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SPECULAR REFLECTION FTIR: A NON-CONTACT METHOD FOR ANALYZING COATINGS ON PHOTOGRAPHS AND OTHER CULTURAL MATERIALS

Arthur A. McClelland, Elena Bulat, Brenda Bernier, Erin L. Murphy

ABSTRACT

Cultural heritage objects present a special set of challenges to analyze chemically. Often micro-sampling or even contacting the object is not appropriate or deemed too risky for fragile surfaces. Fourier Transform Infrared (FTIR) spectroscopy is a commonly used analytical technique for organic compound identification, either in a micro-sampling or Attenuated Total Reflection (ATR) mode both of which inherently require some measure of contact with the sample.

Presented here is a case study of the use of specular reflection FTIR spectroscopy; an FTIR collection modality that allows positive chemical identifications in a *non-sampling* and *non-contact* way. Although this paper focuses on the case study of coatings on 19th century photographs, the specular reflection FTIR modality is applicable to surface coatings on any artifact where molecular composition identification is needed but micro-sampling or physical contact with the sample have been ruled out. The main limitation of the specular reflection modality has traditionally been the lack of specular reflection FTIR reference libraries. As a result, the analytical project presented here first required generation of a specular reflection FTIR spectral library for historical coating materials used on 19th century prints by creating modern reference samples. The project is a result of collaboration between conservators at the Weissman Preservation Center at Harvard Library and materials scientists at Harvard's Center for Nanoscale Systems to analyze original coatings on 19th century salted paper photographs in the collection of the Harvard University Archives.

1. INTRODUCTION

With cultural objects it is often desirable to identify the materials used in a completely non-destructive way. Specular reflection FTIR has the distinct advantage of being a totally non-contact and non-sampling method of chemical identification, but until recently this modality has not been widely used with cultural material. This is primarily due to the fact that few specular reflection FTIR spectral libraries have been developed. In addition to the lack of spectral libraries, interpretation of the spectra gathered in this mode requires consideration of the spectra as a holistic chemical signature rather than interpretation of single peaks as is more common in FTIR-ATR and transmission FTIR. Presented here is a case study of a non-destructive method for identifying single-component coatings on historical salted paper prints using specular reflection FTIR including the creation of a spectral library and a reliable method of data capture and interpretation. Although this case study focused on coatings on photographs, this modality may be used

to analyze any surface. Conservators and conservation scientists, therefore, may find additional applications for specular reflection FTIR within their own disciplines.

1.1. THE VALUE OF COATINGS ANALYSIS

Examining the physical elements of historic photographs can provide researchers with insights into their identification, attribution, and preservation as well as broader art history and cultural issues pertaining to the development of nineteenth-century visual communication. When applied

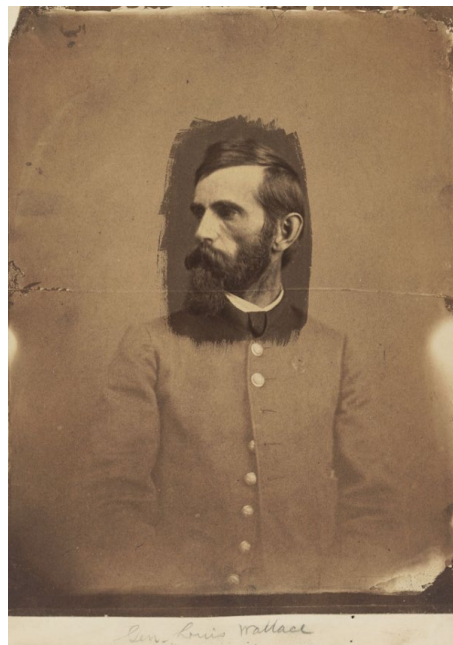


Figure. 1 A salt print portrait of General Louis Wallace, Lew Wallace, Author of Ben Hur, Harvard Fine Arts Library, Special Collections, 1861-1865. For unknown reasons, only the face in this print was coated. The image preservation properties of the coating are very clear in this example. The coating was positively identified as gum Arabic with the specular reflection FTIR library developed by the Weissman Preservation Center, 2018. Courtesy of Special Collections, Fine Arts Library, Harvard University

by the original photographer or studio, coatings are an integral part of a photograph and should be considered as part of the artist's intent and working method.

Since the introduction of the salted paper print in 1839 by William Henry Fox Talbot, photography has been a means of artistic expression, of documenting the world around us, and preserving visual memory. In an era where images are almost exclusively accessed on screens, historic photographs endure as complex three-dimensional objects made of layers of organic and inorganic materials. Because salted paper prints do not have a separate emulsion layer (the image-forming particles are distributed in the uppermost layers of the paper fibers) the photographs have a naturally matte appearance. This physical attribute of the salted paper print made it easy and often desirable for photographers to apply coatings, hand-coloring, or varnishes to their finished prints.

Nineteenth-century photography manuals and other publications (McCabe 2005; Pauli 2011; Reilly 2012; Waldthausen 2014) indicate that coating a salted paper print was a common practice among photographers. A thin coating with transparent materials such as waxes, proteins, polysaccharides, or resins was used individually or in mixes and served aesthetic function. A final transparent coating could dramatically change the appearance of a print as it filled in the tiny areas created by the paper fibers on the print surface. In this manner, the naturally matte surface of the salt print took on a rich, saturated appearance creating the illusion of a sharper image.

Based on the 1855 report on the "Fading of Photographs" by the Photographic Society of London, it is also clear that nineteenth-century photographers were aware that salted paper prints were sensitive to light, humidity, temperature, and pollutants and that a final coating could also offer significant protection against fading and other damage.ⁱ (Reilly 2012). An excellent example of the protective power of a surface coating can be seen in the portrait of General Louis Wallace from the Harvard Fine Arts Library (Figure 1). In this portrait, the photographer used gum Arabic to selectively coat only the image area of the face while leaving the remainder of the portrait uncoated. Why the photographer chose to only coat the face is unclear. The result however, following approximately 150 years of aging, is that the sitter's face is remarkably well-preserved while the rest of the photograph has faded significantly.

Although coatings were traditionally used for preservation of artifacts, often the coatings themselves have been found to deteriorate upon aging. (Figure 2). Issues such as cracking and discoloration, as seen in Figure 2, are due to a wide variety of reasons beginning with original application method and progressing through subsequent storage conditions and use. In addition to the art historical benefits of understanding coating materials, these preservation issues argue for the need to develop a non-invasive method for positive chemical identification of the historic coatings to aid in the best practices in



Figure. 2 A portrait [HUD 254.705 P (HUA)], from the Harvard University class albums showing severe cracking of the coating. Courtesy of Special Collections, Harvard University Archives

conservation treatments and preservation planning (McCabe 2005). Traditional techniques such as transmission FTIR or any of the mass spectroscopy techniques require removing a sample of the object of interest. The widely used attenuated total reflectance (ATR-FTIR) is a non-sampling method, but the contact of the ATR crystal to a delicate glossy surface has the inherent risk of leaving a noticeable mark on the photograph (See Figure 4).

1.2. SALT PRINT SURVEY at HARVARD UNIVERSITY

Starting in 2008, the Weissman Preservation Center at Harvard Library has undertaken a multiyear project seeking to enhance our understanding of salted paper prints and to ensure their long-term preservation. This comprehensive project encompasses an integrated approach to photograph preservation: survey, conservation treatment, housing and storage, cataloging, digitization, scientific analysis, and interpretation, with the goal of enhancing access to salted paper prints at Harvard University. Around fifteen thousand salted paper photographs were identified in twelve separate repositories. They include some of the earliest photographs ever taken and are among the most valuable photographs the University holds. There are early experimental photographs by Fox Talbot and his contemporaries from the Horblit collection at Houghton Library, “Imperial Portraits” by Mathew Brady, the Portrait Collection at The Fine Arts Library, class pictures by John Whipple at the Harvard University Archives and many others. The survey team, which included conservators, curators, and scientists, gathered significant data regarding process, format, size, paper thickness, color, mounting technique, and condition. This data both sharpens and

broadens the conservators' understanding of the physical and chemical nature of salt prints and will help in targeting preservation efforts. In addition, the information will contribute to our collective understanding of the history of early photography, a subject continually revisited by historians, curators, and collectors.

2. EXPERIMENTAL

Although visual examination is a first step when attempting to identify coatings, correct identification of coatings is a challenge to even a highly-trained eye (Waldthausen 2014). The use of mixtures of waxes or resins as coatings and very thinly applied layers barely perceptible to the human eye make it difficult to accurately identify the material used for a coating or perhaps even the presence of a coating. In addition, coated salt prints look very similar to many early albumen prints or salt prints that have additional paper sizing such as starch, gelatin or albumen. Since photographic process variations took place rapidly during the 1850s and the early 1860s, many photographs are hybrid approaches to achieving the desired aesthetic. Proper identification is important in order to accurately identify the images, to credit photographers with the kinds of processes they were using, and to make the best choices for their preservation. In light of these challenges, the survey team sought a more objective, analytical method of identifying coatings.

2.1. HARVARD UNIVERSITY ARCHIVES' SALTED PAPER PHOTOGRAPH COLLECTION

Most published resources on the history of photography cite the dates for the salted paper process from about 1840 until the mid-1850s, when albumen prints were introduced and rapidly gained popularity. However, the survey of salt prints in the Harvard collections indicates that dates are often dependent on geographical regions and photographer's preferences. In fact, some photographers in the collections used the salted paper process well into the middle of the 1860s when the albumen process gained popular commercial use.

During the survey, Harvard University Archives was identified as among the largest collections of salt prints in the University. The Archives houses 75 historic class albums dating from 1852 to 1864, as well as a large collection of loose prints which are duplicates or variants of the prints in the albums. These class albums contain salted paper prints produced annually over a period of 13 years by three prominent Boston photographers; John Adams Whipple, James Wallace Black, and

George Kendall Warren, all of whom used the process continuously until 1864, well into the albumen era. ('Preserving Collective Memory: Nineteenth- Century Harvard Class Books and Albums' 2015)

The Archives holds several albums from each year and as a result, the collection contains many identical images with known creation dates and provenances but with a variety of storage and use histories. The albums are various sizes (the largest album from 1863 contains 211 pages), and arrived in the collection from different sources, including families of Harvard graduates of the time. Each album is unique in that the photographs contained have been individually selected by the student. During the survey it was noted that while elements of the albums, such as cover style, size and choice of portraits may have varied between albums, most of the photographs had been coated. This homogeneity indicates that the photographs were likely coated before the albums were assembled for the individual student.

These annual class albums provide a glimpse into the technical evolution of the salt print process as practiced by some of Boston's pioneering photographers and became the springboard for analytical investigations by the survey team.

While the duplicate images with different use and storage histories would make an interesting case study into the different chemical degradation pathways of the coatings, the focus of this study was to develop a methodology to positively chemically identify the coatings in a non-sampling non-contact way.

2.2. INTRODUCTION TO FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

Fourier Transform Infrared (FTIR) spectroscopy is an analytical technique that can be used to make positive chemical identifications of materials by comparing the spectrum from an unknown sample to a reference library of spectra collected from known samples. FTIR can be performed in several different modes, the three most common modes being transmission, attenuated total reflection (ATR), and specular reflection.

Transmission FTIR requires infrared light to be completely transmitted through the specimen, which is not possible for many art objects. For transmission FTIR, a small sample is typically collected, ground to a powder, mixed with potassium bromide (KBr) and then pressed to form an

optical window for transmission of the infrared light. Transmission FTIR can also be done by pressing a small sample of the object of interest between two diamonds until it is thin enough to be transparent to infrared light. Drawbacks to this method include the need to destructively sample an object. Sampling is typically done at sites on the object with previous damage, but this invariably leads to question as to the validity of the sampled area in relation to the entire object. Transmission mode was the first FTIR technique developed and as a result most of the available reference libraries are of transmission FTIR spectra.

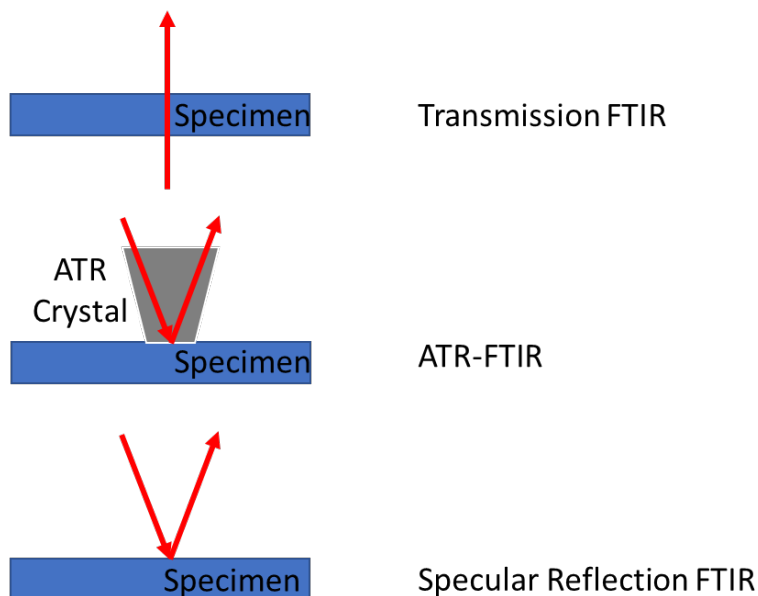


Figure. 3 Schematics of common FTIR sampling modalities. In transmission FTIR the specimen must be transparent to infrared light or a sample must be taken from the object of interest and thinned to the point of being transparent to infrared light. In attenuated total reflection (ATR-FTIR), an ATR crystal must come in contact with the specimen (or a sample from the object of interest) to optically couple infrared light from the crystal to the specimen and back to the detector. In specular reflection FTIR the specimen can be opaque to infrared light and nothing needs to physically contact the object of interest. The infrared light frequencies that are strongly absorbed by the molecular vibrations of the specimen are missing from the reflected infrared light and hence the chemical composition of the specimen can be deduced.

To mitigate the requirement that a specimen be infrared transparent or be destructively sampled Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy was developed. In ATR-FTIR an infrared transparent crystal is placed in contact with the specimen and the infrared light is sent in at an angle such that the light totally internally reflects from the interface between the specimen and the ATR crystal. An evanescent electric field penetrates approximately 500 nm into the sample interacting with the molecular vibrations of the topmost material. This requirement of optical coupling between the crystal and the specimen for the technique to work means that the ATR crystals must be in close physical contact with the object which may result in damage to the surface of the object. (Figure 4). For some artifacts, this physical contact may be well-tolerated while for others with very delicate surfaces, such as photographs, a non-contact method of instrumental analysis is preferred. ATR crystals can be as small as 120 microns, approximately the width of a human hair, but on a glossy surface the imprint

is still noticeable to the unaided human eye. Another advantage of ATR-FTIR is that the spectra can easily be mathematically corrected to match the transmission spectra in commercially available reference spectral libraries. There are also ATR-FTIR specific spectral libraries available commercially.

In specular reflection FTIR, the specimen is illuminated with broadband infrared light and the reflected light is collected. If a molecular vibration in the specimen absorbs a specific frequency of light strongly then that frequency will be missing in the reflected infrared light. Specular reflection does not require the specimen to be infrared transparent or need to physically contact the specimen. The peaks in specular reflection FTIR are far less distinct than in other FTIR modalities (Figure 4), leading to the wide spread perception that it was not as useful. This in turn discouraged researchers from developing specular reflection spectral reference libraries. While there was some interest in reflectance FTIR in the late 1980s (Baker 1989; Perron 1989) the technology was not mature enough yet and the idea largely fell into disuse. Specular reflection FTIR has been occasionally revisited (Cattaneo 2008; Rosi et al. 2011) but has not gained much use compared to ATR-FTIR. The broad overlapping bands with reststrahlen or derivative like spectral features seem to continually discourage researchers.

For projects where the chemical interpretation of individual peaks is needed, such as understanding the chemical pathway of degradation of a coating, the broad peaks in the specular reflection FTIR spectra certainly present interpretation challenges. For projects where the entire spectrum is simply compared to a reference library of spectra, the lack of individually resolved peaks is not such an issue as the overall shape of the specular reflection spectra still contains unique chemical information (Figure 6).

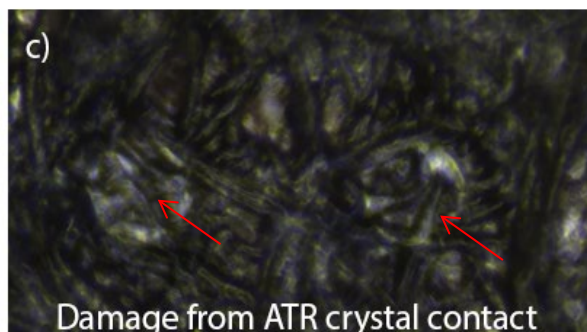
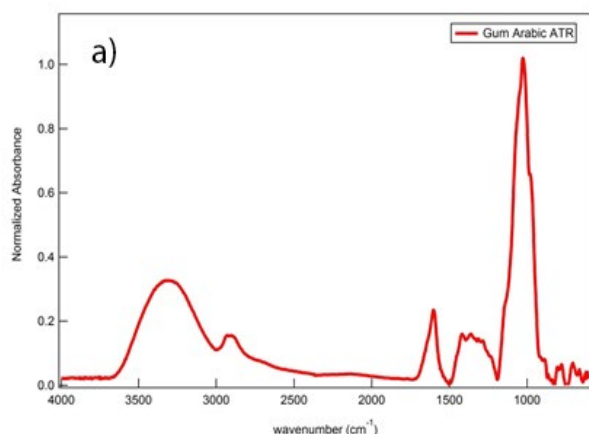
Hyperspectral reflectance imaging spectroscopy in the visible, near infrared, and short wave infrared spectral regions, which has been rapidly gaining popularity in art conservation, (Delaney and Loew 2018; Delaney, Ricciardi, et al. 2016; Delaney, Thoury, et al. 2016; Delaney et al. 2017; Delaney et al. 2010; Dooley et al. 2013; Favero et al. 2017; Grabowski et al. 2018; Mounier and Daniel 2015; Rebollo et al. 2013; Suzuki et al. 2018) has similar challenges of broad spectral shapes and a lack of a widely available commercial spectral reference libraries. One could argue the specular reflection FTIR presented here is a type of hyperspectral reflectance spectroscopy in the mid-infrared spectral region.

Mid-infrared fiber optic reflectance spectroscopy (FORS) is fundamentally the same idea to the specular reflection FTIR presented here just using a fiber optic cable to illuminate a specimen with infrared light and collect the reflected infrared light instead of a microscope. FORS has been applied to cultural heritage specimens (Ploeger et al. 2011; Ploeger, Scalarone, and Chiantore 2010; Poli et al. 2011). For three dimension works of art the flexibility of positioning the fiber optic seems wonderful. The quality of the spectrum that is collected though is highly dependent on the positioning of the mid infrared fiber optic probe though (Ploeger et al. 2011; Ploeger, Scalarone, and Chiantore 2010). The quality of the specular reflection FTIR from the salt prints examined in this project was also very sensitive to the focus of the microscope. The white light optical image obtained through the FTIR microscope allowed easy and repeatable positioning of the specimen at the optimal position for analysis.

Diffuse Reflectance Infrared Fourier Transform Infrared Spectroscopy (DRIFTS) is typically done in a sampling modality where a small amount of sample is removed from the object of interest and ground into a powder. The powder sample is then mixed with KBr powder and placed in a special accessory. The accessory is illuminated with broadband infrared light. The diffusely reflected light is collected by an integrating sphere and analyzed by the spectrometer. Recently handheld FTIR spectrometers able to collect diffusely reflected light have enabled an *in-situ* version of the technique (Steger et al. 2018; Wertz et al. 2018; Arrizabalaga et al. 2014; Arrizabalaga et al. 2015).

The Bruker Lumos FTIR microscope with specular reflection capability was available for use on this project at Harvard University's Center for Nanoscale systems. Specular reflection FTIR has the distinct advantage for cultural heritage objects of being a totally *non-contact* and *non-sampling* method of chemical identification. Spectra can be collected from multiple positions on an object ensuring that the data collected is representative of the chemistry of the object as a whole and local areas which appear different can also be selectively targeted for analysis. For these reasons, specular reflection FTIR was used for analyzing coatings on salt prints at Harvard University Archives.

ATR FTIR



Specular Reflection FTIR

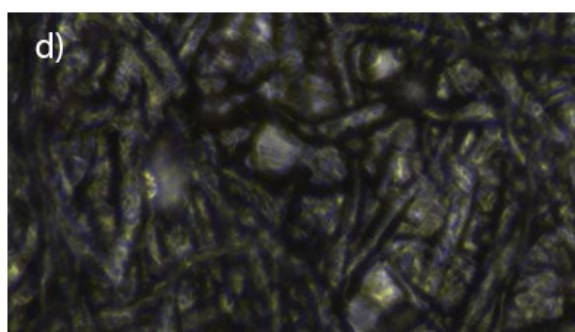
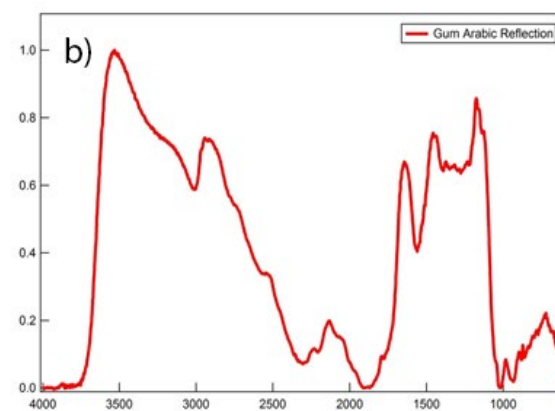


Figure. 4 Comparison of ATR-FTIR and specular reflection FTIR spectra and potential damage to the object. a) ATR-FTIR spectrum of gum Arabic coating on a modern salt print. b) Specular reflection FTIR spectrum from the same gum Arabic coating on a modern salt print. c) Damage marks (120 microns in diameter) left by the ATR crystal on the gum Arabic coated modern salt print. d) Area of gum Arabic coated modern salt print after specular reflection FTIR analysis.

2.3. PRODUCTION OF SAMPLES FOR REFERENCE LIBRARY

To analyze the unknown coatings on historic photographs at the Harvard University Archives using specular reflection FTIR, it was necessary to create a specular reflection FTIR spectral reference library of known materials. To do this, a set of modern reference prints with different coatings was created and spectra were collected from the freshly coated prints, naturally aged prints, and artificially aged prints.

(Figure 5) Based on a literature review, (McCabe 2005; Pauli 2011; Reilly 2012; Waldthausen 2014) the most common

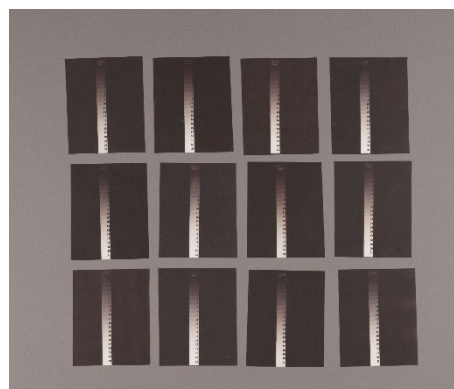


Figure. 5 Modern reference set of salt prints with different coatings

nineteenth-century coatings were found to be: bees wax, white wax, gum Arabic, dextrin, albumen, gelatin, casein, dammar, sandarac, shellac, and Canada balsam.

Most contemporary papers used for printmaking have optical brighteners in varying amounts. “Crane’s Pearl White”, a 100% cotton paper commonly used for alternative photographic processes was chosen to make the reference salt prints using a historically accurate recipe edited by Mark Osterman, (Osterman 2007; Osterman 2002) the photographic processes historian at the George Eastman Museum.

Bulk raw coating materials were purchased from suppliers TALAS and Kremer Pigments and each material was mixed with water, alcohol, or turpentine depending on the solubility properties. Coatings were applied to one half of each sample print using a polyurethane cosmetic sponge. The application method was intended to replicate that of a 19th century photographer by thinly applying the material in order to saturate the image and enhance detail.

To address the issues of how different aging conditions may affect the specular reflection FTIR spectra, two identical reference sets were made and aged under different conditions. The first sample set was naturally aged outdoors for two weeks in fluctuating high temperature (T) and relative humidity (RH) conditions. The second set was aged in accelerated aging oven at the Image Permanence Institute under high humidity testing conditions: 77 degrees F and 85% RH for 4 weeks. Both aged reference sets were then analyzed with FTIR using specular reflection modes with a Bruker Lumos FTIR microscope with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector from 4000 – 600 cm^{-1} at Harvard University’s Center for Nanoscale Systems (CNS).

Spectra from all three sample sets, naturally aged, artificially aged, and unaged, became the basis for the new specular reflectance FTIR spectral reference library.

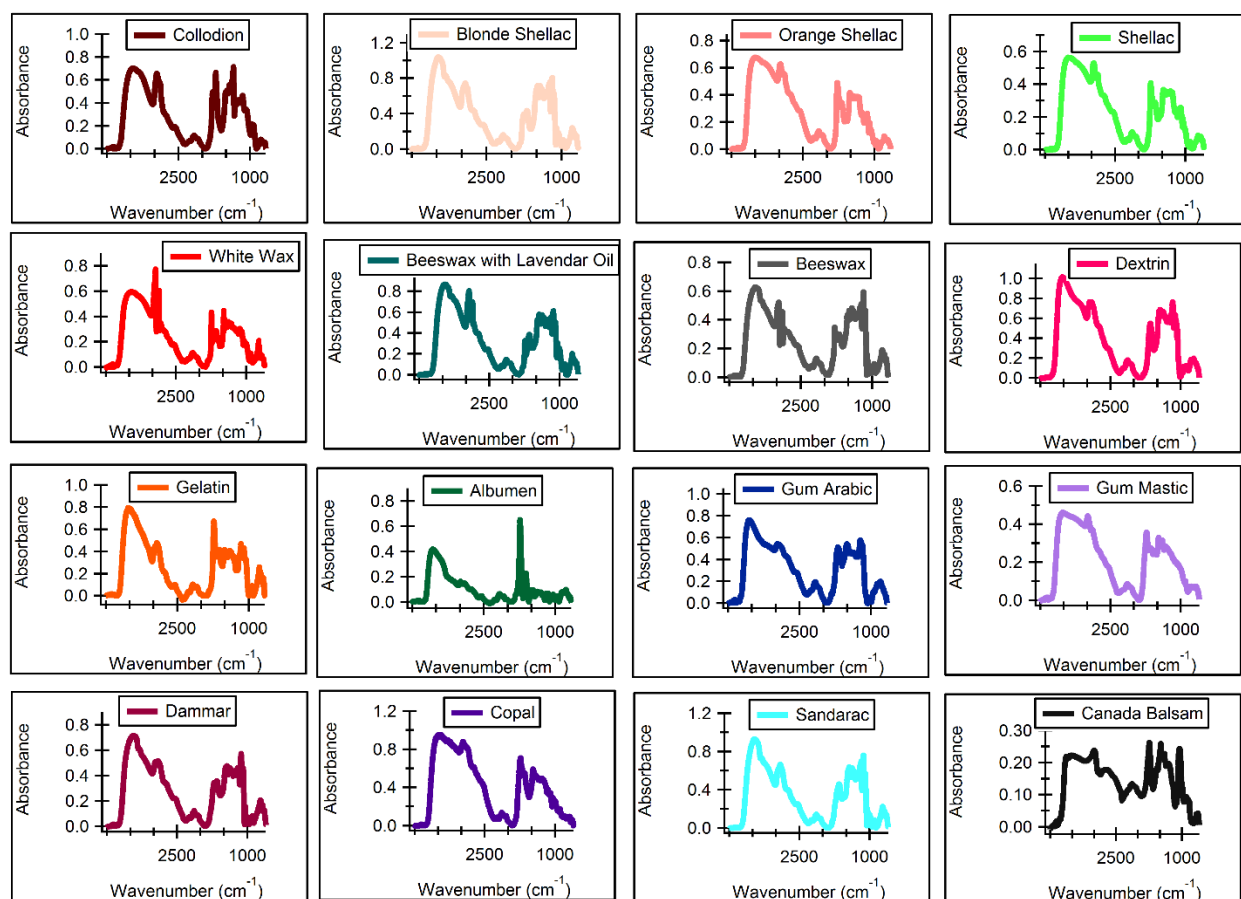


Figure. 6 Illustrative examples from the specular reflection reference library of different fresh coatings on modern salt prints. The data has all be baseline corrected.

Example specular reflection FTIR spectra of the different modern coating reference samples are presented in Figure 6. The clear differences in shape of the specular reflection FTIR spectra of the modern reference coatings allow for the positive chemical identification of the coating using this approach. Further discussion of the differences between the spectra are in the supporting information at the end of this article.

The full data set is available for download from the Harvard Dataverse data repository:

“Harvard Specular Reflection FTIR Library 2019”, <https://doi.org/10.7910/DVN/WARHO2>

3. DATA COLLECTION, PROCESSING and INTERPRETATION

Fourteen photographs from albums and thirteen loose prints from Harvard University Archives were chosen for the coatings analysis. The prints were chosen based on a variety of visual

characteristics observed in the coatings layers of the photographs, such as the uneven, discolored, or cracked coating shown in Figure 7. Many of the loose prints were identical to images in the albums, but exhibited much more significant deterioration, such as cracked and discolored coatings, than those stored in albums.

In addition to coated salt prints, two albumen photographs and all photographic mounts were analyzed with specular reflection FTIR. The albumen prints were included in order to challenge the ability of the library to match known material. Spectra from the mounts were collected in order to determine contribution to the final spectra. Interpretation of the data indicated that the mount paper did not influence the final spectra.



Fig. 7 A portrait from the Harvard University class albums [HUD 254.705 P, (HUA)]. The cracking of the coating is apparent. Courtesy of Special Collections, Harvard University Archives

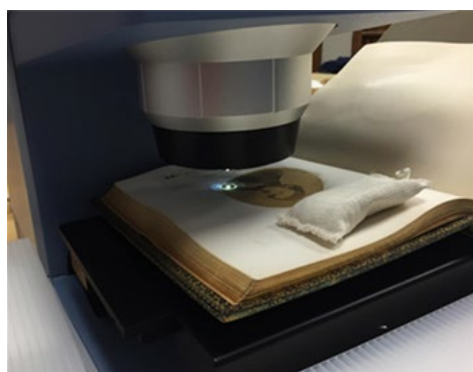


Figure. 8 One of the Harvard University class albums containing salt prints undergoing specular reflection FTIR analysis.

Data collection involved approximately one day of work for a conservator and a scientist and was performed in a conference room at the Harvard University Archives (Figure 8). Sixteen scans were averaged together at six different points on each print. Actual data collection of all six points took about 1.5 minutes per photograph. Data processing and comparison to the reference spectral library took just a few minutes and could be done immediately after collection of the spectrum from the historic print.

Operating the Bruker Lumos FTIR microscope is not overly complicated and the system is portable, so it could be taken into the archives. There are several other FTIR instruments on the market that are also portable and have a specular reflection modality. The Bruker Lumos has a liquid nitrogen cooled MCT detector, that dramatically improves sensitivity compared to a room temperature detector. The coated salt prints in this study had a total reflectivity of just a few percent of the incident light so the increased sensitivity was important in the quality of the spectrum collected. Some of the other portable systems are truly

handheld, but liquid nitrogen cooling is not practical in a handheld system. The lack of an optical microscope for checking focus, which turned out to be critical in collecting good spectra and targeting specific areas of interest are also limitations of the handheld systems. The handheld systems have been recently used to good effect in other studies (Wertz et al. 2018; Arrizabalaga et al. 2014; Arrizabalaga et al. 2015; Steger et al. 2018).

3.1 DATA PROCESSING

In an effort to enhance ease of use of the specular reflection spectral library and eliminate artifacts that could be unintentionally introduced with various data processing steps, it was decided to do only a baseline correction on the spectra that populated the library. The mathematical transformation known as Kramers-Kronig is sometimes applied to specular reflection FTIR spectra in an effort to make them appear more similar to the traditional transmission FTIR spectra. Applying Kramers-Kronig transformations to the data in this case study was deemed an unnecessary complication. As can be seen upon close examination of Figure 6, the specular reflection FTIR with only a baseline correction provides a unique spectral signature for each of the coatings.

Signal contributions from paper in the reference samples were ignored since there would be a similar spectral contribution from the paper in the historic samples. Tests revealed that the signal contribution from optical brighteners in the modern paper was negligible. This seems to be a valid method as can be seen in Figure 9, the overlay of the specular reflection FTIR spectrum of the modern Crane's Pearl White and an uncoated section of a historic salted paper print (HUD 253.703 P) match well.

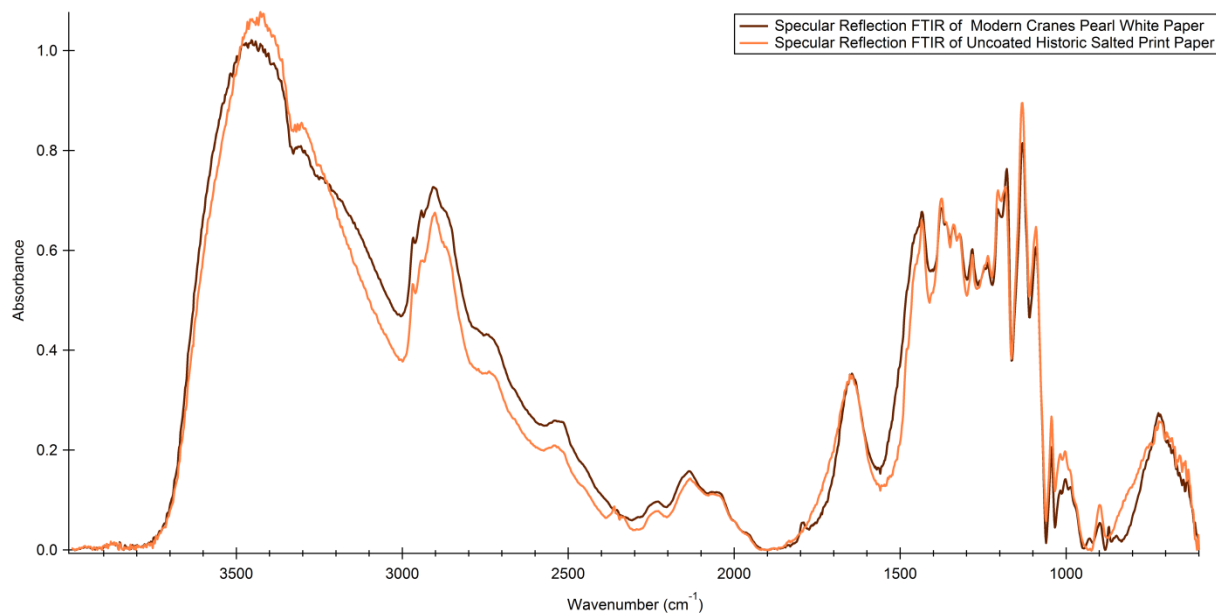


Figure. 9 Specular reflection FTIR match between modern reference sample paper and historic uncoated salted print paper, HUD 253.703 P

The spectra in the library were plotted as wavenumber versus absorbance in order to give the spectra a more “familiar” appearance with the signal being peaks instead of dips. The data collection software (Opus 6.3) simply assumes that any light that was not reflected was absorbed by the sample.

To test the robustness of the technique, spectra were collected from both light and dark areas of the prints. The spectral reference library successfully matched the coatings regardless of whether or not they were collected on a light or dark area of the print.

4. RESULTS

Specular reflection FTIR spectra were successfully used to make positive chemical identifications of coatings on the salted paper prints in the Harvard class albums using the spectral library generated from modern reference samples and the standard OPUS library search algorithm.

Table 1 Call numbers, visual observations, and chemical identification of the album prints used in the case study here.

TABLE 1- Harvard University Class Albums analysis, 1/14/2015			
Call number	Identified coating	Notes	
HUD.253.705	Gum Arabic	Surface cracking, discoloration	
HUD.254.704.3	Gum Arabic	No surface cracking, discoloration	
HUD.254.704.5	Gum Arabic	Surface cracking, discoloration	
HUD.255.705.2	Gum Arabic	Surface cracking, discoloration	
HUD.256.704.4b1	Gum Arabic	Surface cracking, discoloration	
HUD.258.704.1F	Gum Arabic	Surface cracking, discoloration	
HUD.258.704.4b1	Gum Arabic	Surface cracking, discoloration	
HUD.259.704.3PF	Gum Arabic	No surface cracking, discoloration	
HUD.259.704.3PF	Gum Arabic	No surface cracking, discoloration	
HUD.261.04.2Fb1	Gum Arabic	Surface cracking, discoloration	
HUD.263.04.FAb1, print 1	Dextrin	No surface cracking, no discoloration	
HUD.263.04.FAb1, print 2	Dextrin	No surface cracking, no discoloration	
HUD.264.04.2P-F	Albumen	Albumen emulsion	
HUD.264.04.2P-F	Gum Arabic	Surface cracking, discoloration	

Table 2 Call numbers, visual observations, and chemical identification of the loose prints used in the case study here.

TABLE 2- Analysis of loose prints from Harvard University Archives, 5/28/2015			
Call number	Identified coating	Notes	
HUV-39 (4-7)	Gum Arabic	Surface cracking, strong discoloration	
HUV-39 (1-2)	Unknown	Surface cracking, strong discoloration	
HUV-39 (1-5)	Gum Arabic	Surface cracking, discoloration	
HUV-39 (10-2A)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (2-6B)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (1-3)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (2-1)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (1-2)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (1-5)	Albumen	No surface cracking, slightly yellowed	
HUV-20 (2-5a)	Gum Arabic	Surface cracking, strong discoloration	
HUV-20 (1-1)	Gum Arabic	Surface cracking, strong discoloration	
HUP Hall, Charles Henry, class of 1860	Gum Arabic	Surface cracking, strong discoloration	
HUP Hall, Richard Fitch, class of 1854	Gum Arabic	Surface cracking, strong discoloration	

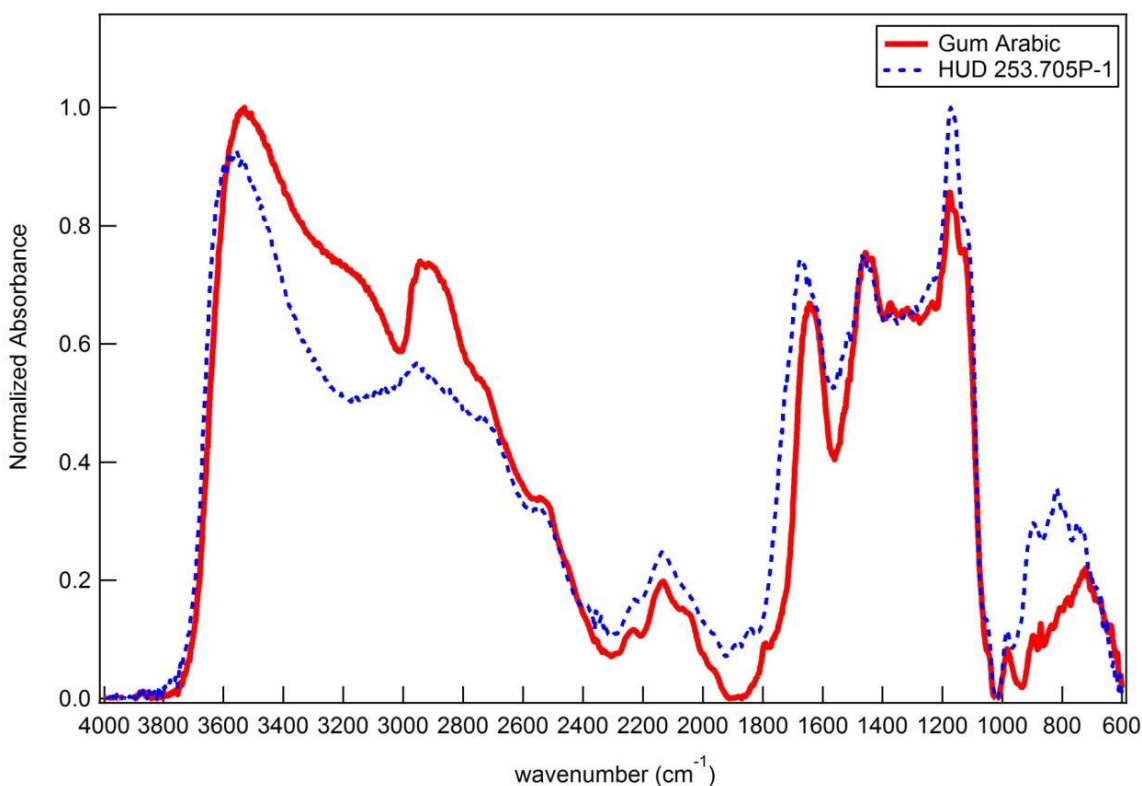


Figure. 10 Specular reflection FTIR comparison of historic photograph with modern reference providing positive chemical identification of the coating as gum Arabic

Of the 14 photographs analyzed in the albums (Table 1) and the 13 loose prints (Table 2) 96% were identified as having a coating of gum Arabic (Figure 10). This result is in keeping with initial visual identification of the prints and with published historical accounts of the use of gum Arabic as a common coating used by artists and photographers (McCabe 2005). The albumen photographs from the collection did result in positive identification for albumen. Two of the photographs were identified as being coated with dextrin. Finally, one coating from the photographs analyzed could not be identified. It is probable that this material is not currently in the spectral library or it could be a mixture, which at the time of the analysis was not part of the spectral reference library. This argues for continued work building larger spectral libraries for specular reflection FTIR.

These initial findings correlated well with expectations and have encouraged further exploration of the use of specular reflection FTIR for positive identification of single component coatings and coating mixes. The information gathered is being used to determine appropriate treatment options,

to monitor further possible deterioration of coatings on historic photographs in the collection and to build a profile of coatings types based on date, photographer or intended aesthetic result in a final print.

During this experiment, significant differences in library matches was not observed between aged and fresh coating materials. The one coating in the modern reference set that changed significantly over time was dammar.

5. CONCLUSIONS

Chemical characterization of photographic coatings is an important tool for dating and identifying individual photographs, contributing new scholarship to the understanding of the history of photography, indicating possible deterioration tendencies particular to each coating material, and making preservation decisions and suitable conservation treatment approaches.

The use of specular reflection FTIR for the identification of organic materials in conjunction with historic or artistic works is still in its infancy but as more conservators and scientists collaborate, the technique will find greater use in, and value for, the cultural heritage sector. In this case study, coatings on historic photographs were positively identified chemically without sampling, contacting, or even leaving the archives, using specular reflection Fourier transform infrared spectroscopy and a relevant spectral library which was created from modern reference samples.

The specular reflection FTIR modality was demonstrated to be a highly effective method of chemical identification by interpreting the spectrum as a holistic chemical signature rather than individual peak assignments. Although in this specific case the specular reflection FTIR technique was applied to single layer coatings on paper, the technique can be used with other materials. At the current time, however, the existing spectral library is limited to coatings on cotton paper and may therefore find direct application to other works on paper with unknown binders or surface treatments. For works on other support materials or for more modern coatings and fixatives, relevant reference samples would need to be made and a corresponding specular reflection FTIR library generated. As this paper provides a useful roadmap on how to build a reference library and the validity of using modern reference materials, this obstacle should not be seen as insurmountable.

Following the encouraging results from analysis on the Harvard University Archives photographs, the authors collaborated with conservation scientists from the Straus Center for Conservation and Technical Studies at Harvard Art Museums and the Getty Conservation Institute at the J. Paul Getty Museum to test the robustness of the technique. Small sections of each reference sample were sent to both institutions and analyzed using specular reflection mode on different FTIR instruments operated by different users. Results and observations from these test runs were incorporated into a protocol document which provides instructions for troubleshooting common errors and adapting the specular reflection library and methodology for different instruments. This protocol document is available electronically as supplemental material to this article.

Finally, this case study shows the value of an interdisciplinary team of conservators and scientists working closely together for successful chemical analysis of cultural heritage materials. The authors have found that data collection and material preparation is relatively easy and the analytical findings support visual identification and expected historical practices.

6. FUTURE DIRECTIONS

Although this initial test group was small and contained information only applicable to single coatings on historic photographs, there is significant potential for further research using this methodology with the expansion of the materials in the spectral reference library. The initial reference library used for this study has since grown to include spectra from additional reference samples from the Weissman Preservation Center, the Rijksmuseum, and from the private research collection of photograph conservator, Clara von Waldthausen. Most recently, the library was populated with spectra from 23 uncoated historic salt prints from the Harvard Fine Arts Library Portrait Collection.

Currently the authors are collaborating with Straus Center Fellow, Laura Panadero, on analysis of coatings mixtures used on several paper negatives by 19th century French photographer, Frédéric Flachéron, held by Houghton Library, Harvard University. This research aims to correlate findings using specular reflection FTIR with a previous study of these negatives in 1999 using GC-Mass Spectroscopy and FTIR in transmission mode (Daffner 2003). Results of this study including additional research into working Flachéron's methods will be published in the near future.

The authors have also been testing Principal Component Analysis (PCA) techniques to compensate for correlation functions commonly used for spectral library matching which can be biased towards the largest peaks in a spectrum ignoring minor components. This technique allows for spectra comparison and classification without this largest peak bias. Initial tests show promising applications for the use of PCA on specular reflection FTIR spectral data sets of more chemically complicated samples such as mixes or varnishes as well as “transitional prints”, a term used to describe hybrid photographs produced during the transition from the salt print era to the albumen era. Other researchers in the hyperspectral reflectance spectroscopy area are trying similar approaches to paintings, which are usually mixes of several pigments and binders (Grabowski et al. 2018).

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Brenda Bernier: As the Malloy-Rabinowitz Preservation Librarian, Brenda Bernier is the Director of Harvard Library's Preservation Services, where she leads teams committed to the preservation and conservation of general library collections, as well as the rare and unique books, photographs, works on paper, audiovisual materials, and digital content from the University's vast library system. Prior positions at Harvard include the James Needham Chief Conservator, serving as Head of the Weissman Preservation Center and Collections Care, and the Paul M. and Harriet L. Weissman Senior Photograph Conservator. Brenda held previous posts at the National Archives and Records Administration, the U.S. Holocaust Memorial Museum, and

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Erin L. Murphy is the Paul M. and Harriet L. Weissman Senior Photograph Conservator and interim James Needham Chief Conservator at Harvard Library. Erin received her Masters of Art degree with a certificate in Art Conservation from Buffalo State College in 2001 and has trained at the Metropolitan Museum of Art, The J. Paul Getty Museum, The Conservation Center for Art and Historic Artifacts and the Museum of Modern Art. Prior to her position at Harvard Library, Erin served as Photograph Conservator at the New York Public Library.

SUPPORTING INFORMATION

Data Collection

For software to make a good match between the unknown sample and the spectral reference library, it is also important that the unknown sample spectrum is a nice “clean” spectrum (Figure 11). The software will have trouble making a good match with a noisy data set. Several factors can contribute to the noise in the spectra. The biggest user controlled factor is the focus on the sample. The sample must remain in focus while the specular reflection FTIR spectrum is being collected. Some gentle weights on the pages of the class albums helped to keep the samples from moving out of focus during sample acquisition Figure 8.

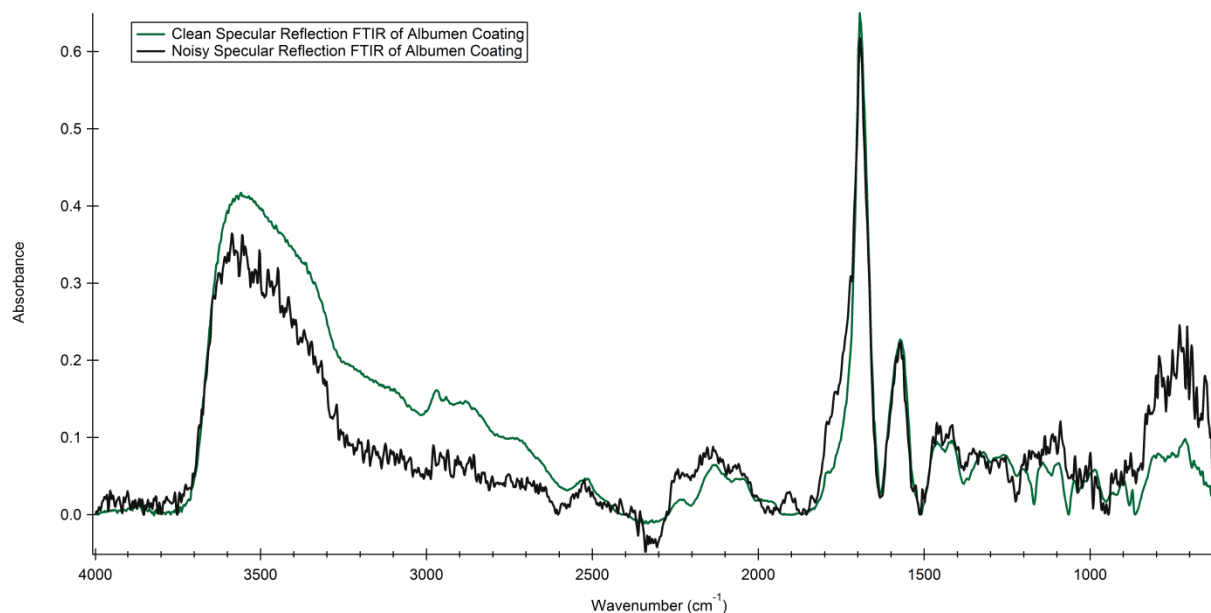


Figure 11 Example of a noisy specular reflection FTIR as compared to clean specular reflection FTIR spectra.

Other factors that a user may not have any control over are the detector on the system that they are using. Signal will need to be collected and averaged for a much longer time on a room temperature DTGS detector to achieve the same noise level as a liquid nitrogen cooled MCT detector. It is recommended to average spectra from multiple locations on the sample to minimize the effects of any inhomogeneity in the coating. For generating the library, 16 scans at 6 different locations on the sample were averaged together. The number of scans needed to get a good signal to noise ratio will be instrument dependent.

For specular reflection, the background measurement should be taken on a clean gold mirror. If dust or fingerprints have accumulated on the gold mirror, it is recommended to clean the mirror with lens cleaning tissue (such as Thorlabs Lens tissue MC-5) and isopropyl alcohol. Evidence of a dirty mirror will usually be negative peaks in the hydrocarbon region ($2,800\text{--}3,000\text{ cm}^{-1}$) as the signal here will be overcompensating for the contamination on the mirror. Other issues with background subtraction not working correctly are evidenced by two peaks around $2,350\text{ cm}^{-1}$

corresponding to atmospheric CO₂ and a series of spikes between 1,500-1,800 cm⁻¹ and 3,200-3,600cm⁻¹ corresponding to atmospheric water vapor. If the CO₂ and water vapor peaks are observed it is best to retake the background spectra and the sample spectra before proceeding to trying to use the reference library Figure 12.

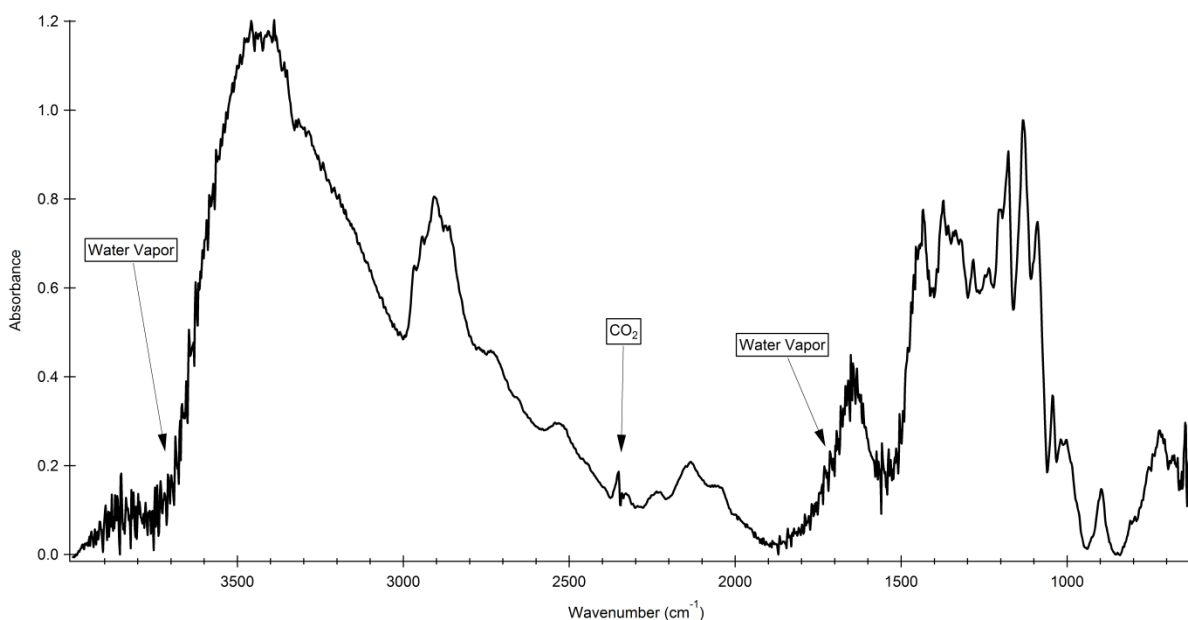


Figure 12 Bad background subtraction showing water vapor and atmospheric carbon dioxide peaks.

The reference library was generated with to 4 cm⁻¹ resolution. Checking that your instrument is also set to 4 cm⁻¹ resolution will help the software match the spectra to the reference library. (The default resolution on most FTIR systems is 4 cm⁻¹.)

Data processing

Once a set of good quality specular reflection spectra from multiple spots are acquired, they should be averaged together and a base line correction should be performed. This can usually be done in the same software that was used to collect the spectra. The reference spectra in the specular reflection FTIR library have been baseline corrected. In order for the software to make a good

match a baseline correction needs to be performed on the unknown sample data (Figure 13).



Figure 13 Baseline correction of the specular reflection is needed to help make matches to the specular reflection library.

Data Interpretation

The main interest of this case study is a positive chemical identification of the coatings on the historic coated salted paper prints. Each peak in a spectrum was not identified but rather the spectrum as a whole was taken as a signature for a specific coating. Below are some notes that were noticed about the different classes of coatings that were included in the library.

Proteins

The Amide I and Amide II bands are the signature peaks of a protein coating. The Amide I and Amide II bands are indicative of the secondary structure of the protein. The specular reflection FTIR seems to have no issues distinguishing between albumen and gelatin coatings on the salted paper prints Figures 14 and 15. The gelatin or starch used for sizing the paper is in small enough quantities as to not interfere with interpreting the composition of the coatings. Questions about the subtle chemical differences due to paper sizing would require a PCA approach.

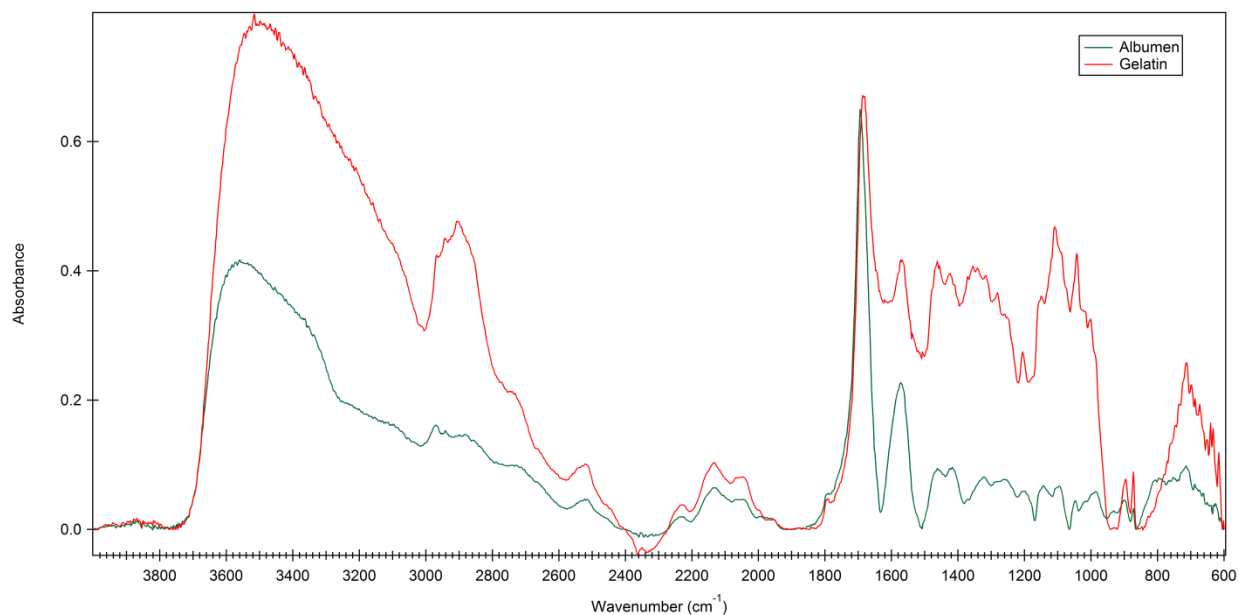


Figure 14 Full range of albumen and gelatin coatings on salted paper prints collected in specular reflection FTIR. Some diagnostic features are also in the 2,800-3,000 cm^{-1} range.

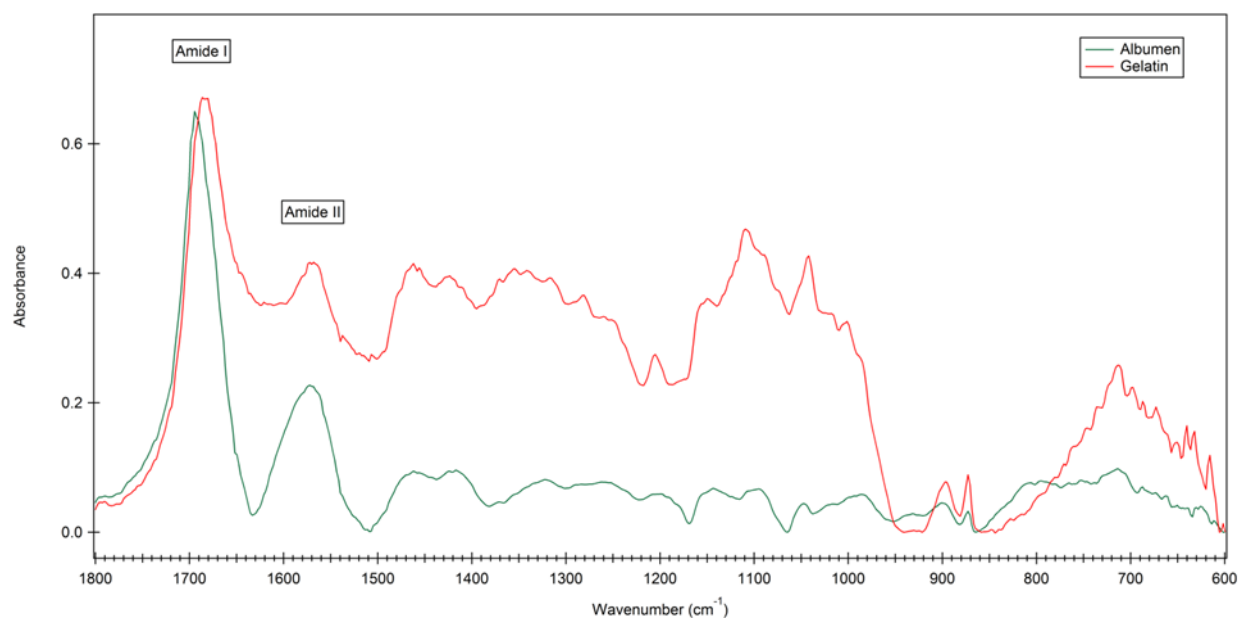


Figure 15 Fingerprint region of albumen and gelatin coatings on salted paper prints collected in specular reflection FTIR.

Waxes

The specular reflection FTIR spectra of wax coatings have a distinctive derivative shapes in the CH_2 stretches 2850 cm^{-1} and 2920 cm^{-1} . White wax and beeswax can be distinguished by looking at the fingerprint region Figures 16 and 17.

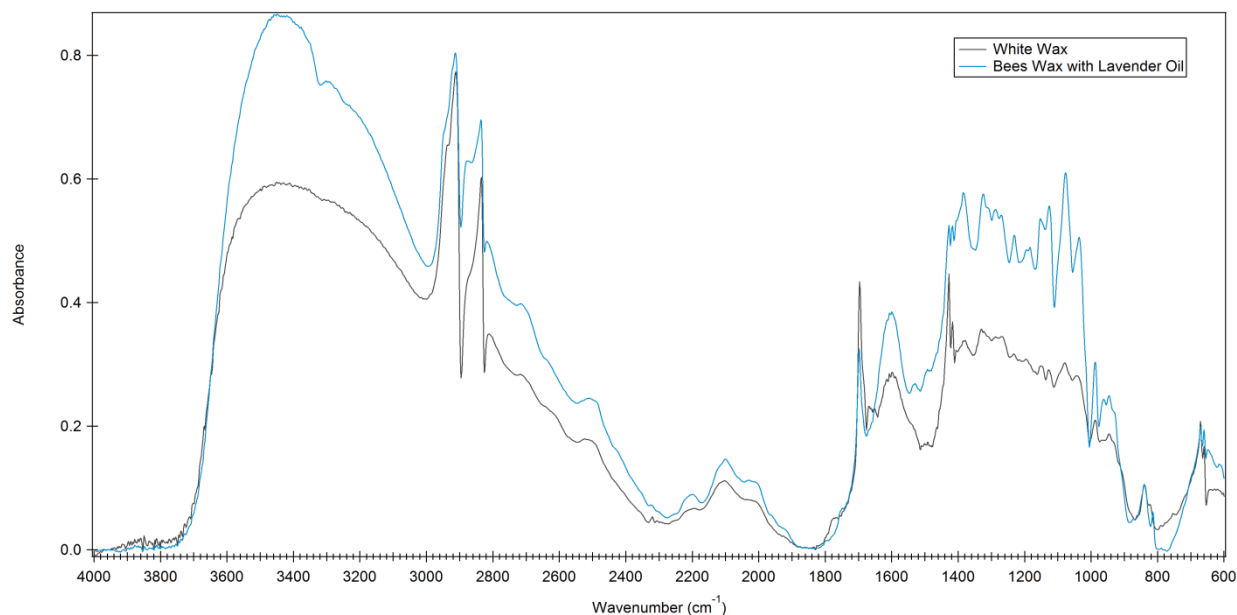


Figure 16 Full specular reflection FTIR of white wax on salted paper print and beeswax with lavender oil on salted paper print

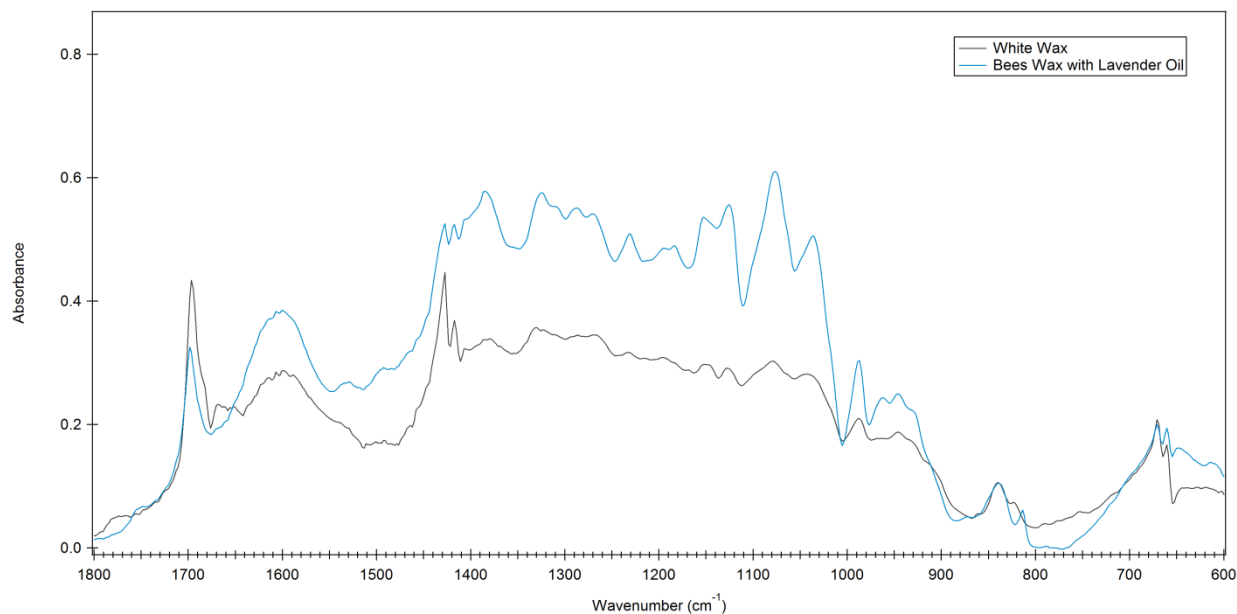


Figure 17 Fingerprint region of specular reflection FTIR of white wax and beeswax with lavender oil on salted paper print

Polysaccharides

The polysaccharides have a single broad peak around 1650 cm^{-1} . Dextrin has a very sharp peak at 1000 cm^{-1} that is distinct from gum Arabic Figures 18 and 19.

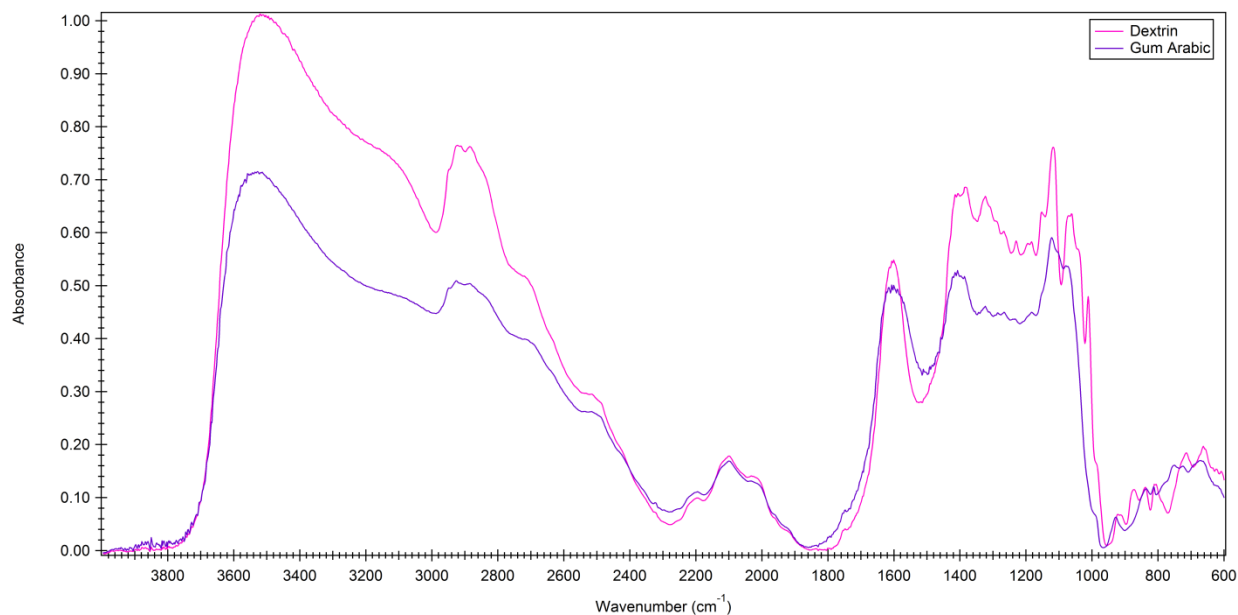


Figure 18 Full range of specular reflection FTIR of dextrin and gum Arabic.

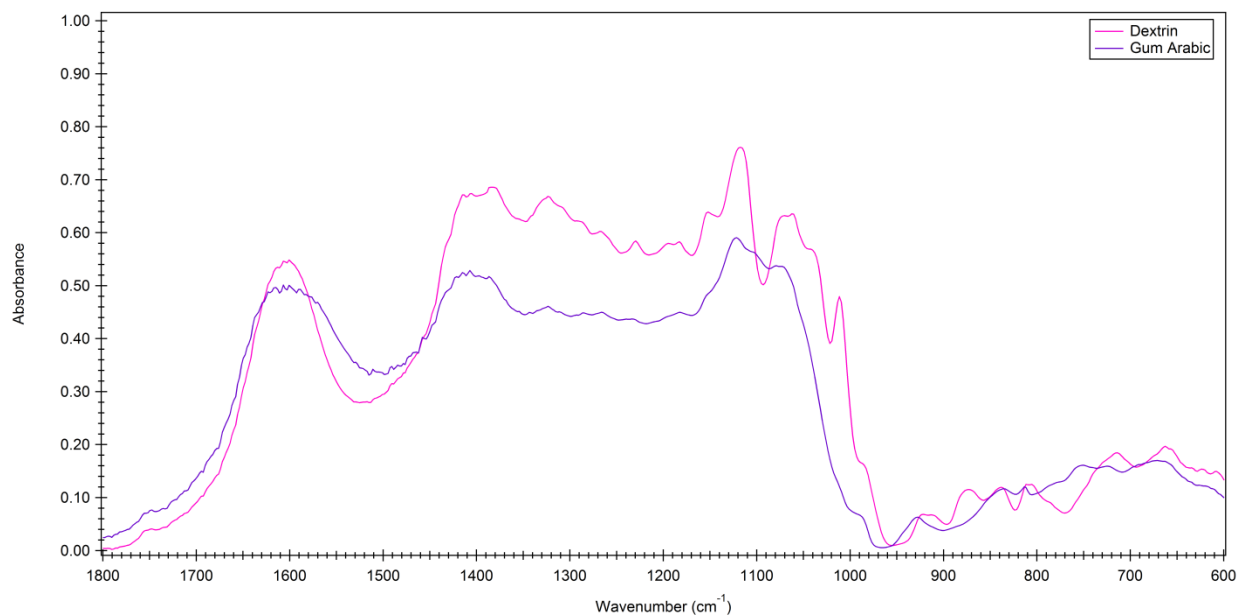


Figure 19 Fingerprint region of specular reflection FTIR of dextrin and gum Arabic.

Resins

The dammar reference sample presented the most problems of all the coatings in this case study as it seemed to be unstable with the spectra changing over the course of a year to the point that it did not reliably match with the fresh or accelerated aging samples. In general resins were distinguishable from each other but the differences were subtler, with occasional multiple suggestions from the spectral library if the collected spectra were sub-optimal. The spectra regions between 1,500-1,800 cm^{-1} and 2,800-3,000 cm^{-1} seem to be particularly useful for distinguishing the different resins Figures 20 and 21.

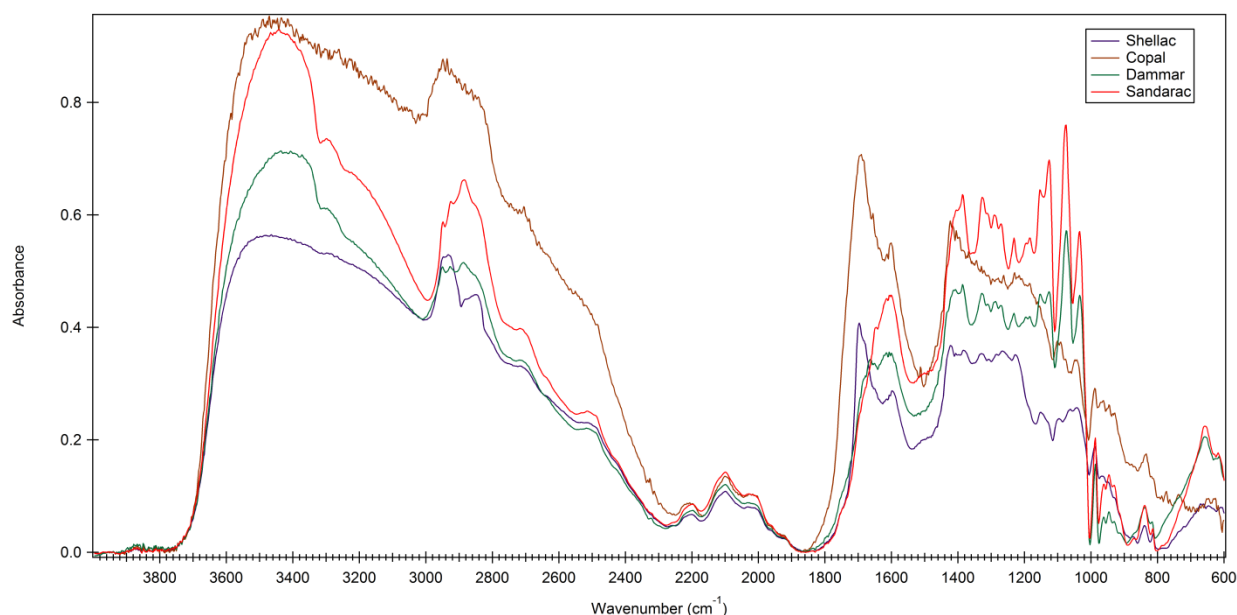


Figure 20 Full Range spectral reflection FTIR of resin coatings (shellac, copal, dammar, sandarac) on salted paper prints.

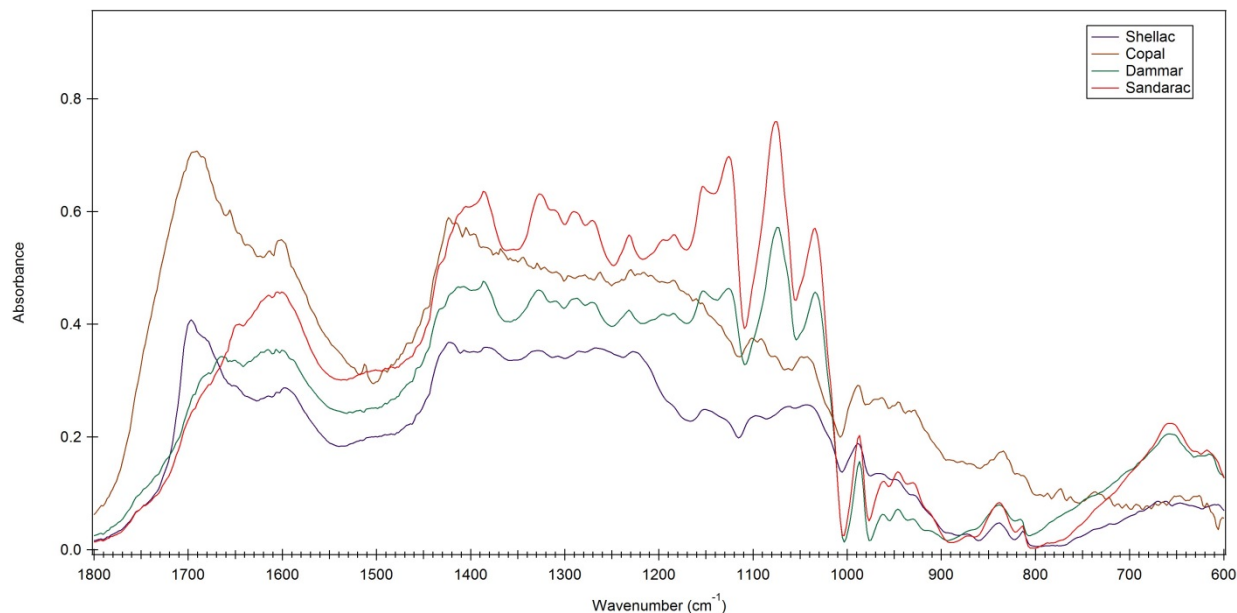


Figure 21 Fingerprint region of specular reflection FTIR of resin coatings on salted paper prints

MODERN REFERENCE PRINTS: FORMULA AND METHODOLOGY

An attempt to find paper free from optical brighteners was not 100% successful. It was discovered that most of contemporary papers used for prints making have optical brighteners in different amount. “Cranes Pearl White”, a 100% cotton paper used to make the reference salt prints using a historically accurate recipe edited by Mark Osterman, the photographic processes historian at the George Eastman Museum.

The recipe used to produce salted paper sample sets:

Salting the paper:

2 g sodium chloride

2 g gelatin

100 mL distilled H₂O

Sensitizing the paper:

20 g silver nitrate

100 mL distilled H₂O

granular citric acid (if needed)

Place paper and negative/objects with sensitized paper

----- PRINT -----

Approx. 5-10 min. for UV unit; Sun is approx. 2x as fast

Washing excess silver:

Wash sensitized print in 2 baths (1 min. each) of water with a pinch of sodium chloride until milky white, silver chloride precipitate no longer appears to evolve from the paper.

Gold tone prints:

30 mL gold chloride, pH ~8

1000 mL distilled H₂O

Bathe print to desired color for 5 min. agitating carefully and continuously.

Wash prints in 2 baths of tap water

Fix:

1000 mL warm water

150 g sodium thiosulfate ("hypo")

2 g sodium bicarbonate

After washing out excess silver, place print in fix for 5 min. agitating the tray continuously.

Pre-final wash in tap H₂O:

Place prints in two baths of tap H₂O for 1 min each.

Final tap H₂O wash:

Place prints in circulating wash for 30 min.

Blot prints and then allow to dry flat

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ⁱ In 1855, the Photographic Society of London established a committee to investigate and report on the "Fading of Photographs". The Committee reported in late 1855 that the causes of fading were due to multiple factors, including poor washing leaving harmful chemical residues in the paper and the presence of pollutions in Victorian London.

The Committee made four suggestions:

- That the greatest care should be bestowed upon the washing of the prints after the use of hyposulphite of soda, and for this purpose hot water is very much better than cold.
- The majority of the Committee think that gold, in some form, should be used in the preparation of pictures, although every variety of tint may be obtained without it.
- That photographs be kept dry.
- That trials be made of substances likely to protect the prints from air and moisture, such as caoutchouc, gutta percha, wax, and the different varnishes.