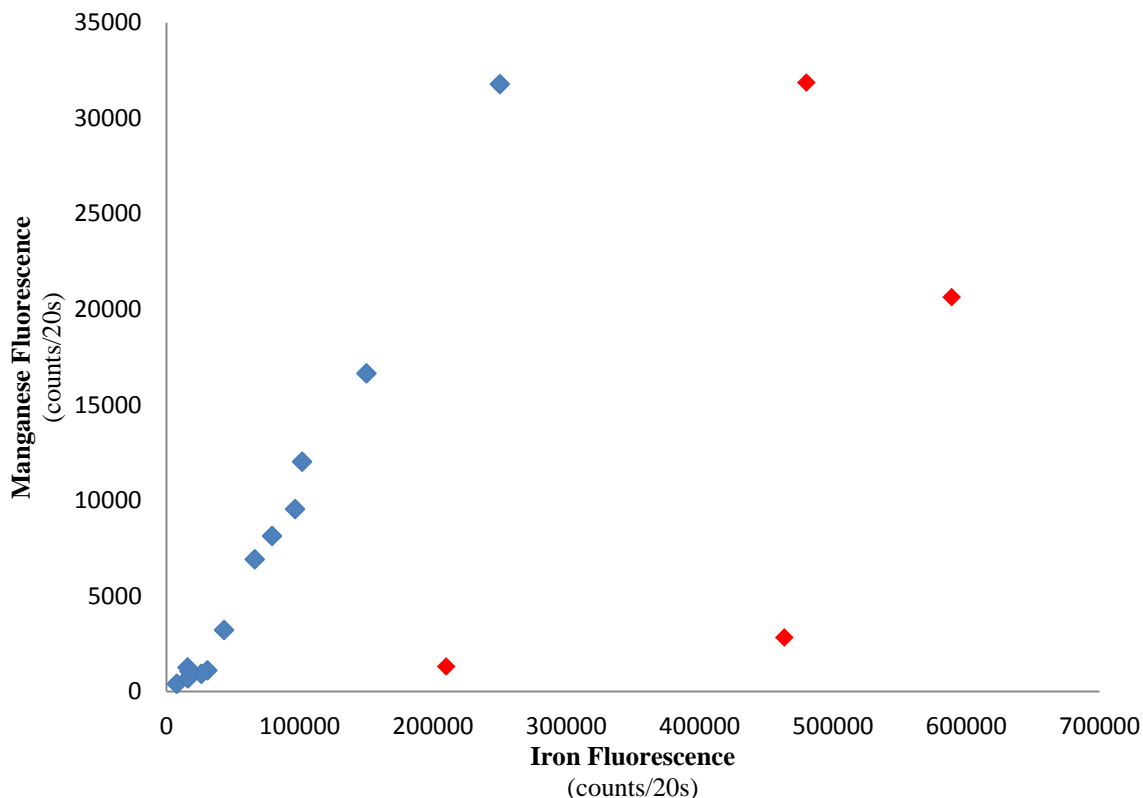
Figure 28. The relationship between iron and manganese in the dark green areas of the foliage, including the corners. The blue points represent dark green areas within the main area of the painting (sample points 1, 2, 3, 11, 20, 23, 25, 26, 27, 32, 38, 39, and 40), while the red points represent the corners (sample points 10, 15, 21, and 24)

Preparation and Analysis of Cross-Sections

Cross-sections of the painting were acquired in four spots, as indicated in Figure 29. Due to the delicate and brittle nature of the cross-sections, they were suspended in a resin prepared by mixing 10 mL of Extec Polyester Clear Resin with 8 drops of Extec Polyester clear hardener. A mini ice-cube tray was used as a mold, and each cube filled half-way with resin mixture and the resin mixture allowed to dry. Each cross-section was then positioned each in a separate cube which was filled the rest of the way with the resin mixture and allowed to dry over a period of several days. Each cube was removed from the tray and sanded with increasingly fine sandpaper from 50 to 2400 grit. Photographs of the cross-sections were taken in visible light using a Zeiss

Primo Star digital microscope at 10x magnification. The photographs of the cross-section at point 1 were discarded as the cross-section splintered and could not be properly mounted. In cross-section 2 (Fig. 30) at least two layers of tinted ground are visible. The tint is consistent with red ochre and chunks of which are visible within the ground layers. Some black and white pigments are also mixed in, possibly from leftover palette scrapings of a previous painting. Tintoretto was known to employ colored grounds as well as palette scrapings in the ground layer [16]. Over the ground layers appears to be a glaze of copper resinate, which has clearly discolored. Discolored copper resinate has been shown to appear orange in visible light [31]. Cross-section 3 (Fig. 31) does not contain the ground layers, but does show the discolored varnish layer on top of the discolored copper resinate. It also shows some blue pigment chunks mixed in, which could be leftover verdigris from which copper resinate is formed. Verdigris is bluer and less prone to discoloration than copper resinate. Cross-section 4 (Fig. 32) shows the paint layers with large umber pigments and a discolored copper resinate layer on the top.

Figure 29. Locations of cross-section samples taken from the painting.
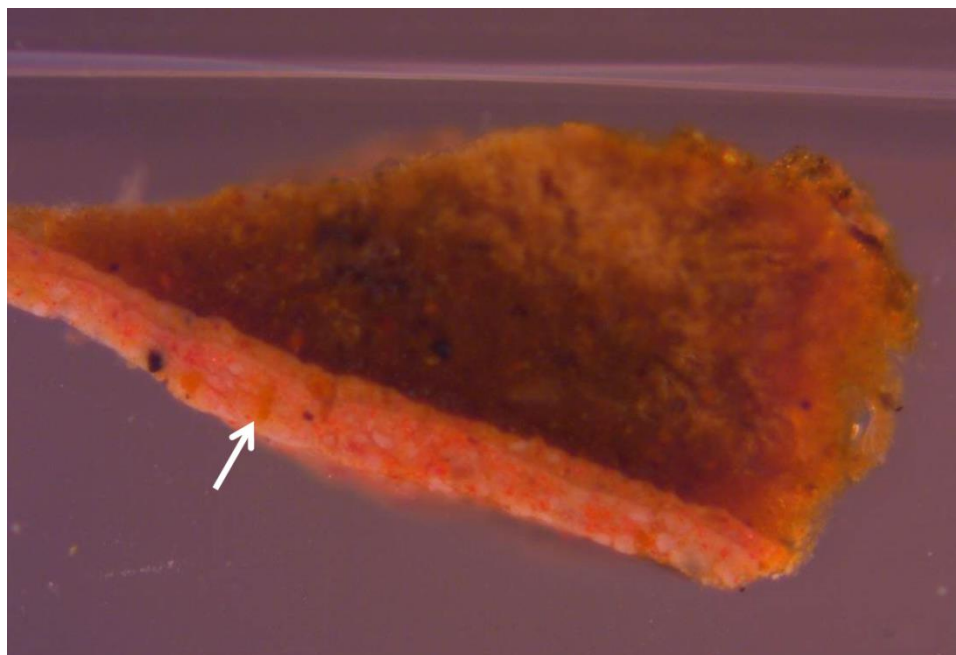
Figure 30. Cross-section of point 2. At least two layers of ground are clearly visible and are characteristic of Tintoretto's tinted grounds from palette scrapings. A chunk of red ochre is identified in the ground layer. Some white and black pigments are also visible in the ground layers.
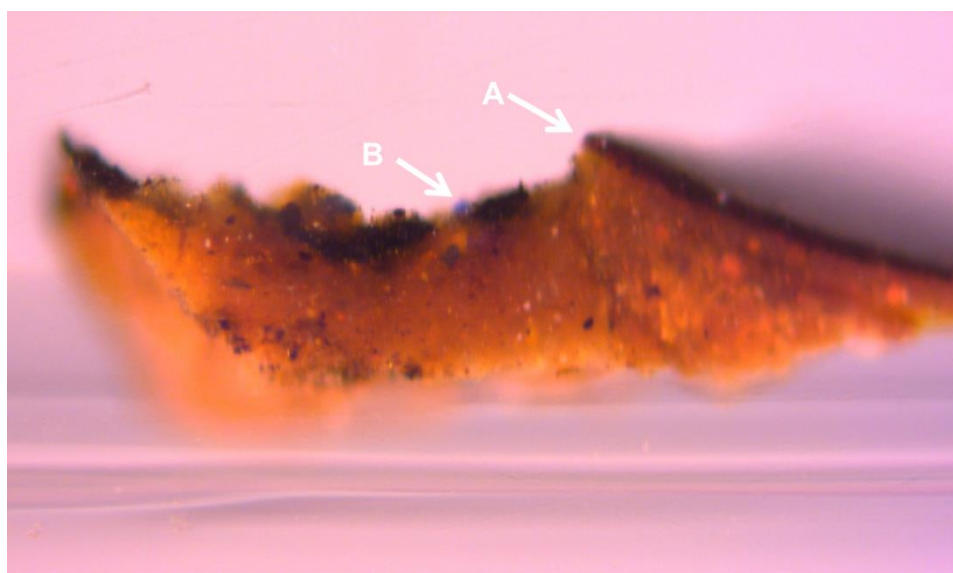
Figure 31. Cross-section of point 3. The dark discolored varnish layer is shown on top (A) with the discolored copper resinate below as well as some blue pigments (B) dispersed within the paint layer. Discolored copper resinate has been shown to appear orange in visible light [31].

Figure 32. Cross-section of point 4. More discoloration of the copper resinate is shown (A) as well as a large chunk of umber in the paint layer (B).

Conclusion

The visual, microscopic and elemental observations of *Allegorical Figure of Spring* illuminate the process Tintoretto may have used, as well as changes the painting may have undergone over time. The pigments employed to create each color have been assigned using XRF as well as the composition of the various layers of the painting. The pigments identified in the main portion of the painting are consistent with Tintoretto's palette and technique, incorporating innovative organic dyes [1, 3, 8], bold new purple tints pioneered by his teacher [16, 28], and his characteristic palette scrapings for the ground layers [16]. The copper-based green that was used could be copper resinate, verdigris or malachite based on historical evidence and the elemental evidence from the XRF. However, copper resinate was known to discolor from green to brown and the mechanism for this discoloration will be discussed in Chapter III.

Evidence of damage and more modern pigments suggests certain areas of repair and retouching. Additionally, observations of the painting deterioration and XRF analysis of the pigments provides proof that the corners and top and bottom strips were added after the painting was finished and that the painting was originally lozenge-shaped. For the next step in this investigation, laboratory chemical analysis of the green pigment will be conducted to determine how this painting may have discolored over time.

CHAPTER III

CHARACTERIZATION OF COPPER RESINATE

As a depiction of spring, Tintoretto's *Allegorical Figure of Spring* (Fig. 1) seems rather dark and morose. The darkened color palette does not match the images of verdant bounty represented by the youthful woman with sprigs of colorful flowers issuing from her fertile womb [13]. Nor do the colors coincide with the bright, vivacious colors used in the companion piece *Allegorical Figure of Summer* (Fig. 1). The somber colors could be partially due to Tintoretto's characteristically shadowy palette, but even his shaded eye would not likely have conceived of brown leaves in spring. The more likely explanation is a degradation of the original green pigment over time.

It was determined in Chapter I through XRF analysis of the painting that the green pigment is most likely copper-based. Two popular green pigments of the Renaissance were verdigris and copper resinate (a combination of verdigris and acidic resins) and Tintoretto was known to employ both of them [32]. These pigments were especially popular in the wine-making regions during the Renaissance [32]. The historical synthesis of verdigris consisted of suspending strips of copper metal in a container of vinegar and then burying the container under dung for several weeks. Bluish green basic and neutral salts of copper and acetate accumulate on the copper during this time and can be scraped away [32]. Verdigris is also formed when metallic copper is allowed to react over time with vinegar to form a salt with varying ratios of acetate, hydroxide and aqua ligands which cause the color to range from blue to blue-green [32]. The

primary product, copper(II) acetate, is a dimer of two copper atoms with four acetate ligands and two axial water ligands [33] (Fig 33).
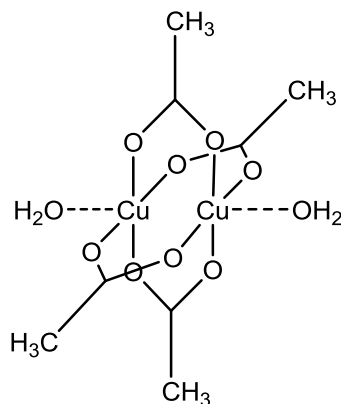
Figure 33. The structure of neutral copper(II) acetate.

Copper resinate is prepared by combining basic verdigris with resins such as Venice turpentine to form a green pigment [4, 14, 27]. Venice turpentine is made from the resin of the western larch tree *Larrix occidentalis*. When boiled together with verdigris, copper salts of abietic acid are believed to be formed. A historic recipe for copper resinate can be found in Theodore Turquet de Mayerne's well-known manuscript, *De Mayerne Manuscript,* of 1620:

Bouffalt, a very excellent workman, gave me these secrets on his deathbed. A beautiful green. Take of Venice turpentine two ounces, spirit of turpentine and ounce and a half, mix them, add two ounces of verdigris, reduced to small fragments. Place these ingredients on hot ashes , and let them gently dissolve. Try the color on glass. Pass it through linen. [27]

The resulting main product is believed to be copper(II) abietate, which may have a similar structure to that of copper(II) acetate, with the abietates replacing the acetates with water

or some other molecule occupying the axial position [33] (Fig. 34). The exact structure of copper(II) abietate has not been elucidated, however, and it is unclear how completely the abietates will replace the acetates (Fig. 35).
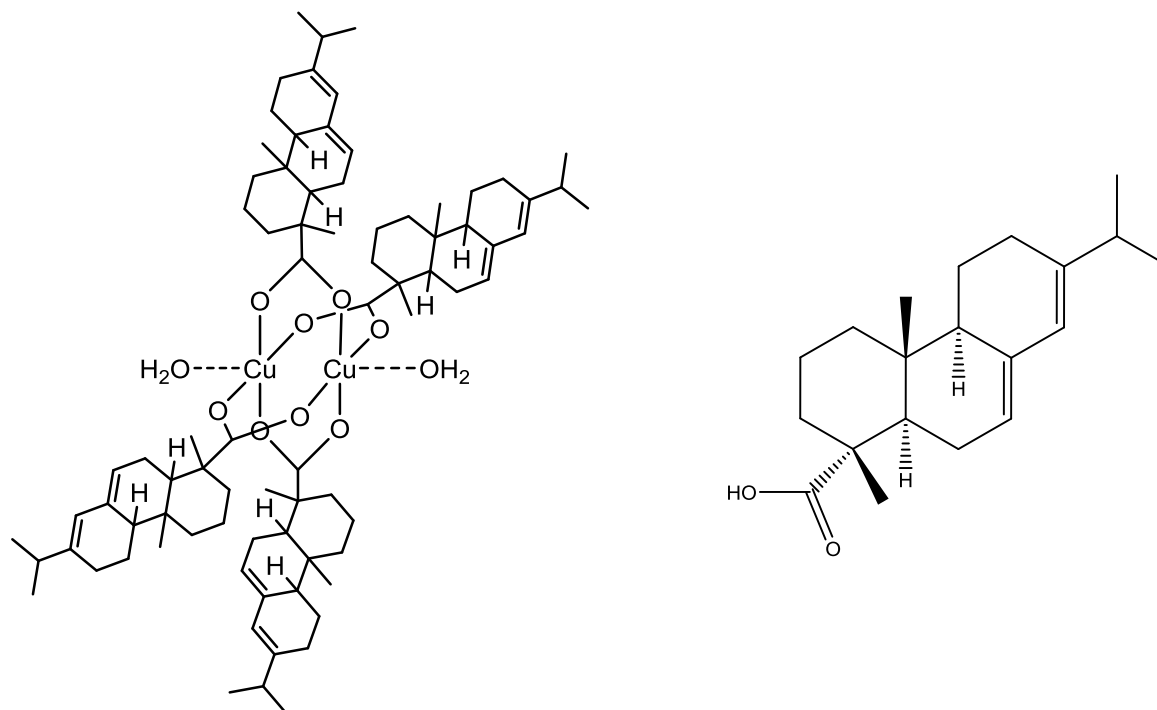
Figure 34. The suggested structure of copper(II) abietate (left) with the structure of abietic acid (right) which forms the ligands on copper(II) abietate.

$$Cu_2Ac_4 \cdot 2H_2O \ + \ Ab^- \ \rightleftharpoons \ Cu_2AbAc_3 \cdot 2H_2O \ + \ Ac^-$$

$$Cu_2AbAc_3 \cdot 2H_2O \ + \ Ab^- \ \rightleftharpoons \ Cu_2Ab_2Ac_2 \cdot 2H_2O \ + \ Ac^-$$

$$Cu_2Ab_2Ac_2 \cdot 2H_2O \ + \ Ab^- \ \rightleftharpoons \ Cu_2Ab_3Ac \cdot 2H_2O \ + \ Ac^-$$

$$Cu_2Ab_3Ac \cdot 2H_2O \ + \ Ab^- \ \rightleftharpoons \ Cu_2Ab_4 \cdot 2H_2O \ + \ Ac^-$$
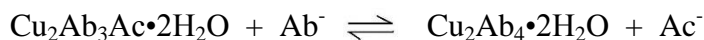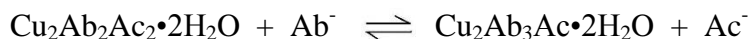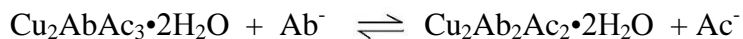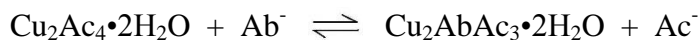
Figure 35. Proposed mechanism for the replacement of acetate ligands (Ac) with abietate ligands (Ab) in the formation of copper resinate. Various compounds may result with copper(II) abietate being the most abundant product.

Copper resinate, as prepared above, is an amorphous, glassy mixture which was usually applied fresh [34]. No distinct pigment particles are observable under a microscope [32] except in rare cases where the copper resinate was allowed to dry and then ground to a powder and suspended in drying oil [33]. In contrast, verdigris is prepared for oil painting by grinding copper(II) acetate in a drying oil (usually linseed) to create a suspension. Under a microscope, one can often distinguish the individual pigment particles of verdigris in the oil medium. Verdigris will occasionally react over time with fatty acids of the oil binder (in linseed oil these are triglycerides of unsaturated linolenic, linoleic and oleic acids with some small amounts of saturated stearic and palmitic acids) to give the glaze-like appearance of copper resinate [32, 35]. The best way to distinguish whether an artist used verdigris or copper resinate originally is to identify the presence of resin acids using gas chromatography [32] or GC-MS [33, 36].

Verdigris and copper resinate range in color from blue to bluish green when wet and turn to a yellow-green upon drying and exposure to atmospheric conditions [32, 35, 37]. This color change upon drying was well known by the artists using the two copper pigments. In fact, the color-fastness of verdigris and copper resinate were of great concern to the artists of the time, who warned of verdigris "poisoning" the colors of other pigments and recommended a separate palette for the pigment and allowing all other paint layers to dry before applying a verdigris glaze [32, 34]. Laboratory studies have shown, however, that verdigris only causes discoloration in sulfur-containing pigments like ultramarine or orpiment in aqueous media but not in oil [32]. Leonardo da Vinci warned against the combination of orpiment and verdigris in oil [34] and discoloration from this combination has been confirmed in Marco Marziale's *Christ and the Woman Taken in Adultery* (c. 1505) where the verdigris glaze over orpiment has turned entirely black [34]. Furthermore, although some experts at the time warned against such mixtures [34], it

was common in Italy to mix verdigris and copper resinate with lead white or lead-tin yellow to improve the opacity of the paint, and neither laboratory tests nor historic examples indicate any harm from the combination [14]. In fact, in some cases it appears that mixing the verdigris with lead white may aid in its protection from discoloration. In Titian's *Venus and Adonis* from 1554, painted in almost exactly the same time and place as Tintoretto's *Allegorical Figure of Spring*, leaves of grass near Adonis's foot were painted with a mixture of lead white and copper resinate and show no discoloration. But in the same painting, areas painted with verdigris and copper resinate mixed and layered with yellow ochre showed significant discoloration [29].

As opposed to its interactions with other pigments, which appears to be much less of an issue than artists thought at the time [14], the browning tendencies of verdigris and copper resinate themselves is significant. Indeed, although the pigments were commonly used in Europe in the Renaissance, they are rarely found in paintings after the seventeenth century as their instability was confirmed and a more stable pigment called emerald green became available [32]. Not all examples of verdigris and copper resinate have undergone browning, however, and it is difficult to discern the conditions under which the discoloration will occur. Sometimes, both in cases where verdigris was employed and in cases where copper resinate was employed, areas of browning and areas that remain green will even coexist in the same painting [32, 37].

When browning does occur in a painting, the copper greens hidden by the frame are frequently still green [32, 38], as in Jan Van Rillaer's triptych, *St. Eustachius* in Zichem Church, painted around the time of *Allegorical Figure of Spring* [38]. Similarly, the copper pigment is protected from browning when painted over with certain other pigments as in the case of Colijn de Coter's *Life of St. Rombout,* in St. Rombout's Cathedral in Mechelen, also painted around the time of *Allegorical Figure of Spring* [38]. In this panel, an area of green drapery is painted with

a layer of copper resinate, followed by a layer of lead white, followed by another layer of copper resinate. Optical microscopy of a cross-section reveals that, while the upper layer of copper resinate has entirely browned, the layer protected by the lead white has stayed green [38]. Another cross-section taken from a different area of the same painting shows copper resinate green in areas covered by a layer of vermilion and red lake, but discolored where the cover of red pigment is not present [38]. Sometimes browning occurs only on the outer surface of the copper resinate layer [38, 39, 40] as found in Jan Van Eyck's *Mystic Lamb,* completed in 1432 [38]. Lab simulations of the aging of copper resinate support the idea that degradation may begin at the surface and work its way in over time. A combination of copper resinate and boiled linseed oil mounted on a glass support were aged by UV irradiation (254 or 365 nm) after which micro-FT-IR-ATR indicated a great variation in color on the outer surface of the paint compared with the inner layers [39]. Another study found that copper resinate in linseed oil that was artificially aged using SO_2 and NO_2 pollutants and water condensation alternated with UV radiation produced similar results. In this case, penetration of the pollutants was found at the surface layer of the paint layer, further suggesting that degradation may occur by outside pollution [40]. Notably, however, the same results were not observed in fresh samples or samples naturally aged for two years [40]. Other paintings, such as Pedro Campaña's *Conversion of the Magdalen*, are browned throughout the entire layer of copper glaze [41]. Another painting, *Adoration*, by an unknown Flemish artist of the sixteenth century, is also browned almost entirely [38]. When analyzing a painting that appears to have browned over time, it is important to determine whether the brown color is intentional or not [32, 38]. A brown glaze may have been added over a green glaze intentionally, either as a varnish for protection or to temper the blueness of the green. Leonardo da Vinci recommends aloe and water to the artists of this time to accomplish the latter

[38]. Another possibility is that a brown glaze was added to the painting later to hide an overly abrasive cleaning [38]. These superimposed brown glazes can be distinguished from surface browning of copper glazes by microscopy [32, 38].

Because the patterns and circumstances of browning are so variable, it has been difficult to elucidate the mechanism or causes of the discoloration. Many studies on the pigment have attempted to determine certain characteristics or proposed mechanisms for degradation, but to my knowledge, no definitive description of the degradation process has been proposed and widely accepted. One of the most explored mechanisms of discoloration is through the well-known light-induced yellowing of oleoresinous binders such as linseed oil. This mechanism is supported by the fact that copper pigment browning is often reduced or absent from areas of paintings protected by the frame from light. Furthermore, some older paintings in egg tempera from the Middle Ages show less browning than the oil paintings of the Renaissance, suggesting that oil may indeed play a role in the browning [37]. Over time, drying oils form fragmented pieces of the oil fatty acids that appear yellow [42] (Fig 36). Linseed oil is especially susceptible because of its high concentration of the pentadiene fatty acid, lineolate, which easily forms radicals [42]. Copper(II) has been shown to participate in the oxidation of lipids by acting as an oxidizing agent to provide a more direct route to the fragmented products of oil degradation [42, 43] (Fig 36). Combinations of linseed oil and copper(II) have been shown to produce a yellowish green color [35] and the addition of copper(II) acetate to linseed oil does increase the number of oil degradation products [43]. It has been proposed that linseed oil may act to extract Cu(II) ions from copper(II) acetate, making them more available to act as oxidation agents but this same effect has not been observed in copper abietates [35].
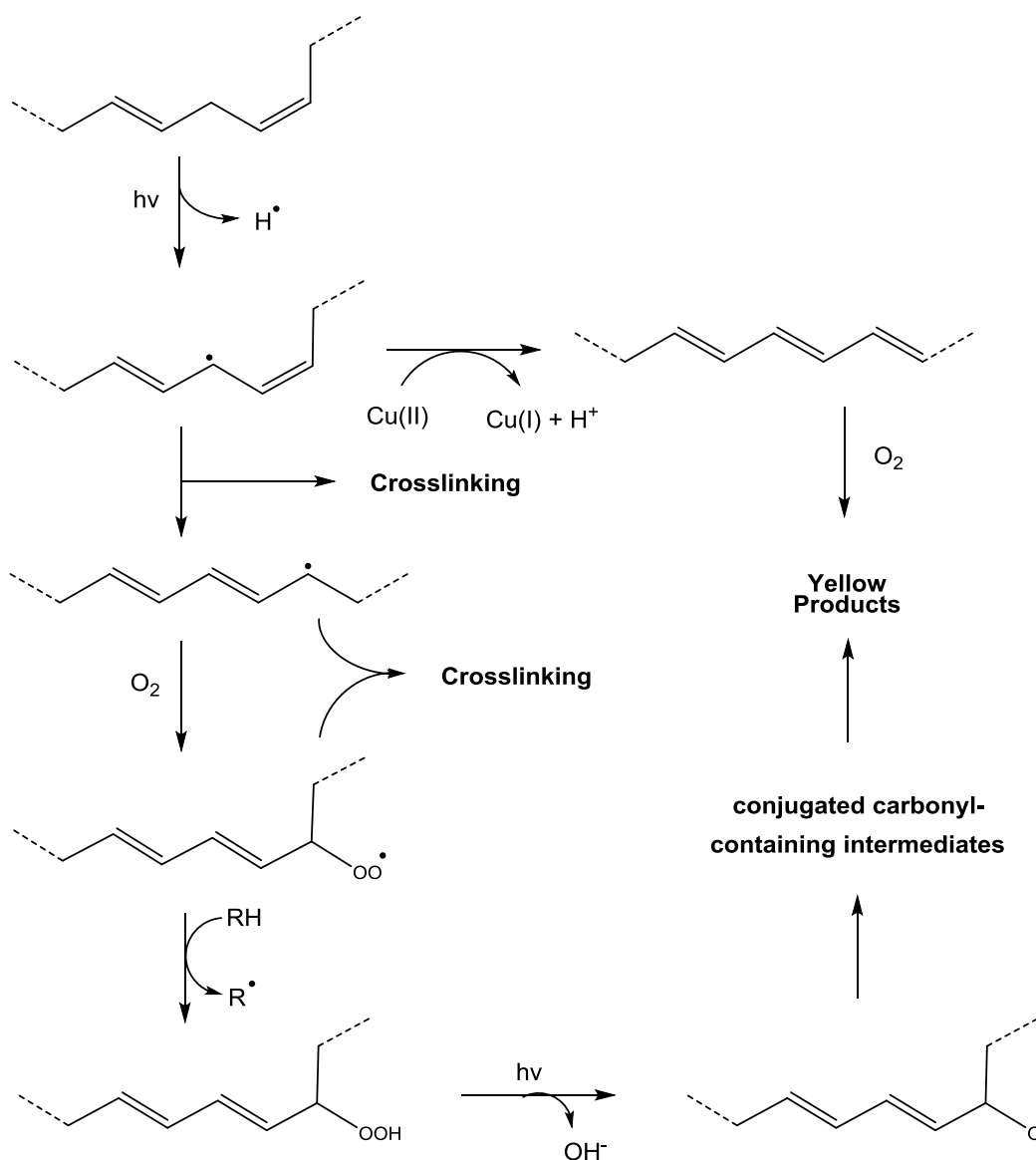
Figure 36. A comparison of the photo-oxidized mechanism for lipid yellowing and the abbreviated mechanism brought about by the presence of copper(II). Adapted from Boyatzis et al.

The main argument against the light-induced, Cu(II)-catalyzed mechanism of browning is that no evidence of Cu(I) has been found in aged samples of copper resinate [36, 40]. Furthermore, implicating oil as the browning culprit in the paintings is contrary to the practical knowledge of the time which recommended grinding the copper pigments in oil and immediately

covering them with varnish to protect them from air and humidity [29, 30]. Evidence also indicates that the oil actually helps to protect the pigment from browning. Under artificial aging conditions, evidence of degradation was found only on the surface of the copper resinate glaze indicating that the degradation agents cannot easily penetrate the oil binder [40].

Other possible mechanisms proposed for copper resinate discoloration involve combinations of thermal aging, UV aging, oxygen, pollutants and humidity. Samples of copper pigment aged artificially with heat show significant browning [36, 37, 43]. However, a proposed mechanism for thermal degradation still utilizes copper(II) as the oxidizing agent [37] which has been brought into question by the lack of copper(I) found in aged copper resinate samples [33]. Samples aged artificially with UV also showed browning [43] but significantly less so than the thermally aged samples [37]. Studies also show that an increase in thermal and UV exposure increased the rate of oil degradation [43] and both heat and UV have also been shown to transform free and bound forms of abietic acid, resulting in large increases of 7-oxo-dehydroabietic acid [36]. One promising study also showed combinations of sunlight, gaseous pollutants such as NO_X and SO_2 and high humidity induced color changes similar to those seen in copper resinate darkening [39].

The one constant in all examples of green pigment browning is copper. No browning of green pigments is observed without its presence [37]. Based on the historical and chemical evidence, we may be reasonably certain that copper resinate was the pigment used by Tintoretto in *Allegorical Figure of Spring*. In this chapter, the chemical properties of this pigment were investigated in order to gain a better understanding of its discoloration by attempting to synthesize pure copper(II) abietate and observing the compound under various conditions such as humidity, UV light and basic environments.

Synthesis of Copper(II) Acetate

The synthesis of $Cu_2(Ac)_4 \cdot 2H_2O$ is adapted from the literature procedure of Solomon et al. [44]. 3.125 g $CuSO_4 \cdot 5H_2O$ was dissolved in 60 mL of distilled water while stirring. A 3 M ammonia solution was added dropwise to the Copper(II) sulfate solution, with constant stirring until the solution turned from a powdery blue with the first few drops of ammonia to a dark translucent blue. Approximately 1.25 g of NaOH pellets were dissolved in approximately 5 mL of distilled water and the NaOH solution was added all at once to the copper ammonia solution, which was then stirred for 5-10 minutes. The precipitate was collected by vacuum filtration and washed with approximately 5 mL of distilled water. The wet precipitate was scraped into a beaker and dissolved with 10% acetic acid (approximately 10 mL) until a more translucent, turquoise color was observed. The solution was air dried. This procedure resulted in a 64.6% yield of 1.61 g copper(II) acetate. The procedure was repeated with all amounts doubled resulting in a yield of 91.1% yield of 4.55 g copper(II) acetate.

Synthesis of Copper Resinate

Synthesis 1: 4:1 Molar Ratio of Abietic Acid and Copper (Adapted from Gunn et al.). The synthesis of copper abietate from the stoichiometric reaction of abietic acid and copper(II) acetate was adapted from the synthesis used in Gunn et al. [35]. Two solutions were prepared in 100-mL beakers: a solution of 0.5 g of abietic acid in 15 mL of 100% ethanol, and a solution of 0.07 g sodium hydroxide pellets in 10 mL of 100% ethanol. The sodium hydroxide solution was poured into the abietic acid solution. With occasional swirling, fine crystals precipitated in the solution over the course of 15 minutes. A solution of 0.165 g copper(II) acetate in approximately

20 mL of ethanol was prepared in 125-mL round-bottom flask. The solution was stirred, and extra ethanol was added as necessary to dissolve the copper(II) acetate. This mixture was added dropwise to the basic abietic acid solution. The new solution was stoppered and stirred for at least 48 hours.

Once the copper resinate was synthesized, it was extracted to observe the organic and nonorganic parts separately. An aliquot of the copper resinate was dissolved in ethanol/hexane and extracted multiple times with water in order to isolate the nonpolar copper(II) abietate in the hexane layer. Another aliquot was dried on a rotary evaporator and the residue placed in a dessicator at room temperature.

Synthesis 2: 8:1 Molar Ratio of Abietic Acid and Copper (Adapted from Gunn et al.). The synthesis of copper abietate from excess abietic acid and copper(II) acetate (8:1 ratio) was adapted from the synthesis used in Gunn et al. [35]. Two solutions were prepared in 100-mL beakers: a solution of 1.0 g of abietic acid in 30 mL 100% ethanol, and a solution of 0.14 g sodium hydroxide pellets in 10 mL 100% ethanol. The sodium hydroxide solution was poured into the abietic acid solution. With occasional swirling, fine crystals precipitated in the solution over the course of ~15 minutes. A solution of 0.165 g copper(II) acetate in 20 mL of ethanol was prepared in 125-mL round-bottom flask. The solution was stirred, and extra ethanol was added as necessary to dissolve the copper(II) acetate. The copper(II) acetate solution was added dropwise to the basic abietic acid solution. The mixture was stoppered and stirred for at least 48 hours.

An aliquot of the copper resinate was dissolved in hexane and extracted multiple times with water. Another aliquot was dried on a rotary evaporator and the residue placed in a dessicator at room temperature.

IR spectra of Copper Resinate and Copper(II) Acetate

Infrared spectra in KBr were obtained of copper(II) acetate, abietic acid, and the evaporated residues of 8:1 and 4:1 copper(II) abietate using a Thermo Nicolet AVATAR 370 FTIR spectrometer.

The IR spectrum of copper resinate (Fig. 37) appears to be consistent with a pure sample of copper(II) abietate [14, 36, 45]. The bands around 1610 cm^{-1} and 1460 cm^{-1} are indicative of an organic carboxylate ligand [14, 36] where the band around 1610 cm^{-1} is due to symmetrical stretching of the COO$^-$ groups and the band around 1460 cm^{-1} is due to the symmetrical scissoring of CH$_3$ groups [45]. The asymmetrical stretching of the COO$^-$ groups may result in a shoulder around 1618 cm^{-1} [45]. The band around 2930 cm^{-1} is due to asymmetrical stretching of CH$_2$ and CH$_3$ groups while the broad band around 3430 cm^{-1} could be due to OH stretching of an aqua ligand [45]. The complex ligand in copper(II) abietate, also accounts for the complicated fingerprint region of the spectrum, from approximately 1300 cm^{-1} and below.

The spectrum differs from the spectrum of copper(II) acetate reported in the literature [14, 46] and the spectrum of my synthesized copper(II) acetate (Fig. 38). Copper(II) acetate will have a band between 1560-1610 cm^{-1} caused by the stretching vibration of the COO$^-$ group [14], CH vibrations at 2985, c. 2935, 1445, 1356, 1053, and 1032 cm^{-1}, and a C-O symmetrical stretching band from the acetate group at 1421 cm^{-1} [46]. As expected, the bands observed for

copper abietate were similar, but with a marked difference in the band around 2932 cm^{-1} representing symmetrical stretching of CH_2 and CH_3 groups. This band was very strong in the copper abietate sample but much weaker or not present in the copper acetate spectra [14], as expected based on the greater number of CH_2 and CH_3 groups in abietate compared with acetate. Additionally, the shift in the band showing the symmetrical stretching of the COO$^-$ group (band III at 1579 cm^{-1} in copper abietate and 1601 cm^{-1} in copper(II) acetate) indicates that the ligand has changed. The fingerprint region is also much less complex in copper(II) acetate compared with copper abietate.
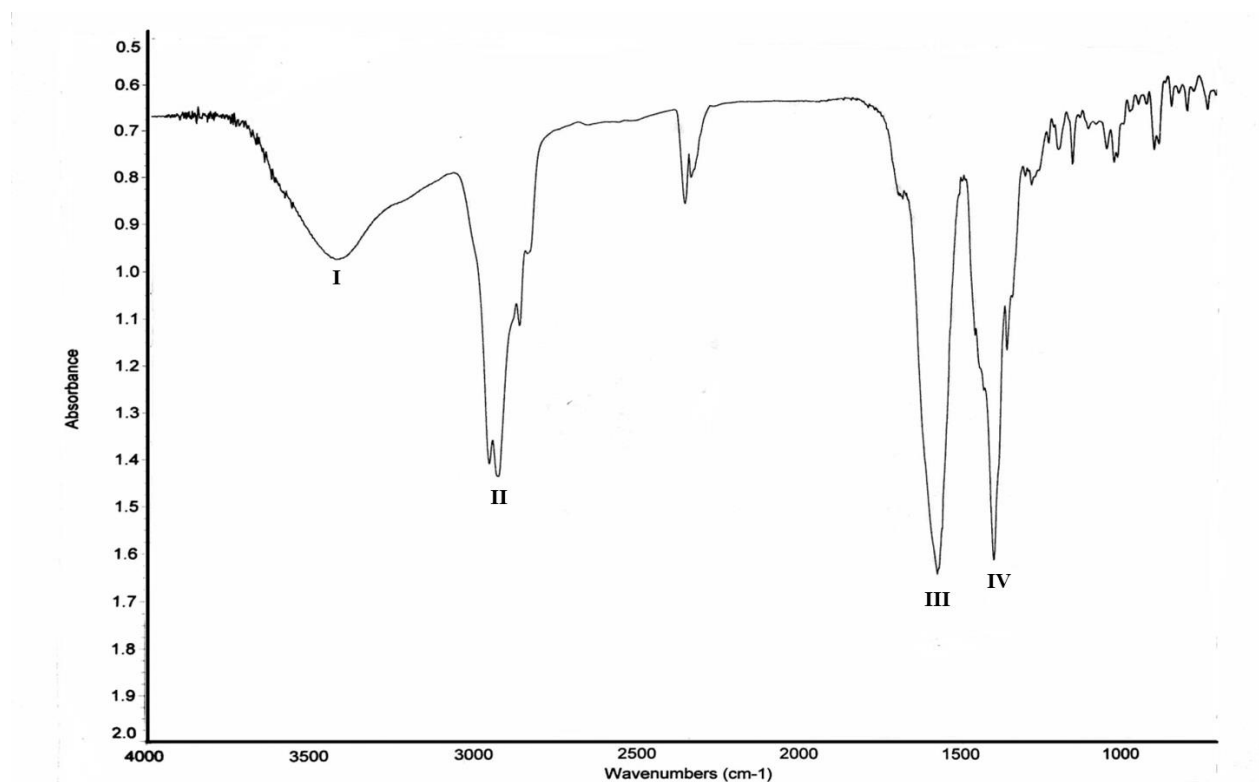
Figure 37. IR spectrum of synthesized copper abietate. The broad band around 3430 cm^{-1} (I) is due to OH stretching of the water, the band around 2930 cm^{-1} is due to asymmetrical stretching of CH_2 and CH_3 groups, the band around 1610 cm^{-1} is due to symmetrical stretching of the COO groups and the band around 1460 cm^{-1} is due to the symmetrical scissoring of CH_3 groups.
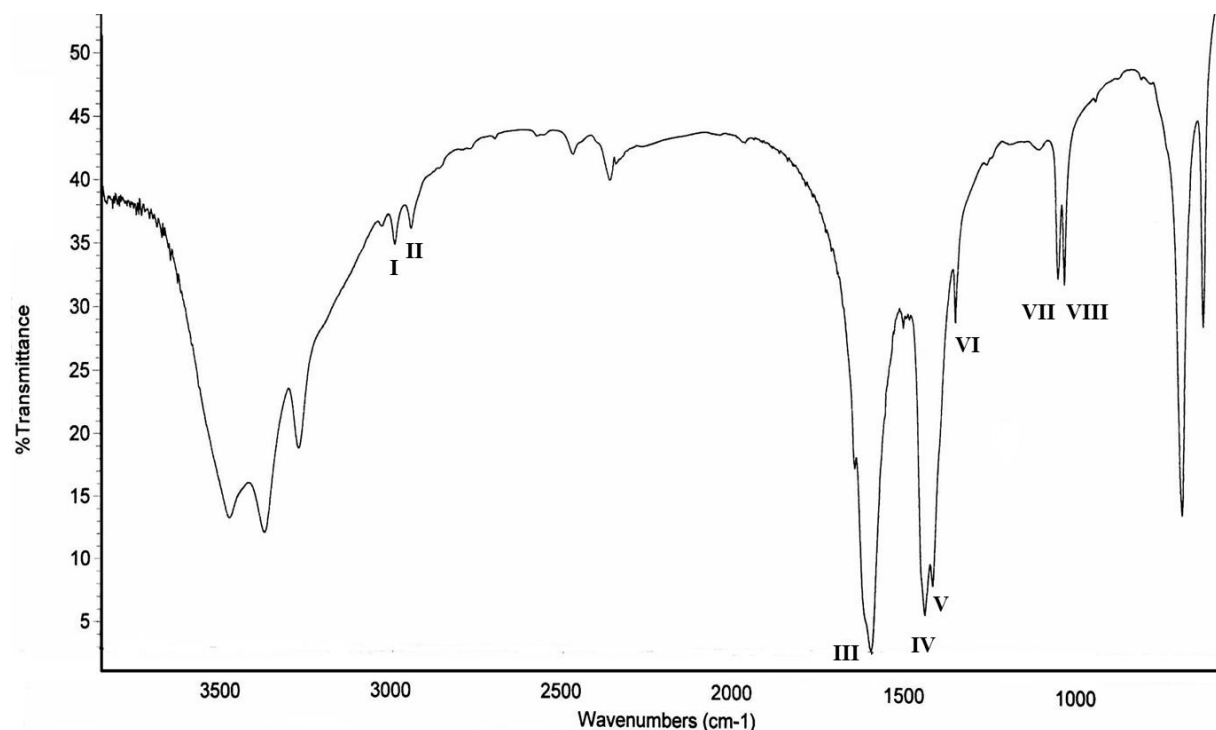
Figure 38. IR spectrum of synthesized copper(II) acetate. Copper(II) acetate will have a band between 1560-1610 cm^{-1} (III) caused by the stretching vibration of the COO group, CH vibrations at 2985 cm^{-1} (I), c. 2935 cm^{-1} (II), 1445 cm^{-1} (IV), 1356 cm^{-1} (VI), 1053 cm^{-1} (VII), and 1032 cm^{-1} (VIII), and a C-O symmetrical stretching band from the acetate group at 1421 cm^{-1} (V).

Verification of Copper Resinate with Mass Spectrometry

Positive-ion ESI-mass spectrometry was conducted on a API 2000 LC/MC/MC in order to identify the compounds present in the synthesized copper abietate mixture, commercially available copper resinate from Kremer, and pure abietic acid (the main component of Venice turpentine). Various combinations of solvents, temperatures and voltages were tested but the best results were obtained in ethanol at 200°C and 3500-4000V.

Our synthesized copper resinate yielded a spectrum (Fig. 39) indicative of a mixture of several copper complexes with varying ratios of abietate and acetate substitutions consistent with the proposed mechanism (Fig. 35). The sodiated ions present are $[Cu_2Ab_4Na]^+$ (1354 m/z), $[Cu_2Ab_3AcNa]^+$ (1111 m/z), and $[Cu_2Ab_2Ac_2Na]^+$ (868 m/z) but $[Cu_2AbAc_3Na]^+$ (627 m/z) was not observed. Therefore, it appears that in the formation of copper resinate from copper(II) acetate and resin acids, abietate ligands do not always fully replace acetate ligands, resulting in different combinations of copper, acetate and abietate. If axial aqua ligands were present as in copper(II) acetate, they were apparently lost during ionization in the mass spectrometer. Clusters of copper, abietate, acetate, and solvent were also noted at 918 m/z representing the $[Cu_3Ab_2Ac(OEt)Na]^+$ ion. Similar mixed clusters have been observed with copper(II) acetate in methanol [47].

The mass spectrum of pure abietic acid (Fig. 40) showed evidence of clusters of up to three sodiated abietic acids. The clustered ions observed were $[AbHNa]^+$ (325 m/z), $[(AbH)_2Na]^+$ (627 m/z) and $[(AbH)_3Na]^+$ (929 m/z). Sodiated abietic acid was also observed to form clusters with the ethanolic solvent yielding $[AbH(EtOH)Na]^+$ (371 m/z). Additional masses are consistent with progressive oxidation of the abietic acid clusters in the instrument.

The spectrum for commercially available copper resinate from Kremer (Fig. 39) contained ions found in both the spectra of pure abietic acid and the synthesized copper(II) abietate as would be expected from the recipe for copper resinate. The strongest peaks were solvent clusters including $[EtOHNa]^+$ at 69 m/z, $[(EtOH)_2Na]^+$ at 115 m/z, $[(EtOH)_3Na]^+$ at 161 m/z, and $[(EtOH)^6Na]^+$ at 299 m/z. Ethanol also clustered with abietic acid producing ions like $[AbH(EtOH)Na]^+$ at 371 m/z and $[AcH(EtOH)_3Na]^+$ at 221 m/z. The sodiated abietic acid clusters that were observed in pure abietic acid were found in the commercial copper resinate

(Fig. 40) as $[AbHNa]^+$ at 325 m/z, $[(AbH)_2Na]^+$ at 627 m/z and $[(AbH)_3Na]^+$ at 929 m/z.

Similarly, the same sodiated copper compounds of varying acetate and abietate ligands that were
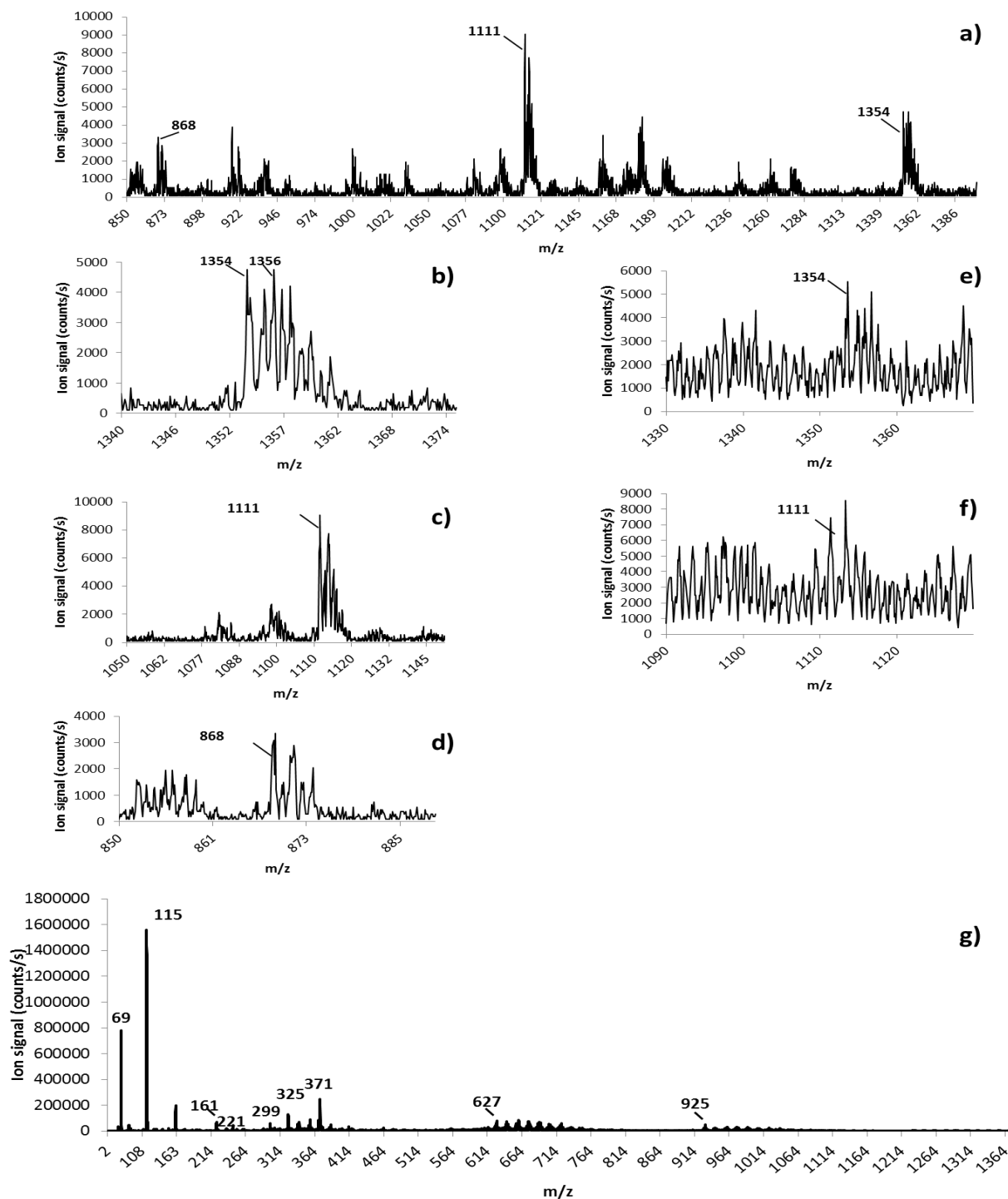
Figure 39. Mass spectra of the synthesized copper resinate (a-d) and the commercially available copper resinate (e-g). Shown are (a) the overall spectrum of synthesized copper resinate with the compounds highlighted, (b) $[Cu_2Ab_4Na]^+$ (1354 m/z), (c) $[Cu_2Ab_3AcNa]^+$ (1111 m/z) and (d) $[Cu_2Ab_2Ac_2Na]^+$ (868 m/z). Also present in the

commercially available copper resinate are (e) $[Cu_2Ab_4Na]^+$ (1354 m/z)and (f) $[Cu_2Ab_3AcNa]^+$ (1111 m/z). The full spectrum of commercially available copper resinate from Kremer (g) is shown with solvent clusters including $[EtOHNa]^+$ (69 m/z), $[(EtOH)_2Na]^+$ (115 m/z), $[(EtOH)_3Na]^+$ (161 m/z), $[(EtOH)_6Na]^+$ (299 m/z), $[AbH(EtOH)Na]^+$ (371 m/z) and $[AcH(EtOH)_3Na]^+$ (221 m/z). Masses were calculated using Cu-63 but peaks from Cu-65 can also be observed for example in (b) at 1356 m/z.
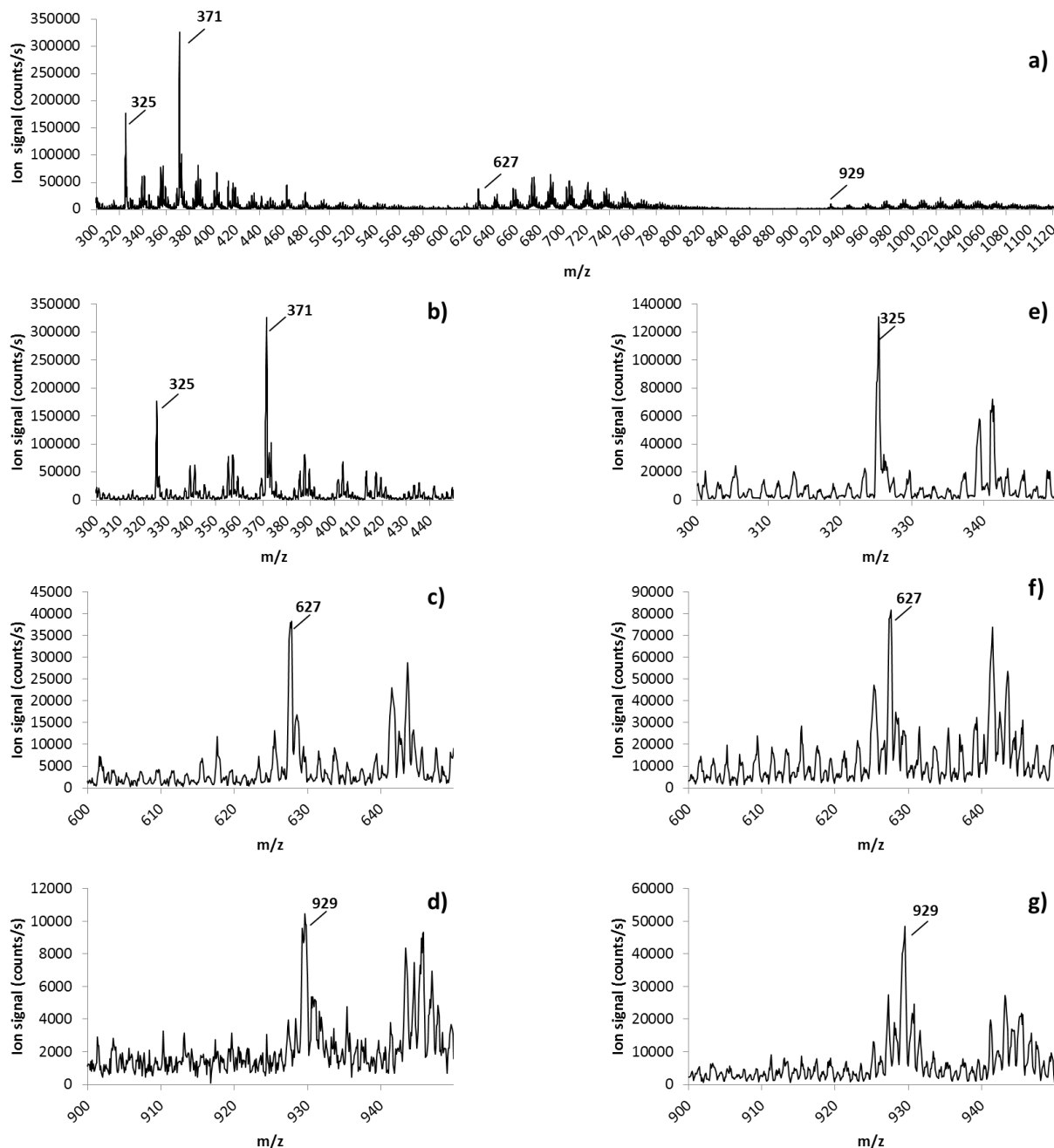
Figure 40. The mass spectra of abietic acid in pure abietic acid (a-d) and commercially available copper resinate (e-g). Shown are (a) the entire spectrum of pure abietic acid with highlighted points for (b) compound $[AbHNa]^+$ (325 m/z) and $[AbHEtOHNa]^+$ (371 m/z), (c) $[(AbH)_2Na]^+$ (627 m/z) and (d) $[(AbH)_3Na]^+$ (929 m/z). Also present in the commercially available copper resinate are (e) $[AbHNa]^+$ (325 m/z), (f) $[(AbH)_2Na]^+$ (627 m/z) and (g) $[(AbH)_3Na]^+$ (929 m/z).

observed in the synthesized copper resinate were also observed in the commercial copper resinate (Fig. 39) as $[Cu_2Ab_4Na]^+$ at 1354 m/z, and $[Cu_2Ab_3AcNa]^+$ at 1111 m/z. The compounds $[Cu_2Ab_2Ac_2Na]^+$ at 868 m/z and $[Cu_2AbAc_3Na]^+$ at 627 m/z were not observed. Based on these results, it can be concluded that copper abietate was successfully synthesized in the lab and that it contains less free abietic acid than the commercially available copper resinate from Kremer. Furthermore, it has been shown that free abietic acid may form solvent clusters of at least three abietic acids and that copper resinate consists of a variety of copper compounds with varying ratios of abietate and acetate ligands.

Observations of Copper Resinate Color by Extraction and Rotavapping

When extracted with hexane and water, the 4:1, the 8:1 and the commercially available copper resinate solutions separated into distinct blue organic and yellow aqueous layers (Fig. 41), indicating that the green of copper resinate pigment is not from the copper complex alone, but rather from a combination of the blue and yellow substances. The organic layer would include any copper compounds with acetate or abietate ligands (Fig. 35), in agreement with the MS results of copper(II) abietate and commercial copper resinate. However, the blue component is unlikely to be copper(II) acetate, which is sparingly soluble in hexane. The yellow layer must therefore contain the salts of the unreacted abietic acid. Accordingly, an aqueous solution of NaOH and abietic acid appears yellow and almost identical to the polar layer of the extraction (Fig. 41). These color observations are consistent with other green pigments, which usually absorb in the blue and yellow range rather than the green [48].
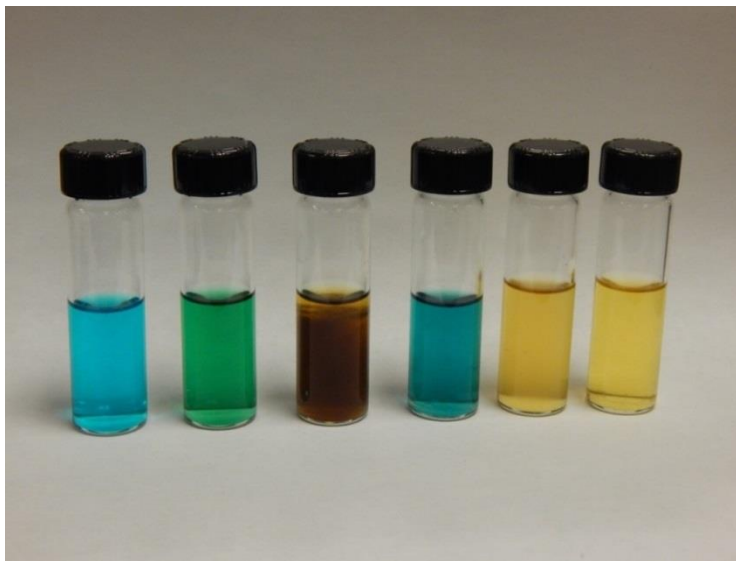
Figure 41. Color comparison of various copper solutions. From left to right: copper(II) acetate, copper resinate mixture, copper resinate in basic solution, organic blue layer of copper resinate extraction, inorganic yellow layer of copper resinate extraction, abietic acid. All solutions are in ethanol except the extraction layers which are in hexane (organic layer) and ethanol/water (inorganic layer).

The combination of yellow abietate and blue copper(II) abietate to make the green of copper resinate is further verified by UV/visible absorbance spectrum (Fig. 42). Pure abietate appear yellow-orange because it absorbs in the blue-violet range. Copper(II) acetate and the 8:1 copper(II) abietate mixture absorb in both the blue-violet and yellow ranges. The slight absorbance of copper(II) acetate in the blue range is why verdigris appears slightly green-blue rather than pure blue. The blue-violet absorbance of the excess abietate in the 8:1 copper abietate mixture gives a more green color than copper(II) acetate or copper(II) abietate alone. Perhaps most importantly, the observed λmax for the two copper compounds are different from one another. The λmax of copper(II) acetate is 708 nm while the λmax of 8:1 copper abietate reaction mixture is shifted to 692 nm, indicating that the blue component of copper resinate is not copper(II) acetate but a new compound or compounds of copper(II) and abietate. Therefore, the

UV/visible spectra confirm that the green color of copper resinate is due to a combination of blue copper abietates and yellow abietic acid.
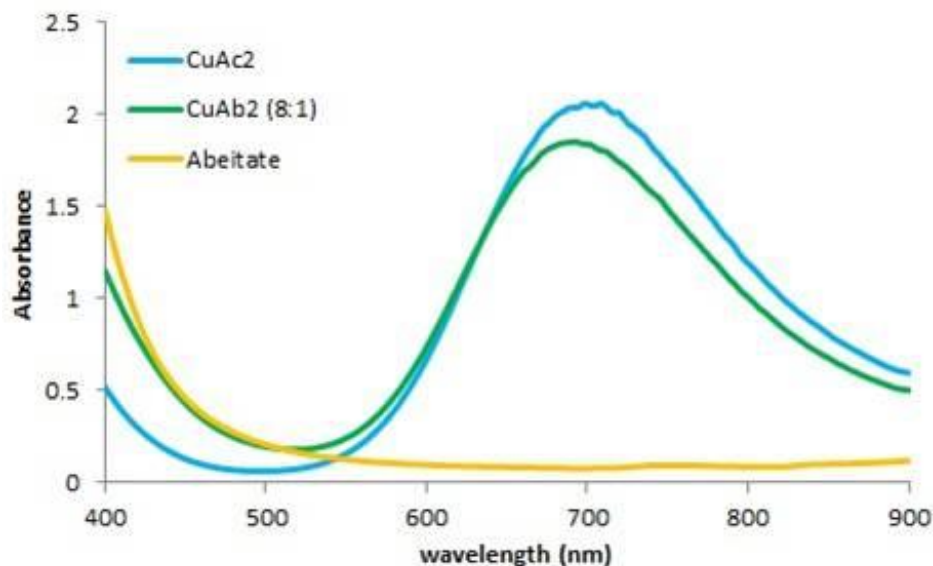
Figure 42. UV spectrum of copper(II) acetate (λ_{max}=708 nm), 8:1 synthesized copper abietate (λ_{max}=692 nm), and pure abietate all in ethanol.

Further color changes are observed when copper resinate is rotavapped. Both the 4:1 and 8:1 copper resinate solutions stayed bright green until the very end of evaporation, at which point they both revealed turquoise blue crystals around the edges of the flask, and a small amount of viscous green substance at the bottom. When the turquoise crystals were stoppered and left overnight, after which time they were observed to be bright green again and had lost the crystalline appearance to become uniformly shiny and sticky. However, if they were then placed in a dessicator, the sticky substance turned blue again, but maintained its sticky consistency. Additionally, when they were placed in the dessicator immediately after rotavapping, before they had turned green again, the crystals and the sticky substance both turned blue and maintained their respective textures.

Water may be crucial to the green color of copper resinate. Indeed, when blue copper resinate crystals are placed in the presence of water, they turn green again, possibly indicating that water molecules are being added or removed in the axial position of the Copper(II) abietate complex, or that water displaces the abietate ligands, resulting in a green combination of blue copper compounds and yellow abietic salt.

Color Observations of Copper Resinate by Drying and Dessication

The influence of water on the structure of copper resinate is further elucidated by the failure of commercial copper resinate to turn yellow-green and dry when placed in a dessicator. To test the effect of water on the drying process of copper resinate, commercially available copper resinate from Kremer was painted on a primed canvas and placed one sample in a dessicator and left one sample to dry normally. It has already been noted that copper resinate transforms from a blue-green to a yellow-green color upon drying over several months [32, 35]. However, my results show that copper resinate fails to make this transition (or makes it at a much slower pace) when placed freshly painted and not yet dried in a dessicator, and remains sticky and blue-green (Fig. 43).

Notable color changes were also observed in copper resinate samples that were allowed to air dry. For these observations, commercial copper resinate from Kremer and painted onto prepared canvas in 1" x 1" squares. One square was placed in direct sunlight to dry with heat and UV exposure while one square was allowed to dry without light at room temperature. My results indicate that copper resinate dried in the dark remains much bluer than copper resinate dried in direct sunlight. Therefore, UV light and temperature may play a role in the

transformation of the copper complex, or these observations may be a reflection of the well-documented [42, 43] UV-induced yellowing of fatty acids in the resin.
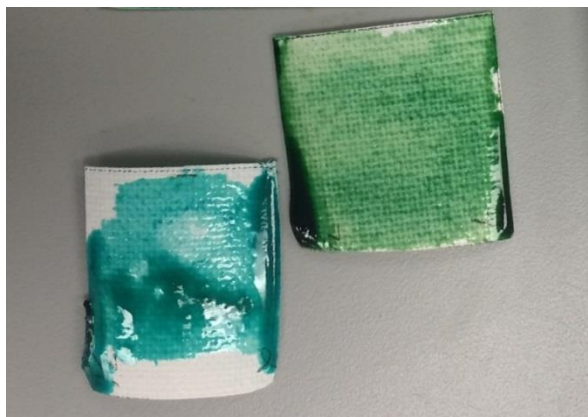
Figure 43. Comparison of copper resinate left in a dessicator for two weeks (left), versus copper resinate dried in open air for two weeks (right).

I propose that water plays a crucial role in the degration of copper resinate pigments of historical paintings like Tintoretto's *Allegorical Figure of Spring*. Copper resinate and verdigris have been shown to form CuS compounds over time when combined with sulfur-containing pigments in aqueous media [32]. Although Tintoretto painted *Allegorical Figure of Spring* in oil media, it was painted in an especially humid environment, which may have exposed it to significant amounts of water. Verdigris has been shown to be especially susceptible to damage and discoloration under humid conditions [49]. Furthermore, the experimental techniques for painting with copper pigments, such as Da Vinci's method of overpainting with aloe and water [38], may have exposed the copper resinate glaze to water even before it was fully dry.

Proposed Mechanism of Discoloration of Copper Resinate

During my attempts to extract copper resinate with various solvents, I happened to add both solutions of 8:1 and 4:1 copper resinate to a NaOH solution in water and effects similar to the browning of copper resinate seen in paintings was observed. When an ethanolic solution of copper resinate was combined with aqueous NaOH, it first turned yellow, and then after several minutes, an orangish-brown precipitate of CuO formed (Fig. 41). A similar reaction was observed with copper(II) acetate. The base displaces the acetate and abietate ligands of the blue copper(II) carboxylate molecules to rapidly form CuO particles. The color and appearance of the solution is very similar to that of the formerly green areas of Tintoretto's *Allegorical Figure of Spring*, which suggests a slow substitution of the acetate/abietate ligands in the blue portion of copper resinate by water to form brown CuO is the cause of the discoloration. The humid climate of Venice may have accelerated the process. The environmental exposure to water could also be consistent with the instances where the painting's frame appears to have protected the green copper pigments from discoloration.

Conclusion

Based on the laboratory investigations of copper resinate, I am able to shed light on the properties and composition of copper resinate and propose possible causes of the discoloration observed in Tintoretto's *Allegorical Figure of Spring*. My foremost conclusion is that the green color of copper resinate is due to a combination of blue copper abietate and yellow abietic acid. Furthermore, the final green color of the copper resinate is largely dependent upon water and, when deprived of it, remains a bluer green. Prolonged exposure to water and sunlight appears to

affect the final color of the copper resinate glaze, with samples achieving a much yellower color in their presence. Therefore, exposure to excessive water may play a role in the degradation of the color from green to brown. Popular techniques at the time proposed by Da Vinci encouraged saturation of fresh copper resinate with aloe and water [38], and this particular painting was painted and displayed in a humid maritime environment, both of which would have contributed to excessive water exposure. Finally, I was able to achieve a convincing replication of the degraded brown copper resinate by accelerating the degradation with ethanolic base. The result was a brown particulate copper oxide which closely resembles the appearance of the formerly green portions of *Allegorical Figure of Spring*. I therefore propose copper oxide to be the final product of copper resinate discoloration.

CHAPTER IV

CONCLUSION

This work focused on the discoloration of green pigments to brown in a sixteenth century Venetian painting by Tintoretto. In this research, I have examined *Allegorical Figure of Spring* to determine its composition and condition. I determined with a fair amount of confidence that the discolored pigment was copper resinate, and studied its properties, including its structure and stability under various conditions. This research has given insight into the original appearance of the painting, and has also elucidated the process by which copper resinate undergoes its discoloration.

In the physical and chemical examination of the painting, I discovered information about the painting's original shape and appearance, the pigments used to paint it, and what damages and repairs it has undergone over the centuries. Two main areas of damage were found using UV light, one on the arm and one on the dress. Repairs to the damage on the arm were confirmed using XRF by the presence titanium white and zinc white, which were not used until the twentieth and nineteenth centuries, respectively. The physical examination of the painting also revealed large cracks running at 45° angles to each corner and parallel to the top and bottom of the painting. An initial hypothesis that these cracks reveal later additions to the painting was supported by the XRF results which found vastly different elemental profiles in the corners and top and bottom strip compared with the main portion of the painting. Thus, the painting must have originally been lozenge-shaped.

The physical and chemical examination of the painting also supported the hypothesis that copper resinate was the original green pigment used in the painting. The presence of copper in the foliage was verified by XRF analysis, narrowing down the possible green pigments to malachite or copper resinate. Malachite is not known to discolor with age but copper resinate is well known to turn to brown over time [32] and was used frequently by Tintoretto and his contemporaries [4]. Copper abietate, the likely main component of copper resinate, was subsequently analyzed in the lab, revealing information on its composition and stability. In particular, I determined that the green color of copper resinate is not because copper(II) abietate is green, but rather a combination of blue copper(II) abietate and yellow abietic acid. Furthermore, I found evidence for the importance of humidity and light in the drying process of the copper resinate. In the absence of either of these elements, the copper resinate will stay sticky and will fail to achieve the final green shade, instead remaining bluish-green.

I also propose that the degradation of copper resinate is dependent upon water, based on the yellowing of the color that is observed in the presence of humidity, and on the abundance of evidence that this painting was subjected to water during the painting process and from the environment. Da Vinci was widely respected by his contemporaries as the father of the "modern" age of painting [50] and he suggested that the best practice for curing copper resinate was to apply a mixture of aloe and water to the surface of the painting after it was complete [38]. It is likely that Tintoretto followed this advice. Furthermore, having been painted and displayed in the marine environment in Venice, the painting would have been subjected to a highly humid environment anyway. Furthermore, the importance of humidity in the discoloration of copper resinate has been suggested by other research [39].

Finally, I propose that the final product of copper resinate degradation is particulate copper oxide. By accelerating the degradation process using ethanolic base, I obtained a particulate copper oxide that closely resembled the discolored portions of copper resinate on the painting. A previous study found no evidence of copper oxide or copper(I) [33] but the possibility has not been extensively considered.

Although we have made great strides in understanding *Allegorical Figure of Spring* and the structure and degradation of copper resinate, there is still work that could be done. For a better understanding of the painting itself it would be useful to use an IR microscope and/or scanning electron microscopy with energy-dispersive spectroscopy on the cross-sections of the painting to more definitively identify the elemental composition of the layers. It would also be useful to research paintings of similar provenance and background in order to assess the similarities and differences in their structure and condition. In particular, it would be useful to conduct this type of analysis on the other three paintings in this series, *Allegorical Figure of Summer, Allegorical Figure of Autumn and Allegorical Figure of Winter*. Perhaps that most useful work to be accomplished to further the understanding of the copper resinate pigment would be to obtain a crystal structure of the molecule. A full understanding of the structure of this pigment would aid in elucidating whether water is a ligand similar to copper(II) acetate, and the various combinations of copper and abietate ligands.

This work at the intersection of chemistry and art conservation is an important contribution to understanding the life of this painting and others like it. The discoloration of pigments is one of the most difficult problems which face conservators and copper resinate is a well-known culprit of discoloration. Through enhancing the understanding of this pigment's

structure and process of discoloration, we are one step closer to preventing this particular disfiguring consequence of time.

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