QUANTITATIVE ANALYSIS OF THIN-FILM ORGANIC MATERIALS ON PHOTOGRAPHS USING FOURIER TRANSFORM INFRARED SPECTROMETRY

A thesis submitted in partial fulfillment of the requirements
For the degree of Master of Science in Chemistry

By

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ABSTRACT

QUANTITATIVE ANALYSIS OF THIN-FILM ORGANIC MATERIALS ON PHOTOGRAPHS USING FOURIER TRANSFORM INFRARED SPECTROMETRY

By

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Master of Science in Chemistry

In photography various organic materials are used to bind the light-sensitive material to a suitable backing. Binder thickness varies and depends on factors such as the application technique, the type of backing and aging effects on the photograph. The main purpose of this study was to produce a series of quantitative standards for each of the three principal binding materials - albumen, gelatin and collodion- so that reliable quantitative measurements of the binder thickness for historical photographs can be made using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectrometry. Determination of the thickness of the organic layer on a photograph can help conservators identify the coating method and possibly indicate whether additional organic coatings are present on the photograph. A set of quantitative standards will serve
to cross-calibrate ATR-FTIR instruments in different laboratories, thus making comparative studies more meaningful.

Initial work focused on developing a method of preparing a uniform coating of each of the three organic materials with varying thicknesses on a satisfactory support. Satisfactory samples of albumen were prepared on a paper backing by rolling an albumen solution onto the paper and allowing it to dry thoroughly. Standards with a thickness range of 146 – 4518 µg/cm$^2$ were created for albumen. Gelatin samples were prepared in a similar fashion and a set of standards with a thickness range of 1853 – 7055 µg/cm$^2$ were created. All sample preparation methods used were unsuccessful in creating sufficiently thin collodion coatings. Furthermore, a study of numerous collodion photographs using digital and scanning electron microscopy indicated that the coating thickness for these photographs was too great to permit quantitative ATR-FTIR measurements. Consequently, no further work was done to prepare collodion standards of varying thickness.

Calibration curves based on a normalized IR peak area measurement were obtained for the set of albumen and gelatin standards using different ATR-FTIR instruments. These were then used to quantitatively assess the albumen or gelatin thickness for a number of photographs from the Getty Conservation Institute collection. The inter-laboratory results showed a variation of less than 10% for the measured albumen thicknesses. The different instruments produced differences less than 20% for the measured gelatin thicknesses. Details of the standard preparation and the quantitative ATR-FTIR measurements, along with suggestions for additional studies, are presented in this work.
I. Introduction

A photograph generally consists of three basic components: a substrate, an image layer that contains the light-sensitive material and a binder that holds the light-sensitive layer to the substrate. Historically, glass slides were used as the substrate but they were fragile and difficult to transport. Later, paper, which was much easier to transport, was adopted as the substrate for photographs. The light-sensitive materials were metal-containing substances, the most popular of which contained silver. However, other types of materials, including those containing platinum, were also used in the production of early photographs. Acidic solutions containing these metals were often used to sensitize photographs (1, 2). These solutions would deposit the light-sensitive metal onto the substrate thereby enabling the image to appear after exposure and processing.

For paper photographs the binder was a translucent material that kept the light-sensitive material suspended and bound to the paper. The binder had several important functions as part of the photograph. It created a layer around the light-sensitive material that helped to protect it from the environment. In addition, the binder helped to maximize the light absorption of the light-sensitive material by dispersing and suspending it over the support (1). The binder was most often made of organic materials such as gelatin, albumen or collodion. These materials dry into a clear film and thus hold the light-sensitive material in place while not interfering with the image making. A quantitative study of the binder layer, specifically those composed of gelatin, albumen and collodion, is the focus of this work.
In the study of historical photographs, three approaches are generally used to identify the era and construction of the photograph: visual, microscopic and analytical. Some photographs can be identified visually by the color, subject matter and the substrate used in creating the photograph. If the photograph requires further analysis, a cross section of a photograph can be obtained and analyzed microscopically. Under magnification the various layers of the photograph can be identified. Albumen photographs are good candidates for microscopic analysis because the layers are distinct under magnification. While cross section analysis does give the analyst further information about the photograph, it is destructive and must be used carefully. In addition, if the albumen has been coated with a top layer such as a varnish, it can be difficult to separate out the albumen layer from the other coatings, even under magnification. At this point the analysis may benefit from analytical study. By analyzing photographs using techniques such as Fourier Transform Infrared spectrometry (FTIR), the infrared signature and depth of the organic layer can help identify the top layers of a photograph. Techniques such as FTIR can also quantify thin organic layers, including the binder, on photographs, thus providing additional and potentially useful information. Once the trends of an era or a manufacturer have been established for the different organic materials it may be possible that the analyst can use the quantitative data to date the photographs they are studying. However, non-destructive FTIR does have its limitations as an analytical tool as this study shows.
A. Historical Background

1. Albumen

Albumen paper was considered to be “one of the most luxuriously beautiful photographic paper surfaces ever devised” (3). It was a convenient solution to the difficult salt paper printing process and calotype negatives that preceded it. In 1850 Louis Désiré Blanquart-Évard invented the process by which albumen was used to coat photographic paper (4, 5). Initially, this process was very simple. A mixture of egg white and salt was beaten to a froth, and, after the solution settled, the paper was coated by floating it on top of the solution before hanging the paper to dry (4). This quickly became the most popular type of photographic material. Not only were photographers making their own albumen-coated papers, but it was being manufactured on a large scale. By the 1860s, albumen paper was the most widely used manufactured printing paper (3), although in the United States photographers would float their own paper until the Civil War (4). By 1870, with more than 24 manufacturers of albumen paper, Germany emerged as the primary producer, with Dresden becoming the hub for the production of factory-produced albumen paper (6). Albumen paper production remained popular until 1895 and disappeared completely as a commercial product in 1929 (4) due to the numerous advantages offered by the use of other binders.

Specific attention to details during the preparation of the albumen was vital to creating a high quality product. Fresh eggs had to be completely separated; no portions of yolk or other contamination could remain in the albumen solution. Ammonium chloride or sodium chloride was then added to the solution and it was beaten to a froth. The chloride content was important to the sensitivity and contrast of the paper. Paper
with 1-1.5% chloride was less sensitive, but had more contrast, since there was less chloride for the silver to bind to when the paper was sensitized in a silver nitrate solution. On the other hand, paper with 1.5-2.5% chloride content was more common and produced a richer and denser image (4). By beating the solution the large protein molecules were broken down, thereby creating a solution with a more even viscosity. By adding acetic acid the large protein molecules were broken down further by acid-catalyzed hydrolysis (7), thus increasing the viscosity of the solution.

The solution was allowed to settle over night and was strained to remove any froth or particulates that remained. The liquid was aged for about one week before use. Once the albumen solution was ready, it was placed in trays and the paper was floated on top of the solution. The common types of paper used were the Canson feres, Saxe from Malmédy (at the time part of Germany), Rives from France, and Whatman from Britain (3, 6). After the albumen solution was applied, the paper was hung vertically to dry (4). Due to the orientation of the paper during drying the thickness of the albumen over the sheet of paper varied considerably. To compensate for this, another layer of albumen was applied by floating a second time and the sheet was hung upside down to dry (8).

Before a second coat of albumen was applied the paper was allowed to dry in a warm loft for six months (4). This allowed the first coat to completely cure so that it was insoluble and remained on the paper during application of the second coat. Two other approaches were used to cure the first layer in a shorter amount of time. In one approach, the layer of albumen was dried under a current of steam; this would “cook” the albumen. The second method involved immersing the coated paper in a 70% solution of isopropyl
alcohol. Coating the paper twice not only created a more even albumen coating, but also produced a glossier sheet to print on (4) due to the thicker coating.

Recent studies have been performed to gain additional information about the materials used to create these photographs. One study used several imaging techniques including visible microscopy (see Fig. 1), FTIR imaging and scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX) to analyze the various layers of albumen photographs (9). These analyses determined that the albumen layer thickness varied widely among the photographs.

![Figure 1. Micrographs (50x) of albumen photographs. (A) the card support, (B) crystalline layer, (C) paper, (D) albumen layer and (E) epoxy matrix (9)](image)

2. Gelatin

Gelatin is now the most commonly used binder on photographic printing supports such as paper or glass slides. It consists of protein obtained from the ground up bones and hides of cattle (1, 10). The first use of gelatin was in the 1840s when it was mixed with a salt solution and water to create the binder for salted paper photographs, so named
because there was very little gelatin present compared to the later emulsion papers. Just enough gelatin was used to bind the salt solution to the paper. The solution was applied to the paper by floating, as in the method of applying albumen to paper (4).

In 1871 the first gelatin emulsions were made by Dr. R. L. Maddox. This process required the photographer to first melt the emulsion in hot water. Once the emulsion was in its liquid form the photographer coated a glass plate (11). However, photographers found this process to be quite cumbersome and preferred to purchase plates that had been coated with the binder. Pre-coated gelatin plates were produced and sold on a large scale by 1878 in Great Britain (1). Until 1895 copies from gelatin plates were made onto albumen paper, but in 1882 a gelatin-coated paper was introduced (1). The use of gelatin paper became more widespread and manufactured gelatin papers became more popular. By the early 1890s the use of gelatin paper was more popular than the use of traditional albumen papers (12) and by the 1920s, when commercial albumen production ceased, gelatin-coated papers had become the standard photographic paper used worldwide.

3. Collodion

Collodion is a solution of cellulose nitrate dissolved in alcohol and ether and was invented in 1846 (1, 13). It was found to be a good binder for photographs because it reduced the exposure time significantly from previous processes, thus enabling the photographer to take portraits. Collodion was used as a binder for wet-plate negatives, ambrotypes, and tintype photographs along with paper photographs from 1885-1930 (1, 13). Wet collodion negatives were introduced in 1851 by Frederick Scott Archer (13). Initially, a photographer would have to coat glass plates with collodion solution at the time that the photographs were taken because the collodion negatives had to be wet when
used (12). Collodion solution dries quickly so there was not as much of a delay waiting for the plate to set, but it was still a cumbersome process. Photographers had to carry all of their equipment with them when they wished to take photographs outside of their studio. In addition, the collodion solution had to be handled carefully because the ether created the possibility of an explosion (13). In order to coat a plate the photographer would hold it horizontally and pour a small portion of collodion solution onto the plate. He would then slightly lower one side and allow the collodion solution to flow over the plate coating it uniformly and allowing the excess material to drain into a collection bottle (14).

Several different processes of coating paper with collodion were introduced starting in 1853, but it was not until the 1880s that one process was favored and commercial collodion paper was produced on a large scale (15). While collodion papers were popular for a while they were eventually replaced by the silver/gelatin-coated paper which had advantages over both the collodion and albumen photographic paper. In the United States collodion papers were available for purchase until World War I, but in Germany they were made on a commercial scale until the late 1930s. Figure 2 outlines important milestones in the use of binding materials for photographs.
Figure 2. Some important milestones in the use of binding materials for photographs

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
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<tbody>
<tr>
<td>1840</td>
<td>First use of gelatin</td>
</tr>
<tr>
<td>1846</td>
<td>Louis Desire Blanquart-Evard invented albumen coating process</td>
</tr>
<tr>
<td>1850</td>
<td>Albumen manufactured paper used</td>
</tr>
<tr>
<td>1851</td>
<td>Invention of collodion solution</td>
</tr>
<tr>
<td>1853</td>
<td>Collodion coated paper processes introduced</td>
</tr>
<tr>
<td>1860</td>
<td>Wet collodion photographs introduced by Frederick Scott Archer</td>
</tr>
<tr>
<td>1870</td>
<td>Commercial collodion paper was produced</td>
</tr>
<tr>
<td>1871</td>
<td>First gelatin negatives introduced by Dr. R.L. Maddox</td>
</tr>
<tr>
<td>1878</td>
<td>Germany becomes primary albumen paper producer</td>
</tr>
<tr>
<td>1880</td>
<td>Kodak pre-coated gelatin plates sold on a large scale</td>
</tr>
<tr>
<td>1882</td>
<td>Gelatin paper more popular then albumen</td>
</tr>
<tr>
<td>1890</td>
<td>End of albumen popularity</td>
</tr>
<tr>
<td>1895</td>
<td>First gelatin coated paper</td>
</tr>
<tr>
<td>1920</td>
<td>End of albumen paper production</td>
</tr>
<tr>
<td>1929</td>
<td>Commercial collodion paper available in Germany until 1930s</td>
</tr>
<tr>
<td>1930</td>
<td>Commercial collodion paper became the standard coating of photographic paper world wide</td>
</tr>
</tbody>
</table>
II. Materials and Methods

A. Materials

1. Albumen

The albumen used to make the standards in this study was prepared by mixing the egg whites of 12 eggs with 15 grams of ammonium chloride, 15 mL of deionized water and 2 mL of glacial acetic acid. A KitchenAid stand mixer was used to whip the mixture until it formed a meringue-like consistency. The mixture was allowed to sit for 24 hours in a refrigerator and the foam top was removed leaving behind the albumen solution used for coating. This albumen solution was diluted with water to create four solutions of varying concentrations of albumen. The diluted albumen solutions contained 75%, 50%, 25%, and 12.5% of the concentrated albumen solution by volume. Several drops of blue food coloring were added to some of the solutions to attain better visibility of the albumen coating on the support.

2. Gelatin

The gelatin used to make the standards was prepared using Knox brand original unflavored gelatin. One pouch of the unflavored gelatin was sprinkled over ¼ cup of cold water and allowed to stand for 1 min. Another ¼ cup of boiling water was then added to the solution and stirred until the gelatin had completely dissolved. The standards could only be coated when the solution was warm. If the gelatin solution cooled and hardened it could be used by placing the bowl of cooled gelatin into a hot water bath and gently warming the solution. Once the gelatin solution was liquid additional samples could be coated.
3. Collodion

Photographers' Formulary collodion solution, Cat. No. 10-0430, was used to make the collodion standards. The collodion solution was placed in a beaker and the backing materials were dipped directly into the solution.

4. Photographs

The photographs used in the collodion calibration studies and the applied studies were obtained from the Getty Conservation Institute (GCI). Seventeen albumen-coated photographs, eighteen gelatin-coated photographs and twenty-three collodion-coated photographs were selected at random from these categories of photographs in the extensive GCI collection. Each photograph had been analyzed previously and the organic binder had been identified.

5. Backing Materials

Three different backing materials were tested to determine which would provide the most uniform coating. In order to simulate photographs most closely paper was the preferred backing, but additional materials were used in an effort to obtain the most consistent coating over the entire sample. Sections of paper, Strathmore series 500 paper with a thickness of 0.13 mm, were cut into approximately 11-cm x 9-cm squares and used to prepare the standards. Two circular silicon wafers with a diameter of 10 cm and a thickness of 0.48 mm were also coated. Finally, a sheet of polyethylene with a thickness of 0.19 mm was cut into approximately 5-cm x 7-cm squares and coated.
The gelatin and collodion standards were prepared only on the Strathmore series 500 paper because the other two backing materials proved to be more difficult to work with when coated with albumen.

B. Preparation of Standards

Each of the standards produced using one of the methods outlined below was stored in a Gelman filter holder.

1. Albumen Standard Preparation
   a. Paper

Initially, a section of the Strathmore series 500 paper was secured to a thin Plexiglas plate using transparent tape. A Plexiglas box was filled with an albumen solution and the plate holding the paper was submerged in the solution for a specific amount of time ranging from 5 to 90 seconds depending on the sample that was being prepared. The Plexiglas plate and paper were then removed from the box and placed flat on the bench.

Two methods of drying were tried over the course of preparing samples with a paper backing. First, a Bio-Rad Model 785 vacuum blotter was used in which a vacuum system pulls air through the sample to dry it. With this method, the paper sample was removed from the Plexiglas plate after dipping and was placed directly on the top surface of the blotter which was covered except for the section supporting the sample. The second method was to allow the samples to air dry for more than a week. Each sample was placed on a flat, dry surface such as a cutting board or the laboratory bench. The samples were taped or pinned down to the surface to minimize the curling of the paper. It was important to properly secure the paper because curling created a pool of the albumen
solution and a very uneven coating. Once the samples were completely dry, the samples that were taped down were cut out so that all of the transparent tape was removed from the sample.

Due to difficulties in removing the albumen-coated samples from the Plexiglas plate and because of significant pooling found on the dipped samples, an alternative method of applying the albumen solution was explored. The albumen was applied by rolling it on with a two-inch sponge roller. The roller was soaked in the albumen solution, and, while the paper was taped or pinned down to a cutting board, the solution was rolled onto the paper. Each piece of paper was rolled three times in perpendicular directions in an attempt to create an even layer on the paper. The paper was then allowed to dry flat with either the tape or the pins holding the paper in place.

b. Silicon

For the silicon backing, a silicon wafer was taped to a Plexiglas plate and dipped into the albumen solution in the Plexiglas box for 90 seconds. Once the plate was pulled from the Plexiglas box, the silicon wafer was removed from the Plexiglas plate and allowed to dry flat on the bench top.

c. Polyethylene

Pieces of very thin polyethylene plastic were cut and an albumen solution was rolled on to them. The samples were allowed to dry flat on a cutting board. The polyethylene sheet did not need to be taped or pinned down in order to remain flat.
2. Gelatin

Initially, gelatin samples were created by rolling the material with a sponge roller in a fashion similar to that used to apply the albumen. When rolled out the gelatin coating had air bubbles in it so, subsequent samples were created by spreading a few drops of gelatin over the sample paper with the flat side of a knife. This spreading technique was found to create as uniform a coating as when using the roller but without the air bubbles.

3. Collodion

For the collodion samples two pieces of paper were taped back-to-back with transparent tape. They were then submerged vertically into a beaker of collodion solution using tweezers for 5 seconds and then removed. If a second dip followed the sample was turned over and dipped upside down for an additional 5 seconds. Although the sample was completely submerged the collodion solution ran down the paper when it was removed from the liquid so dipping the sample a second time while upside down helped to even out the coating.

The collodion standards prepared from photographs were made by cutting out small sections from collodion-coated photographs in areas that would not disrupt the main image. Each section was less than 0.5 cm by 0.5 cm.

C. ATR-FTIR Measurements

1. Principles

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectrometry utilizes the internal reflectance of an infrared beam within an ATR crystal.
The IR beam is directed up through an ATR crystal into the material through a series of mirrors and then bounces back down to go on to the detector (see Fig. 3).

![Partial image with text](image)

**Figure 3.** Sample in contact with ATR crystal (16)

Total internal reflectance occurs when the refractive index \(n_1\) in Fig. 4 of the ATR crystal is greater than the refractive index \(n_2\) in Fig. 4 of the adjacent material (17). This creates an evanescent wave that penetrates some distance into the sample (see Fig. 4).

![Complete image with text](image)

**Figure 4.** Evanescent wave penetrating a distance \(\Lambda\) into a sample with a lower refractive index than the ATR crystal (18)
ATR crystals come in a variety of materials including diamond, zinc selenide, and germanium and can be found in a variety of attachments from slide-on for an FTIR microscope to multi-bounce for the FTIR. Diamond and zinc selenide ATR crystals were used in this study; each has a refractive index of 2.4, while the refractive index of the analyzed samples was much smaller. The depth of penetration is dependent on many factors, including the crystal material, the angle of incidence and the radiation wavelength. The reported depth of penetration for the ZnSe and diamond crystals is approximately 2.4 µm at a 45° angle of incidence (19). Depending on the sample, various wavelengths of the evanescent wave will be absorbed by the material creating the bands seen in the corresponding FTIR spectrum (20). Since the spectrum depends on the energy transfer between the ATR crystal and the sample, the sample is pressed tightly against the crystal (17). This method enables the non-destructive analysis of thin layers of solid samples, along with the analysis of powders, liquids, and pastes. It is ideal for the analysis of photographs where non-destructive measurements are preferred.

FTIR spectral bands created from scanning a sample correspond to the vibrational modes of the molecules present. For example, the band chosen to represent the albumen layer was the amide I band at 1642 cm\(^{-1}\). The amide I band is from the C=O (carbonyl) stretch with a small amount of influence from the N-H in-plane bending (see Fig. 5a). The standard carbonyl bond frequency, normally 1715 cm\(^{-1}\), has been shifted to about ~1650 cm\(^{-1}\) (or 1642 cm\(^{-1}\) in our case) due to three different effects: the electronegativity of the nitrogen atom, resonance within the amide bond structure, and hydrogen bonding. The electronegativity of the nitrogen atom will raise the carbonyl bond frequency. This is countered by the resonance structures of the molecule (Figure 5a). The lone pair of
electrons on the nitrogen will give a resonance structure that increases the single bond character of the carbonyl which decreases the carbonyl bond frequency. Intra- and intermolecular hydrogen bonding can form a very strong attraction between the N-H and the oxygen, greatly lowering the carbonyl bond frequency. The net result of these three effects is a lowering of the carbonyl bond frequency to around 1650 cm$^{-1}$. Proteins are secondary amides so the presence of the amide II band at about 1550 cm$^{-1}$ can be seen in all of the albumen and gelatin spectra (see Fig. 6, 7 and Table 1). The amide II band is very distinctive and comes from a combination of C-N stretching and the N-H in-plane bending (see Fig. 5b) (21).

Figure 5. (a) Amide I - carbonyl stretch of the amide bond and resonance of the amide (b) Amide II - C-N stretching and N-H in-plane bending
Figure 6. ATR-FTIR spectrum of albumen with amide bands I and II

Figure 7. ATR-FTIR spectrum of gelatin with amide bands I and II
Table 1. Amide Vibrational Modes and Corresponding Absorption Bands of Albumen and Gelatin

<table>
<thead>
<tr>
<th>Vibrational Modes</th>
<th>Absorption band (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Albumen</td>
</tr>
<tr>
<td>C=O stretch</td>
<td>1642</td>
</tr>
<tr>
<td>C-N stretch and N-H in-plane bending</td>
<td>1530</td>
</tr>
</tbody>
</table>

Collodion is a solution of cellulose nitrate (see Fig. 8) and the absorption band at 1634 cm⁻¹ is the anti-symmetric stretch of the nitrate groups (R-O-NO₂). This is a strong, distinctive IR band. The nitrate group is about 70 wavenumbers higher than the nitro group (N=O) which is usually seen around 1565 cm⁻¹. Since the nitro group has a similar structure to the carbonyl, it stretches and bends in a similar fashion. The absorption bands at 1273 cm⁻¹, 996 cm⁻¹ and 826 cm⁻¹ can also be attributed to the cellulose nitrate of the collodion solution (see Fig. 9 and Table 2).

Figure 8. Structure of cellulose nitrate (22)
Figure 9. ATR-FTIR spectrum of dried collodion

Table 2. Vibrational Modes and the Corresponding Absorption Bands for Collodion

<table>
<thead>
<tr>
<th>Vibration Modes</th>
<th>Absorption band (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>asymmetric NO₂ stretch</td>
<td>1630</td>
</tr>
<tr>
<td>symmetric NO₂ stretch</td>
<td>1273</td>
</tr>
<tr>
<td>cellulose</td>
<td>996</td>
</tr>
<tr>
<td>NO₂ stretch</td>
<td>826</td>
</tr>
</tbody>
</table>

Figure 10 shows an ATR-FTIR spectrum of the paper backing used for the albumen and gelatin standards. The major cellulose absorption at 1028 cm⁻¹ can be seen in many of the albumen and gelatin samples with a paper backing.
2. Instrumentation

Two FTIR spectrometers were used to analyze samples in this work. The majority of the results were made using a Varian Excalibur spectrometer with a PIKE Attenuated Total Reflectance (ATR) attachment (see Fig. 11) and an A2 Sens-IR spectrometer (see Fig. 12). Thirty-two scans were collected for each spectrum with a resolution of 4 cm\(^{-1}\), a sensitivity of 1 and a scan range of 4000-750 cm\(^{-1}\). The PIKE ATR utilizes a ZnSe crystal and with a press to maintain constant contact with the sample while the Sens-IR utilizes a diamond crystal and a press.
Figure 11. (a) Varian Excalibur spectrophotometer (b) PIKE ATR attachment with press

Figure 12. Sens-IR spectrometer at the GCI (photo by Dusan Stulik)
Figure 13. FTIR spectra of albumen sample 11a analyzed using the Varian FTIR and the Sens-IR

Typically, each sample in this study was analyzed using both the Varian FTIR and the Sens-IR instruments. As shown in Figure 13, the spectrum of albumen sample 11a taken using the Varian FTIR is very similar to the spectrum of this same sample taken with the Sens-IR.

3. Quantitative Analysis

a. Coating Thickness of Standards

In order to determine the thickness of the coating on each sample prepared with a paper backing, the surface density of the paper ($\rho_p$), in g/cm$^2$, was first determined. The mass of a piece of paper ($m_p$) with measured area $A$ was determined. The surface density was then calculated as

$$\rho_p = \frac{m_p}{A}$$
After the paper was coated and had completely dried it was cut to the desired size (A’) and reweighed to yield the mass of the coated paper (m_{cp}). The mass of the coating (m_{c}) was obtained by subtracting the paper mass (m_{p}).

\[ m_{c} = m_{cp} - m_{p} = m_{cp} - A'\rho_p \]

The coating thickness (\( \rho_c \)), expressed as a surface density in units of \( \mu g/cm^2 \), was then calculated as

\[ \rho_c = \frac{m_c}{A'} \]

b. Spectral Peak Areas and Peak Heights

FTIR peak areas and peak heights were determined using Win-IR Pro software. Generally the amide I and amide II peaks were positioned on a large shoulder due to IR absorption by the paper backing (see Fig. 14). This caused the amide peak areas to fluctuate significantly and inconsistently. Ultimately the peak height of the carbonyl peak of the albumen or gelatin coating was divided by the peak height of the dominant cellulose peak to provide a relative peak height for the amide I band. This resulted in much more reproducible and consistent measurements for the albumen and gelatin standards.
Figure 14. Expected shoulder under the amide I and II absorption bands of albumen

D. Digital Microscopy

A KH-3000 Hirox digital microscope with a MX-5040RX zoom lens (Fig. 15) was used to measure the thickness of the collodion layer on the GCI photographs at 400X magnification. The digital microscope and accompanying software had been calibrated using a standard microscope slide supplied by the manufacturer. The samples were held in place with a mini vice and the edge of each photograph was analyzed. The thickness of the collodion layer was determined using the measurement tool of the software.
E. Scanning Electron Microscopy

A cross section of one of the collodion photograph samples was analyzed using a Joel SEM 5900LV scanning electron microscope (SEM). This cross section was placed in a small metal vice, which was placed directly into the SEM. An image of the layers was taken utilizing the microscope at low vacuum mode and at a low acceleration voltage. The thickness of the collodion layer was calculated by the instrument at several points along the edge of the paper. Magnification calibration of the Joel SEM 5900LV system is performed per the service contract every 6 months using a certified magnification reference standard. The standard is an MRS-3XY traceable standard from Geller Micro-analytical Lab.
III. Results and Discussion

A. Albumen Studies

In order to prepare and analyze useful standards a great many variables were considered. Most importantly non-uniformity of the albumen coating and fluctuations of the peak area due to variations in the background or pressure applied can result in inconsistent results. All of these issues were addressed so that a meaningful calibration curve could be obtained.

The initial solution of albumen was diluted with water to create four solutions of varying concentrations of albumen. It was expected that the different concentrations would result in differing thicknesses of albumen on the paper. However, each concentration produced such a wide range of albumen thickness that no significant difference between the solutions could be detected. In addition, increasing the dip time did not necessarily create a thicker coating. Although the coatings seemed to have a more consistent thickness across each backing surface when coated with the roller versus dipping them, there was still not enough uniformity in the thickness to create a large sample area for use as a standard.

The drying method also had a significant effect on the thickness of the coating across a sample. In many cases significant albumen pooling occurred during the drying phase. When the vacuum blotter was utilized to dry the samples more rapidly the house vacuum was strong enough to pull the albumen coating into and in some cases through the paper. When the samples that had been dried using the vacuum blotter were analyzed by ATR-FTIR, little or no albumen was found on the surface of the paper (see Fig. 16).
By placing the sample only partially over the drying area some of the albumen remained on top of the paper, but it was unevenly distributed. While the vacuum blotter decreased the drying time, these additional problems rendered this approach ineffective. Eventually, all samples were allowed to air dry in a horizontal position.

![Amide I and II should appear between 1700 and 1500 cm⁻¹](image)

Figure 16. No amide peaks were observed for test sample #4 dried using the vacuum blotter

Samples that were dipped in the albumen solution had to be removed from the Plexiglas plate prior to drying. Removal of the samples from the plate allowed the paper to buckle and create areas where the albumen could pool. In addition, the tape holding the sample to the Plexiglas often would not stick to the drying board and some of the samples curled badly during drying. Samples prepared using the roller method were either taped or pinned down to a cutting board prior to rolling in order to keep the sample attached to the board during drying. This eliminated the curling that produced low spots on the paper where the albumen pooled. It was therefore determined that the most efficient way to create the samples was to apply the coating by rolling and then allow
them to dry flat. This did not eliminate the uneven coating over the entire sample, but it did eliminate the more extreme coating issues of pooling. Rolling the samples also required less of the coating material than did dipping the sample.

Drops of blue food coloring were also added to the albumen solution used to coat some samples. This was done to aid in visualizing the coating. However, it was found that the visibility of these very thin coatings was not significantly improved. The food dye did assist in identifying areas where the coating had pooled.

The problems encountered with preparing coatings on paper prompted consideration of other backing materials. Silicon, in the form of a pure silicon wafer, and a thin sheet of polyethylene were tried as backing material. The coating layer on both the silicon wafers and the polyethylene was uneven, and when the albumen solution dried the coating cracked and flaked off. Neither material was considered further as a replacement for the paper backing.

At first an attempt was made to create samples that were 5.08 cm by 5.08 cm. Samples of this size always displayed a very uneven coating thickness so they were cut into a smaller size by removing the more extreme areas of the coating. The sample was then weighed, measured, and scanned again. Each sample was analyzed at four different locations and an average peak area was determined (see Fig. 17). However, the amide peak areas varied considerably for the four points and no satisfactory calibration curve was obtained (see Fig. 18). In order to reduce the unevenness in the coating, samples measuring 0.5 cm by 0.5 cm or smaller were cut, weighed, and scanned. These much small samples were analyzed at only one location. Regardless of how the albumen
coating was applied, the large variation in the coating thickness across the larger area always resulted in a significant range of coating thickness in the smaller-sized samples.

Figure 17. Amide I peak area (in blue) determined by Win-IR Pro software for an albumen standard.
It quickly became apparent that the amount of pressure applied to each sample in order to maintain contact with the ATR crystal had a noticeable effect on the peak area. The more pressure that was placed on a given samples the larger the peak. Because neither the Sens-IR nor the Varian spectrometer with PIKE ATR has a calibrated press it was impossible to determine the ideal pressure. However, both instruments had a maximum pressure that could be applied without damaging the sample or the ATR crystals. This pressure was utilized each time in order to minimize the variation in the peak area due to pressure differences.
Initially, the combined area of the amide I and II peaks was calculated for each smaller-sized sample. This approach did not yield consistent results, probably due to inadequate compensation for the substantial and sharply varying baseline. Subsequently, each peak was then analyzed separately. This resulted in rather widely scattered data and calibration curves that generally had a significant intercept value regardless of which amide peak area was used (see Fig. 19). Next, the peak height of amide I was determined and these values were used to construct a calibration curve (see Fig. 20). This did not significantly decrease the scatter of the data or the intercept value, again presumably because of inadequate compensation for the baseline caused by the signals from the paper backing (see Fig. 10).

In order to properly allow for the cellulose contribution to the baseline of the amide peak, the peak height of amide I was divided by the peak height of the 1028 cm⁻¹ cellulose peak and plotted against the albumen thickness. The resulting calibration curve displayed much less scatter in the data and a significantly reduced intercept value (see Fig. 21). The data used to construct this calibration curve are shown in Table 3. Figure 22 shows the final set of albumen standards used for this calibration and Figures 23-27 show the ATR-FTIR spectra of these albumen standards obtained with the Varian spectrometer.
Figure 19. Amide I peak area versus albumen thickness for small paper-backed samples

\[
y = 1.20E-03x + 8.56E-01 \\
R^2 = 6.78E-01
\]

Figure 20. Amide I peak height versus albumen thickness for small paper-backed samples

\[
y = 1.75E-05x + 8.23E-03 \\
R^2 = 7.77E-01
\]
Figure 21. Albumen calibration curve based on the 1642 cm\(^{-1}\) peak height/1028 cm\(^{-1}\) peak height ratio versus albumen thickness.

Table 3. Albumen Calibration Curve Data

<table>
<thead>
<tr>
<th>Standard</th>
<th>Albumen thickness* (µg/cm(^2))</th>
<th>1642 cm(^{-1}) peak ht/1028 cm(^{-1}) peak ht</th>
</tr>
</thead>
<tbody>
<tr>
<td>29b</td>
<td>146</td>
<td>0.12</td>
</tr>
<tr>
<td>29a</td>
<td>330</td>
<td>0.20</td>
</tr>
<tr>
<td>36</td>
<td>1200</td>
<td>0.48</td>
</tr>
<tr>
<td>15c</td>
<td>3240</td>
<td>1.17</td>
</tr>
<tr>
<td>11a</td>
<td>4518</td>
<td>1.44</td>
</tr>
</tbody>
</table>

*All thicknesses have an uncertainty of ±3%.
Figure 22. Final set of albumen standards

Figure 23. ATR-FTIR spectrum of albumen standard 29b
Figure 24. ATR-FTIR spectrum of albumen standard 29a

Figure 25. ATR-FTIR spectrum of albumen standard 36
Figure 26. ATR-FTIR spectrum of albumen standard 15c

Figure 27. ATR-FTIR spectrum of albumen standard 11a
B. Gelatin Studies

Once the best method for creating, sizing and analyzing the albumen samples was determined, gelatin samples were created in a similar fashion. The gelatin was rolled or spread onto 5-cm by 5-cm pieces of paper and allowed to dry flat. Once the samples were dry they were cut to smaller samples. There was not as much pooling as with the albumen samples, probably because the gelatin coating dried more rapidly. However, the coating was still not as consistent across the larger area as it was over a 0.5-cm by 0.5-cm sample. As was the case with the preparation of the albumen samples, the large variation in coating thickness across the larger area resulted in a significant range of coating thicknesses in the smaller-sized samples.

Like the albumen samples, the amide I peak area data did not give a linear calibration curve passing through zero. The same analytical method was used on the gelatin samples as was used on the albumen samples. For each sample, a ratio of the peak height of amide I (in this case 1632 cm\(^{-1}\)) and the peak height for the cellulose of the paper (1028 cm\(^{-1}\)) was determined and plotted versus the gelatin thickness (see Fig. 28 and Table 4).
Figure 28. Gelatin calibration curve based on the 1632 cm\(^{-1}\) peak height/1028 cm\(^{-1}\) peak height ratio versus gelatin thickness

Table 4. Gelatin Calibration Curve Data

<table>
<thead>
<tr>
<th>Standard</th>
<th>Gelatin thickness* (µg/ cm(^2))</th>
<th>1632 cm(^{-1}) peak ht/1028 cm(^{-1}) peak ht</th>
</tr>
</thead>
<tbody>
<tr>
<td>53m</td>
<td>2460</td>
<td>0.60</td>
</tr>
<tr>
<td>57m</td>
<td>1850</td>
<td>0.46</td>
</tr>
<tr>
<td>67d-2</td>
<td>3600</td>
<td>1.15</td>
</tr>
<tr>
<td>67b</td>
<td>5400</td>
<td>1.43</td>
</tr>
<tr>
<td>65f</td>
<td>7060</td>
<td>1.95</td>
</tr>
</tbody>
</table>

*All thicknesses have an uncertainty of ±3%.
The gelatin standards used for the final calibration curve were stored in labeled containers (see Fig. 29). Figures 30-34 show the ATR-FTIR spectra of the gelatin standards obtained with the Varian spectrometer.

![Figure 29. Final set of gelatin standards](image)

![Figure 30. ATR-FTIR spectrum of gelatin sample 53m](image)
Figure 31. ATR-FTIR spectrum of gelatin standard 57m

Figure 32. ATR-FTIR spectrum of gelatin standard 67d-2
Figure 33. ATR-FTIR spectrum of gelatin standard 67b

Figure 34. ATR-FTIR spectrum of gelatin standard 65f
C. Collodion Studies

An attempt was made to prepare samples collodion samples by dipping. Two pieces of paper were taped back-to-back and then dipped in a collodion solution. The paper pieces were removed from the solution and then cut apart and allowed to dry flat. The samples were then cut into small 0.5-cm by 0.5-cm squares. The collodion dried very quickly and this seemed to create a much more uniform coating on the samples compared to that found for gelatin and albumen. Each of the samples was analyzed using ATR-FTIR and the height of each absorption peak at 1635 cm\(^{-1}\) was determined. A plot of the peak height versus the collodion thickness (µg/cm\(^{2}\)) was made (see Fig. 35). Since nitrocellulose has significant IR absorption in the region of the cellulose peak at 1028 cm\(^{-1}\), any IR signal from the paper backing is significantly altered. Therefore, a ratio of the collodion peak height to that of the paper at 1028 cm\(^{-1}\) could not be used. As shown in Figure 35, the collodion peak height did not vary significantly from sample to sample. This, along with the absence of any clear signal from the paper backing, suggests that the coating on the surface of the paper was thicker than the depth of penetration of the evanescent wave. Similar results were obtained regardless of how the collodion was applied to the backing; the 1635 cm\(^{-1}\) peak area did not show any consistent correlation with coating thickness.
In order to prepare a suitable set of collodion calibration standards, a different approach was tried in which samples obtained from various collodion photographs were used. Several collodion photographs were obtained from the GCI collection and a small section was cut out of each photograph in a location that would not disrupt the main image (see Fig. 36, 37, 40, 41, 44, 45, 48, 49, 52, 53, 56 and 57). Each of the samples was analyzed using the Varian spectrometer (see Fig. 38, 42, 46, 50, 54, and 58). Each sample was then analyzed using a digital microscope that was calibrated to a magnification of 400x. Each photograph section was placed in a small metal vice with the cross section of the sample facing the microscope. A digital image of the cross section was then recorded at a magnification of 400x. The thickness of the collodion layer (L1 noted on the digital images) was then measured by the software of the digital microscope (see Table 5). Figures 39, 43, 47, 51, 55 and 59 show the digital images of these photograph cross sections. Layer A is the metal vice holding that the photograph,
layer B is the paper support of the photograph and layer C is the collodion layer on the surface of the photograph.

Table 5. Collodion Layer Thicknesses on Photograph Samples Determined by Digital Microscopy

<table>
<thead>
<tr>
<th>Photograph</th>
<th>Collodion thickness (µm)</th>
<th>Peak height 1634 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS3253</td>
<td>4.45</td>
<td>0.221</td>
</tr>
<tr>
<td>DS0347</td>
<td>10.6</td>
<td>0.227</td>
</tr>
<tr>
<td>DS2743</td>
<td>13.9</td>
<td>0.170</td>
</tr>
<tr>
<td>DS0225</td>
<td>15.6</td>
<td>0.247</td>
</tr>
<tr>
<td>DS0231</td>
<td>16.7</td>
<td>0.328</td>
</tr>
<tr>
<td>DS4009</td>
<td>20.0</td>
<td>0.372</td>
</tr>
</tbody>
</table>

Figure 36. Collodion photograph DS3253 with sample removed

Figure 37. Sample from collodion photograph DS3253
Figure 38. ATR-FTIR spectrum of sample from collodion photograph DS3253

Figure 39. Digital image of cross section of collodion photograph DS3253
Figure 40. Collodion photograph DS2743 with removed

Figure 41. Sample from collodion photograph DS2743

Figure 42. ATR-FTIR spectrum of sample from collodion photograph DS2743
Figure 43. Digital image of cross section of collodion photograph DS2743

Figure 44. Collodion photograph DS0347 with sample removed
Figure 45. Sample from collodion photograph DS0347

Figure 46. ATR-FTIR spectrum of sample from collodion photograph DS0347
Figure 47. Digital image of cross section of collodion photograph DS0347

Figure 48. Collodion photograph DS0225 with sample removed
Figure 49. Sample from collodion photograph DS0225

Figure 50. ATR-FTIR spectrum of sample from collodion photograph DS0225
Figure 51. Digital image of cross section of collodion photograph DS0225

Figure 52. Collodion photograph DS0231 with sample removed

Figure 53. Sample from collodion photograph DS0231
Figure 54. ATR-FTIR spectrum of sample from collodion photograph DS0231

Figure 55. Digital image of cross section of collodion photograph DS0231
Figure 56. Collodion photograph DS0231 with sample removed

Figure 57. Sample from collodion photograph DS4009
Figure 58. ATR-FTIR spectrum of sample from collodion photograph DS4009

Figure 59. Digital image of cross section of collodion photograph DS4009
All of the measured collodion thicknesses on the photograph samples appear to exceed the expected penetration depth of the evanescent wave. The absence of any clear IR signal from the paper backing confirms that this is the case. In Figure 60, the spectrum of neat collodion and the spectrum of a collodion photograph have absorption bands that match. There are no addition absorption bands in the collodion photograph that correspond with the paper backing.

The photograph with the thinnest collodion layer (DS3253) was then analyzed on a scanning electron microscope (SEM). A sample of DS3253 was placed vertically in a small vice. An image of the photograph cross section was obtained using the SEM (see figure below).

Figure 60. ATR-FTIR spectrum of neat collodion (blue) and of a collodion photograph (red)
Fig. 61. Layer A is the paper support and layer B is the collodion layer on the surface of the photograph. The SEM instrument calculated the collodion thickness in three locations, as noted by the red lines in Figure 61). At these locations the collodion thickness is 0.002 in (5 µm). As shown by the blue arrows in Figure 61 there are also thicker areas of the collodion layer. Using the SEM measuring scale noted on the image, it is estimated that the thickest section of the collodion layer is 10 µm.

Figure 61. SEM image of the cross section of photograph DS3253 with the measured thickness of the collodion layer (see text for details)

Since the thickness of the collodion layer on typical photographs appears to exceed the penetration depth of the ATR-FTIR evanescent wave, it is not possible to use ATR-FTIR spectrometry to measure quantitative differences in the thickness of the collodion layer among photographs.
D. Applied Studies

The calibration curves initially created using the albumen and the gelatin standards were from spectra created using the Varian spectrometer with a PIKE Attenuated Total Reflectance attachment. Each of the standards was also scanned using the A2 Sens-IR spectrometer and a second calibration curve was created. These calibration curves are shown in Figure 62. The slight differences in the slopes and intercepts reflect differences in the instrumentation and experimental uncertainty and are expected. In a similar way, the final set of gelatin standards was measured using both instruments and calibration curves were prepared (see Fig. 63).

![Figure 62. Comparison of albumen calibration curves using final set of albumen standards.](#)
Figure 63. Comparison of gelatin calibration curves using final set of gelatin standards

In order to test the universal application of these standards a selection of photographs from the Getty Conservation Institute were analyzed for albumen and gelatin using both instruments. The same location on a photograph was scanned with both instruments. The ratio of the peak heights for absorption bands at 1642 cm\(^{-1}\) and 1028 cm\(^{-1}\) was calculated for each spectrum and used with the appropriate calibration curve to determine the albumen or gelatin thickness. The albumen photographs and accompanying spectra are shown in Appendix A, and the gelatin photographs and accompanying spectra are shown in Appendix B. The results for the albumen measurements are shown in Table 6 and those for the gelatin measurements are given in Table 7.
Table 6. Calculated Albumen Thicknesses for Photographs Analyzed

<table>
<thead>
<tr>
<th>GCI Photograph</th>
<th>Albumen thickness* ((\mu g/cm^2)) using Sens-IR</th>
<th>Albumen thickness* ((\mu g/cm^2)) using Varian FTIR</th>
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</thead>
<tbody>
<tr>
<td>DS0264</td>
<td>1940</td>
<td>2110</td>
</tr>
<tr>
<td>DS0598</td>
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<td>4300</td>
</tr>
<tr>
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<td>2600</td>
</tr>
<tr>
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<td>3660</td>
</tr>
<tr>
<td>DS1527</td>
<td>3500</td>
<td>3430</td>
</tr>
<tr>
<td>DS1744</td>
<td>3930</td>
<td>4010</td>
</tr>
<tr>
<td>DS1757</td>
<td>4000</td>
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<tr>
<td>DS1797</td>
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<td>1280</td>
</tr>
<tr>
<td>DS2787</td>
<td>2010</td>
<td>2120</td>
</tr>
<tr>
<td>DS2804</td>
<td>4110</td>
<td>4340</td>
</tr>
<tr>
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</tr>
<tr>
<td>DS3193</td>
<td>1730</td>
<td>1890</td>
</tr>
</tbody>
</table>

* All calculated thicknesses have an uncertainty of ±3-5%.
Table 7. Calculated Gelatin Thicknesses for Photographs Analyzed

<table>
<thead>
<tr>
<th>GCI Photograph</th>
<th>Gelatin thickness* (µg/cm²) using Sens-IR</th>
<th>Gelatin thickness* (µg/cm²) using Varian FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS1924</td>
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<td>4700</td>
</tr>
<tr>
<td>DS1996</td>
<td>8730</td>
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<tr>
<td>DS2093</td>
<td>7790</td>
<td>6560</td>
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<tr>
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<td>6660</td>
</tr>
<tr>
<td>DS2093</td>
<td>7790</td>
<td>6560</td>
</tr>
<tr>
<td>DS2097</td>
<td>4180</td>
<td>4300</td>
</tr>
<tr>
<td>DS2101</td>
<td>6600</td>
<td>5590</td>
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<tr>
<td>DS2103</td>
<td>7850</td>
<td>6450</td>
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<td>DS2531</td>
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<td>4120</td>
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<tr>
<td>DS2091</td>
<td>6810</td>
<td>5360</td>
</tr>
<tr>
<td>DS1929</td>
<td>5990</td>
<td>5500</td>
</tr>
</tbody>
</table>

* All calculated thicknesses have an uncertainty of ±3-5%.

A comparison of the measured albumen thicknesses for a given photograph indicates reasonable agreement between the two instruments. A variation of less than 10% was noted. This suggests that the final set of albumen standards can be used to provide quantitative albumen thickness information that is more reliable than what is generally available to conservators from other means. Use of the two instruments produced differences less than 20% in the measured gelatin thickness.
E. Conclusions and Suggestions for Future Studies

In the course of this study, two sets of calibration standards were created. A set of five standards of albumen coated on paper was prepared. This set produced a reasonable calibration curve that can be used to analyze the thickness of the albumen layer on photographs. Similarly, five standards of gelatin coated on paper were prepared that resulted in a useful calibration curve for determining the thickness of a gelatin layer on photographs. It is expected that these standards can be used by any conservation laboratory that wishes to quantify the albumen or gelatin layer thickness using ATR-FTIR. Some variation in results from instrument to instrument can be expected because these measurements rely on factors which are difficult to control such as the pressure used contact the ATR crystal and sample.

An attempt was made to create a set of collodion standards, however, the thickness of the collodion layer on typical photographs and on standards that were prepared proved to be too thick to quantify by ATR-FTIR because it routinely exceeded the penetration depth of the evanescent wave of the ATR-FTIR.

There are published studies that indicate that the albumen thickness on photographs ranges from 8-10 µm which is greater than 5µm (the maximum depth of penetration expected for the evanescent wave)(9). However, the absorption band for the cellulose of the paper could be seen in the majority of the albumen and gelatin standard spectra, and the intensity of the peak height for the paper backing (cellulose) varied as expected (it decreased with increasing coating thickness) depending on the thickness of
the albumen or the gelatin coating. This strongly suggests that the albumen or gelatin had soaked into the paper backing during drying of the standards. The results of this study suggest that albumen thicknesses previously reported to be greater than 5 µm are not expected to refer to a layer deposited on top of the paper, or they may not be typical of albumen photographs.

It is recommended that additional studies should be done using a SEM or some other type of microscopy. A study of the penetration of albumen and gelatin into paper using fluorescent-labeled molecules would help elucidate the exact location of the coating applied to a paper backing. This might also permit a more precise determination of the linear thickness of these layers. A careful determination of the maximum penetration depth of the ATR-FTIR evanescent wave in the various coating materials would be useful. A larger scale survey of collodion photographs might determine if sufficiently thin collodion layers for quantitative ATR-FTIR measurements are present. If so, then the development of a working methodology for the preparation of collodion standards is needed. In addition, a methodology for preparing standards of the various organic coatings using spin coating techniques should be investigated. Finally, gelatin standards might be prepared on paper coated with a baryta layer (a layer of barium and strontium sulfates). Such standards should be of interest to conservators studying gelatin emulsion photographs since a baryta layer was typically used to brighten images in such photographs.
References


20. [http://www.pecsa.co.za/technical/tatrhatri.htm](http://www.pecsa.co.za/technical/tatrhatri.htm), accessed 2-16-11


22. [http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures---N/Nitrocellulose-Structure.htm](http://chemistry.about.com/od/factsstructures/ig/Chemical-Structures---N/Nitrocellulose-Structure.htm), accessed 6-8-12

Appendix A. Photographic Images and ATR-FTIR Spectra for Albumen Applied Study

Figure A1. Albumen photograph DS0264

Figure A2. ATR-FTIR spectra of albumen photograph DS0264
Figure A3. Albumen photograph DS0598

Figure A4. ATR-FTIR spectra of albumen photograph DS0598
Figure A5. Albumen photograph DS1022

Figure A6. ATR-FTIR spectra of albumen photograph DS1022
Figure A7. Albumen photograph DS1233

Figure A8. ATR-FTIR spectra of albumen photograph DS1233
Figure A9. Albumen photograph DS1527

Figure A10. ATR-FTIR spectra of albumen photograph DS1527
Figure A11. Albumen photograph DS1744

Figure A12. ATR-FTIR spectra of albumen photograph DS1744
Figure A13. Albumen photograph DS1757

Figure A14. ATR-FTIR spectra of albumen photograph DS1757
Figure A15. Albumen photograph DS1797

Figure A16. ATR-FTIR spectra of albumen photograph DS1797
Figure A17. Albumen photograph DS2787

Figure A18. ATR-FTIR spectra of albumen photograph DS2787
Figure A19. Albumen photograph DS2804

Figure A20. ATR-FTIR spectra of albumen photograph DS2804
Figure A21. Albumen photograph DS2963

Figure A22. ATR-FTIR spectra of albumen photograph DS2963
Figure A23. Albumen photograph DS3144

Figure A24. ATR-FTIR spectra of albumen photograph DS3144
Figure A25. Albumen photograph DS3176

Figure A26. ATR-FTIR spectra of albumen photograph DS3176
Figure A27. Albumen photograph DS3177

Figure A28. ATR-FTIR spectra of albumen photograph DS3177
Figure A29. Albumen photograph DS3193

Figure A30. ATR-FTIR spectra of albumen photograph DS3193
Appendix B. Photographic images and ATR-FTIR Spectra for Gelatin Applied Study

Figure B1. Gelatin photograph DS1924

Figure B2. ATR-FTIR spectra of gelatin photograph DS1924
Figure B3. Gelatin photograph DS1929

Figure B4. ATR-FTIR spectra of gelatin photograph DS1929
Figure B5. Gelatin photograph DS1996

Figure B6. ATR-FTIR spectra of gelatin photograph DS1996
Figure B7. Gelatin photograph DS2085

Figure B8. ATR-FTIR spectra of gelatin photograph DS2085
Figure B9. Gelatin photograph DS2087

Figure B10. ATR-FTIR spectra of gelatin photograph DS2087
Figure B11. Gelatin photograph DS2091

Figure B12. ATR-FTIR spectra of gelatin photograph DS2091
Figure B13. Gelatin photograph DS2093

Figure B14. ATR-FTIR spectra of gelatin photograph DS2093
Figure B15. Gelatin photograph DS2097

Figure B16. ATR-FTIR spectra of gelatin photograph DS2097
Figure B17. Gelatin photograph DS2101

Figure B18. ATR-FTIR spectra of gelatin photograph DS2101
Figure B19. Gelatin photograph DS2103

Figure B20. ATR-FTIR spectra of gelatin photograph DS2103
Figure B21. Gelatin photograph DS2525

Figure B22. ATR-FTIR spectra of gelatin photograph DS2525
Figure B23. Gelatin photograph DS2531

Figure B24. ATR-FTIR spectra of gelatin photograph DS2531
Figure B25. Gelatin photograph DS2535

Figure B26. ATR-FTIR spectra of gelatin photograph DS2535
Figure B27. Gelatin photograph DS2658

Figure B28. ATR-FTIR spectra of gelatin photograph DS2658
Figure B29. Gelatin photograph DS2094

Figure B30. ATR-FTIR spectra of gelatin photograph DS2094