The Atlas of Analytical Signatures of Photographic Processes

ALBUMEN

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The Atlas of Analytical Signatures of Photographic Processes is intended for practicing photograph conservators and curators of collections who may need to identify more unusual photographs. The *Atlas* also aids individuals studying a photographer's darkroom techniques or changes in these techniques brought on by new or different photographic technologies or by the outside influence of other photographers. For a complete list of photographic processes available as part of the *Atlas* and for more information on the Getty Conservation Institute's research on the conservation of photographic materials, visit the GCI's website at getty.edu/conservation.

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Front cover: Gustave Le Gray, *The Brig*, 1856. Albumen silver print, 32.1 × 40.8 cm. The J. Paul Getty Museum, Los Angeles.

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ALBUMEN

English: albumen
French: *albumin*
German: Albuminverfahren

HISTORICAL BACKGROUND

The albumen process was invented by Louis Blanquart-Evrard (French, 1802–1872). Some photographic experiments with albumen positives were conducted prior to Blanquart-Evrard's albumen printing process, but he made a major contribution to the invention of the albumen process as it was known and used during the second half of the nineteenth century.

The process was presented by Louis Blanquart-Evrard to the French Academy of Sciences on May 27, 1850, and later published in *Compte rendus des séances de l'Académie des Sciences* 30, no. 21(1850): 665.

The albumen process was the main positive printing photographic process of the nineteenth century. It started around 1850, dominating photographic printing between 1855 and 1890 and surviving in various forms into the late 1920s. (An example from the time is shown in fig. 1.)

Figure 1 Gustave Le Gray, *The Brig*, 1856. Albumen silver print, 32.1 × 40.8 cm. The J. Paul Getty Museum, Los Angeles.

Prior to 1854, all albumen prints were produced using material prepared by a photographer or the photographer's studio staff, often on special paper stock that was available commercially. In 1854 the first commercially produced albumen photographic paper appeared on the market. This was still only a paper substrate coated with salted albumen that needed to be sensitized with a solution of silver nitrate. Only after 1872 did presensitized albumen photographic paper with a longer shelf life start to be sold commercially. Some photographers did not trust the quality of commercially sensitized albumen paper and for economical reasons chose to prepare their own albumen paper.

Figure 2 shows a historical timeline of the albumen (positive) photographic process.

Process Description

Almost all photographers who published their techniques for making and printing on albumen paper proposed highly personalized procedures using different paper substrates and different chemical substances and their ratio, but most published recipes and procedures are essentially similar.

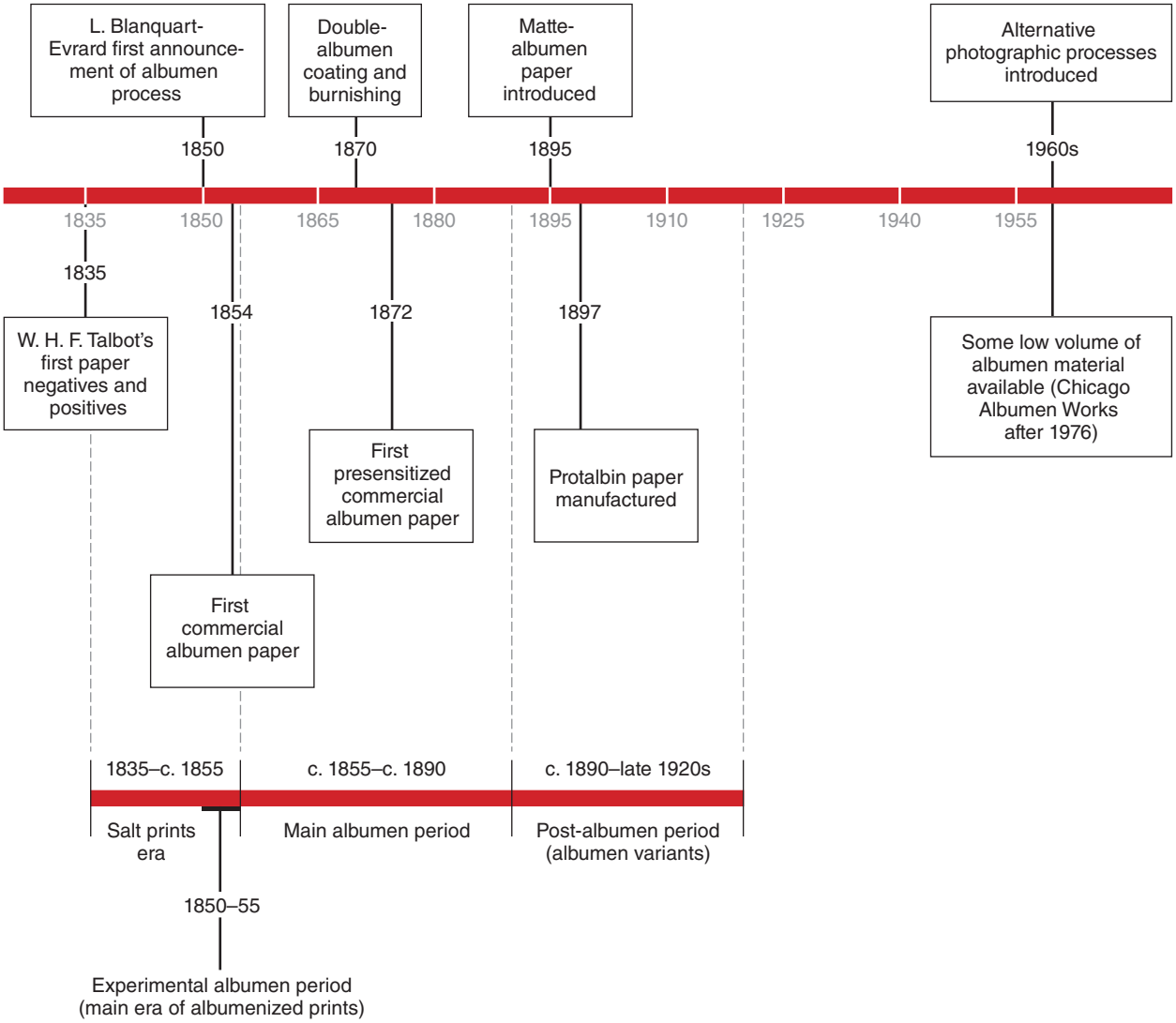

Figure 2 Timeline of the albumen photographic process.

Preparation of handmade (noncommercial) albumen paper involved two steps. First, selection of the paper substrate for albumen printing was as critical as the selection of the paper substrate for older salt paper processes and for many recent alternative photographic processes. A prospective paper for the production of high-quality and highly consistent albumen prints needed to have great wet strength during wet stages of processing, needed to be lightweight to facilitate coating by floating, and needed to be free of metallic impurities that were responsible for the black specks that damaged processed photographs. The paper also had to be free of chemical impurities from chemical processing and bleaching of the paper fibers. Of the many manufacturing facilities that experimented with the production of photographic raw stock for albumen printing, only the Blanchet Frères et Kléber Co. (near Grenoble in France), which produced Rives paper, and the Steinbach paper mill in Germany (in Malmedy in Belgium today) were able to produce an adequate quality of paper substrate for the newly developing photographic industry. Both paper mills prepared machine-produced paper internally sized with starch and resin soaps.

Second, most published recipes for the preparation of salted albumen called for the use of fresh eggs. Egg white was separated from egg yolk, leaving no traces of yolk or blood behind in the egg white. A solution of sodium chloride or ammonium chloride was added to the egg white, and the resulting mixture was beaten to a stiff froth. Left to stand overnight, the froth would liquefy, resulting in a much more homogenized and uniform solution of salted albumen that was usually filtered and mixed with water. The solution was then used for coating albumen paper by floating the paper substrate on a bath of salted albumen. The major difference between many of the different published recipes lay in whether the albumen salt solution was used as prepared, or if it was diluted with various amounts of water. Albumen papers prepared using more diluted coating solutions resulted in less glossy albumen prints. During the early period of albumen printing in the 1850s, the public was accustomed to the matte character of salt prints, and the glossiness of albumen photographs was highly criticized in the photographic literature. That changed over time as the public developed a taste for the high definition and contrast of glossy albumen photographs.

Figure 3 shows a schematic cross section of a typical albumen photograph.

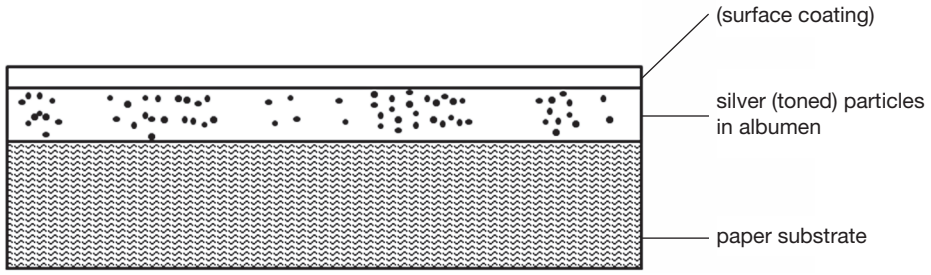

Figure 3 Schematic cross section of a typical albumen photograph.

Main Application of the Albumen Process

The albumen silver positive printing process was the most important positive photographic process of the second part of the nineteenth century. Albumen photographs were used for all kinds of photographic applications, from commercial portrait photography to scientific photography. Albumen photographs were often mounted on mounting boards. Many, but not all, of existing *cartes de visite* (CDV), cabinet cards (CC), and a number of later variants of card photographs contain albumen prints. Albumen photographs were also mounted in early photographic albums and printed in large numbers for trade as portraits of famous people or royalty, as curiosities, or as tourist souvenirs.

Noted Photographers Using the Albumen Process

Philip Henry Delamotte
Roger Fenton
Francis Frith
Hermann Krone
Gustave Le Gray
John Edwin Mayall
Félix Nadar
Charles Nègre
Timothy O'Sullivan
Carleton E. Watkins

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Cartier-Bresson, A. 2008. *Le Vocabulaire Technique de la Photographie*. Paris: Marval, 104–10, 116–17.

Lavédrine, B. 2009. *Photographs of the Past: Process and Preservation*. Los Angeles: The Getty Conservation Institute, 112–23.

Mazurek, J. 2010. "Antibodies and Art: Characterization of Albumen and Gelatin on Paper." *International Preservation News*, no. 50 (May 2010): 17–20.

Albumen Process–Related Patents

Henry F. Anthony, U.S. 41,750 (Mar. 1, 1864)

IDENTIFICATION: ALBUMEN PHOTOGRAPHS

Visual Signatures

Albumen photographs dominated all areas of photography from about 1855 until about 1890, and variants of albumen photographs were produced up until the late 1920s. Several other major positive photographic processes—glossy collodion, printing-out paper (POP) silver gelatin, and developing-out paper (DOP) silver gelatin—were used during that period, producing photographs that were sometimes visually similar to albumen photographs. A combination of visual, microscopic, and analytical signatures of all of these photographic processes allows for the positive identification of each process.

Visual Characteristics

Most albumen photographs were produced by copy printing a negative on a prepared sheet of sensitized albumen photographic paper. As such, most existing albumen prints have the identical size of the camera-produced negatives. Many untrimmed albumen photographs show a dark border around the prints that reflects the size difference between the albumen paper and the negative from which the photograph was produced in the copy frame (fig. 4).

Whereas most albumen photographs were toned, some, namely test photographs, were left untoned. Depending on the quality of the darkroom processing and their state of conservation, albumen photographs can be found in different color tonalities ranging from very light brown, brown, and reddish brown to dark violet-black (fig. 5).

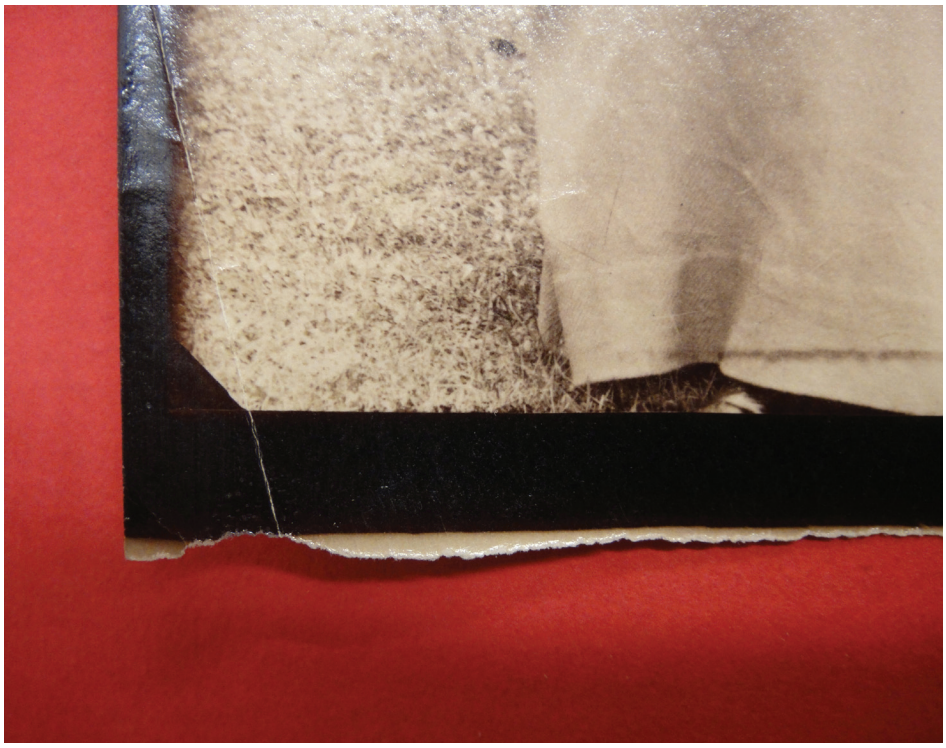


Figure 4 Photograph showing a portion of the dark border of an untrimmed albumen photograph.

Figure 5 Examples of albumen photographs showing a range of color tonalities.

Most albumen photographic papers were thin and had a strong tendency to curl inside, forming tight rolls of unmounted albumen photographs that, when left in such a state after processing, were rather fragile and difficult to handle without special treatment and conditioning (fig. 6).

Most photographs were mounted on special card stock (CDV, CC, and other formats), paper substrates, mounting boards, or album pages. Sometimes the adhesive resulted in a visible tonality change or bleaching of the albumen prints, causing the lines of applied adhesive to show up in the prints as lighter, well-delineated areas that disfigured, to various extent, mounted albumen photographs.

Earlier albumen prints, created before about 1870, were usually less glossy than double-coated albumen photographs and albumen photographs that were made glossy by surface burnishing and varnishing. Preparing albumen photographic papers using aged or partially putrefied albumen also produced higher-gloss albumen prints. When left unmounted but stored flat under weight, these old albumen photographs can remain flat, clearly showing that the albumen paper substrate was usually very thin (fig. 7). Most old albumen photographs show a certain level of yellowing of the albumen layer. This is usually visible in the Dmin areas of inspected albumen photographs (fig. 8).

Figure 6 A conservation scientist sorts through old unmounted albumen photographs that had curled into tight rolls.

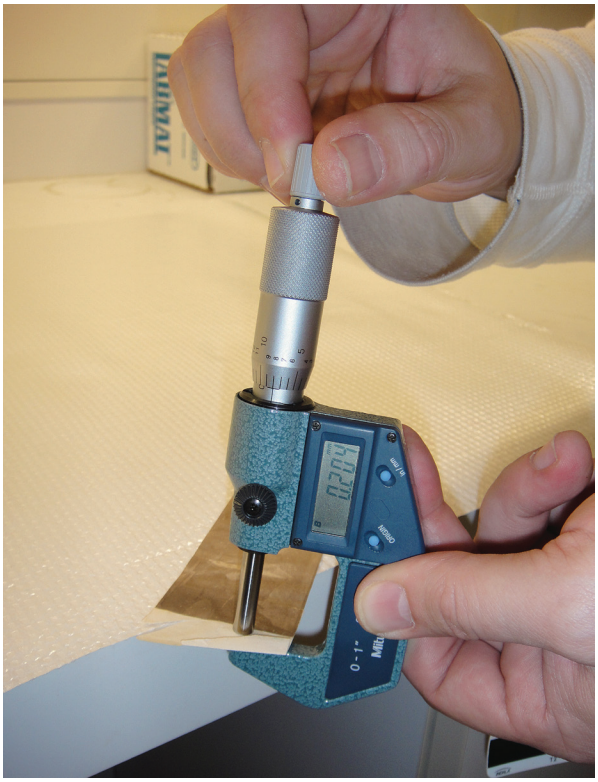


Figure 7 Thickness measurement (0.204 mm) of an unmounted albumen photograph stored flat.

Figure 8 Photograph showing yellowing of the albumen layer.

Figure 9 Nineteenth-century advertisement promoting the tinting of albumen photographic paper to counteract yellowing.

Figure 10 Examples of photographs printed on albumen paper containing pink and blue organic dyes.

The photographic industry was well aware of the problem of yellowing of albumen prints. Some albumen photographic materials that were available commercially were prepared by adding organic dyes to the albumen (fig. 9) to counteract the yellowing. Figure 10 shows photographs printed on the commonly available pink and blue albumen photographic papers. Many of these organic dyes had very low light stability and often faded when exposed to light during display or exhibition. Some areas of original dye may still be visible under a photograph's matte or frame.

Microscopic Characteristics

The most typical microscopic signature of albumen photographs is a fine network of surface microcracks that is rather uniform across the surface layer of the photograph. Figure 11 shows an 1860s uncoated albumen CDV photograph. The microscopic details revealing the surface network of microcracks recorded at different magnifications are shown in figures 12a–c.

Figure 11 Albumen CDV photograph from the 1860s.

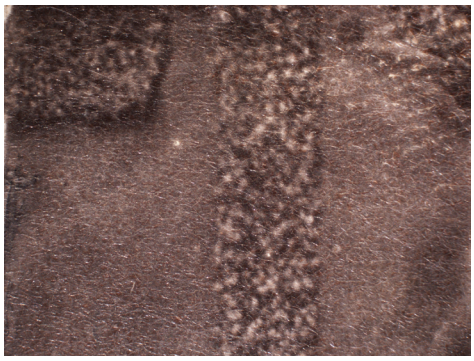


Figure 12a Micrograph showing the network of surface microcracks typical of unburnished period albumen prints in fig. 11 recorded at 10× magnification.

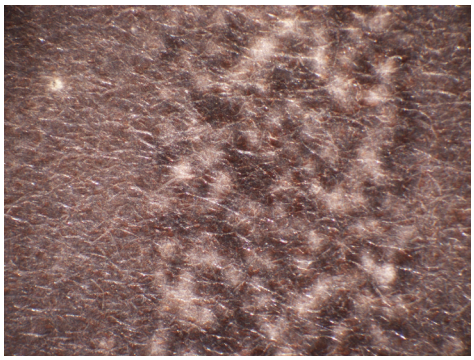


Figure 12b Micrograph showing the network of surface microcracks typical of unburnished period albumen prints in fig. 11 recorded at 25× magnification.

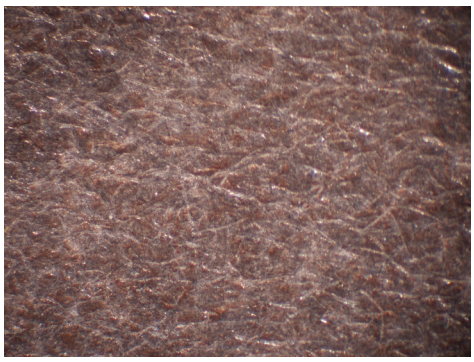


Figure 12c Micrograph showing the network of surface microcracks typical of unburnished period albumen prints in fig. 11 recorded at 40× magnification.

Such a network of surface microcracks can be found in most albumen prints produced before 1870. The surface of albumen prints produced after 1870 that were sometimes burnished and heat treated may not fully exhibit such a microcrack pattern, or surface cracks may not be visible at all. Figure 13 shows a glossy albumen photograph mounted on a CC. Figures 14a–c show the corresponding microscopic images of its surface pattern.

Figure 13 Glossy albumen CC-mounted photograph from after 1880.

Figure 14a Micrograph showing an absence of microcracks, as is typical of burnished albumen prints in fig. 13 recorded at 10× magnification.

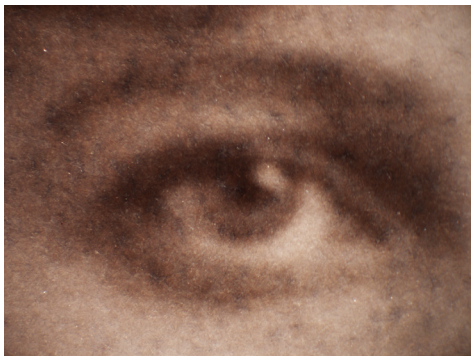


Figure 14b Micrograph showing an absence of microcracks, as is typical of burnished albumen prints in fig. 13 recorded at 25× magnification.

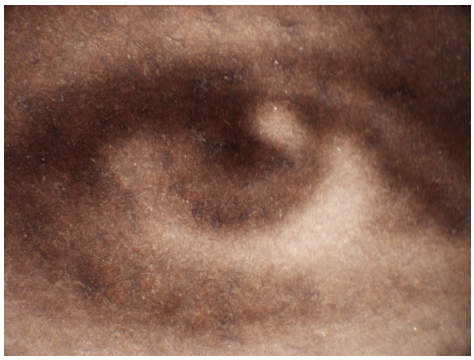


Figure 14c Micrograph showing an absence of microcracks, as is typical of burnished albumen prints in fig. 13 recorded at 40× magnification.

Albumen was usually coated onto untreated paper substrates, causing the photographs to exhibit a so-called two-layer structure that is limited to the paper substrate and albumen layer. The examination of the Dmin area of the photograph should show paper fibers of the paper substrate clearly visible under the albumen layer (fig. 15).

Many old, professional portrait albumen photographs were retouched to eliminate the visual imperfections of the negative or those created during printing and processing. Retouching was also done to enhance or suppress some visual features of a photographed subject or its surroundings. Originally well-retouched photographs did not show any clearly visible retouching marks. The retouching material was usually more resistant against light fading than the image material of the albumen photograph. Today many old, retouched photographs exhibit clearly visible retouching marks superposed over the slightly faded original image (fig. 16).

Figure 15 Paper fibers visible under the albumen layer of a photograph examined using a high-power loupe or microscope (80× magnification).

Figure 16 Retouching marks visible in the image area of a slightly faded photograph.

Analytical Signatures

XRF

XRF analysis of an unmounted, well-processed, and gold-toned albumen photograph usually shows only the presence of silver (Ag), gold (Au), and some, if any, fillers and impurities contained in the paper substrate (fig. 17).

The standard processing of albumen photographs usually called for gold toning before fixing. The resulting toned albumen photographs exhibited a shift of color toward darker-brown or violet-black tonalities. Figure 18a shows a light print and a dark print of a nineteenth-century gold-toned, unmounted albumen photograph. Figures 18b and 18c show the XRF spectra recorded from the dark area of each image. The spectra show the presence of both the image-forming silver: spectral peaks of silver (Ag) Kα at 22.16 keV, Kβ at 24.94 keV, together with the visible Ag Lα at 2.98 keV, and gold (Au) toner (Au Lα at 9.71 keV and Au Lβ at 11.44 keV). Semiquantitative XRF analysis shows that the amount of gold in the Dmax area of the darker photograph is about 2x higher than in the lighter photograph.

Gold toning was by far the most common procedure used when toning albumen prints; however, some toning was also done using platinum (Pt) and a combination of gold and platinum, as in photographs found in an album of the French photographer Eugène Durieu (fig. 19). Platinum toning imparted a dark green-gray tonality to the albumen print. Platinum toning is identified based on the presence of two characteristic spectral peaks of platinum (Pt Lα at 9.44 keV and Pt Lβ at 11.07 keV) (fig. 20). Of the 105 photographs in the Durieu album, 72 were toned using platinum. Several photographs in the album were also the result of combination toning using both gold and platinum.

Another interesting example of gold-platinum combination toning was discovered during the analysis of Felice Beato's photographs from his travels to Japan, Korea, Burma, China, and India. Some of his negatives were sent to England to be printed. The printing and processing were done by the Hering Photographic Printing Company. Only photographs from that printing showed

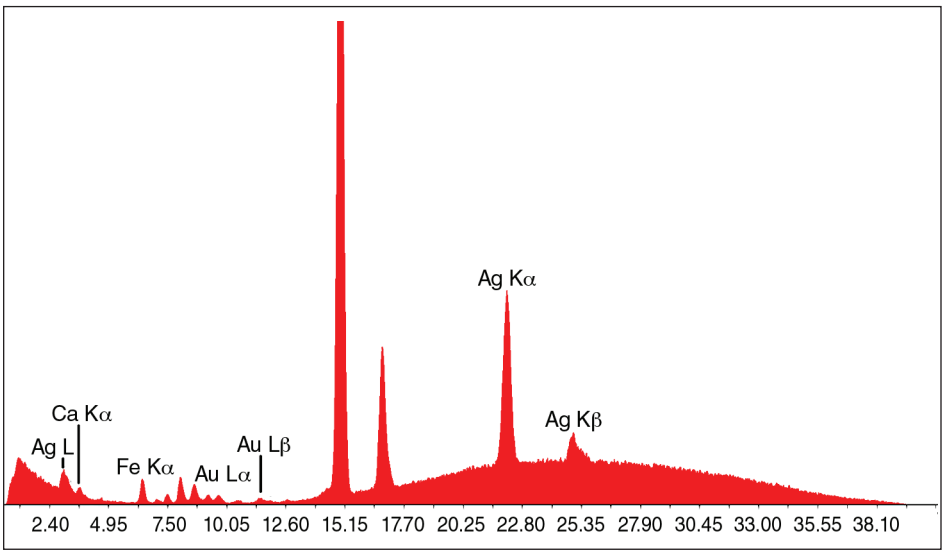


Figure 17 XRF spectrum of a gold-toned, unmounted albumen photograph showing the presence of silver and other impurities.

Figure 18a Light print (left) and dark print of 19th-century gold-toned, unmounted albumen photograph.

Figure 18b XRF spectrum of the dark image area of the light print.

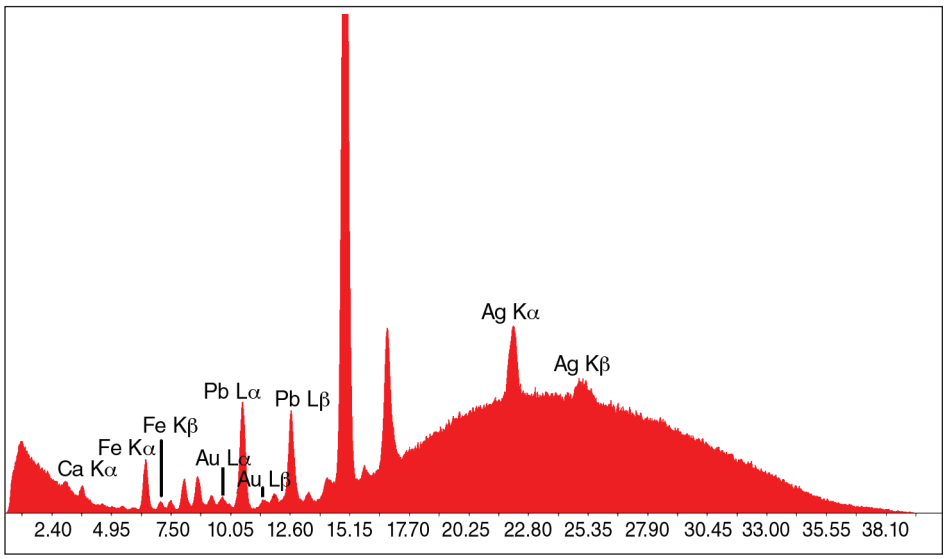


Figure 18c XRF spectrum of the dark image area of the dark print.

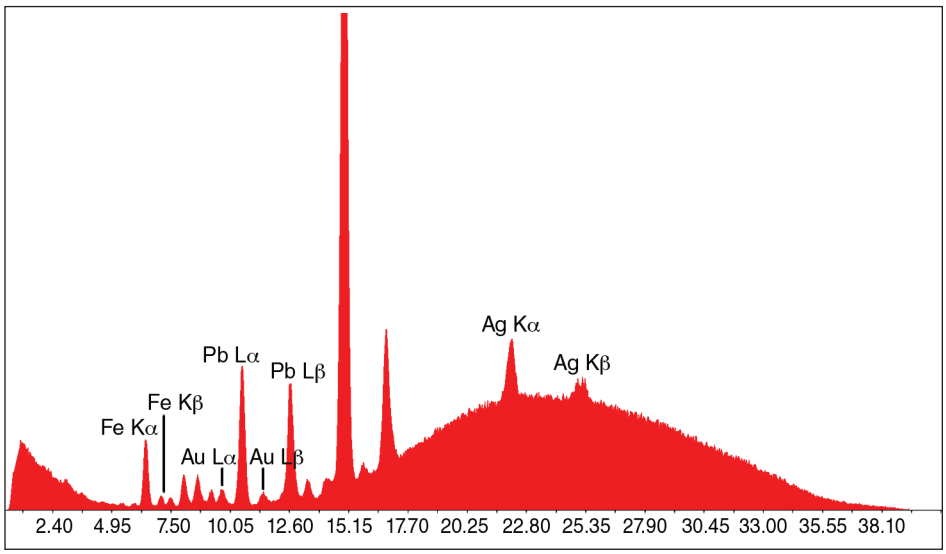


Figure 19 Eugène Durieu, Portrait of a female, c. 1855, Platinum-toned albumen photograph, 7.4 × 5.5 cm (GEH Durieu album print, reg. 1979:0079:0020). Courtesy of George Eastman House, International Museum of Photography and Film.

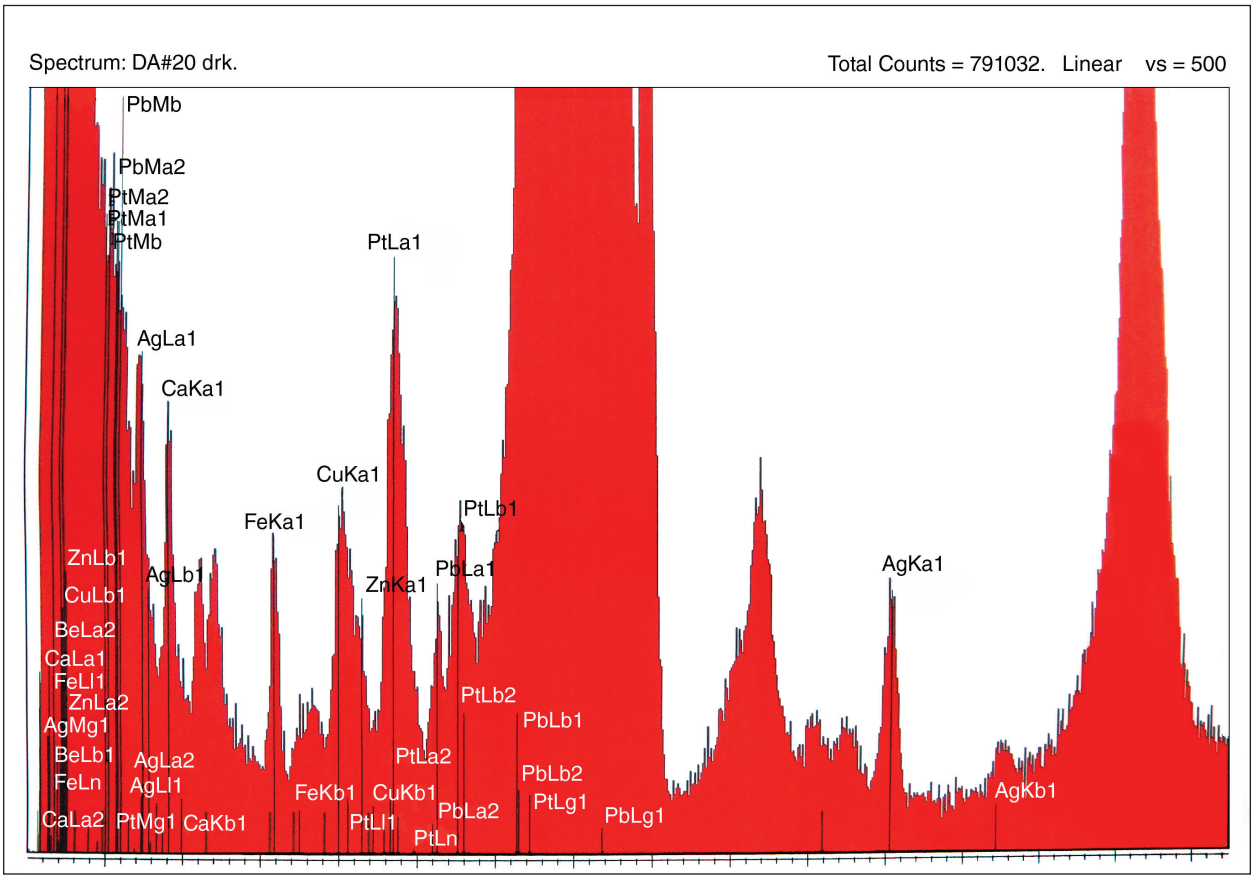


Figure 20 XRF spectrum of the photograph in fig. 19.

the use of combination gold-platinum toning during XRF analysis. The resulting photographs did not show any different color or tonality from other photographs in the series, and a visual examination alone would not be able to detect the toning procedure. Figure 21a shows Beato's albumen photograph that was printed in England using a gold-platinum combination. Figure 21b shows its XRF spectrum.

In the 1850s some photographers started to experiment with uranium in the toning of albumen photographs (fig. 22). The XRF spectrum shows the presence of both silver (Ag) and uranium (U) (spectral peaks of U Lα at 13.61 keV and Lβ at 17.21 keV) (fig. 23). The results of the analysis clearly indicate that uranium was used as a toning element.

Figure 21a Felice Beato, *Views of China* (Interior of North Fort showing Chinese encampment), 1861. Albumen silver print toned using combination gold-platinum toning, 24.4 × 85.9 cm overall. The J. Paul Getty Museum, Los Angeles, Partial gift from the Wilson Centre for Photography.

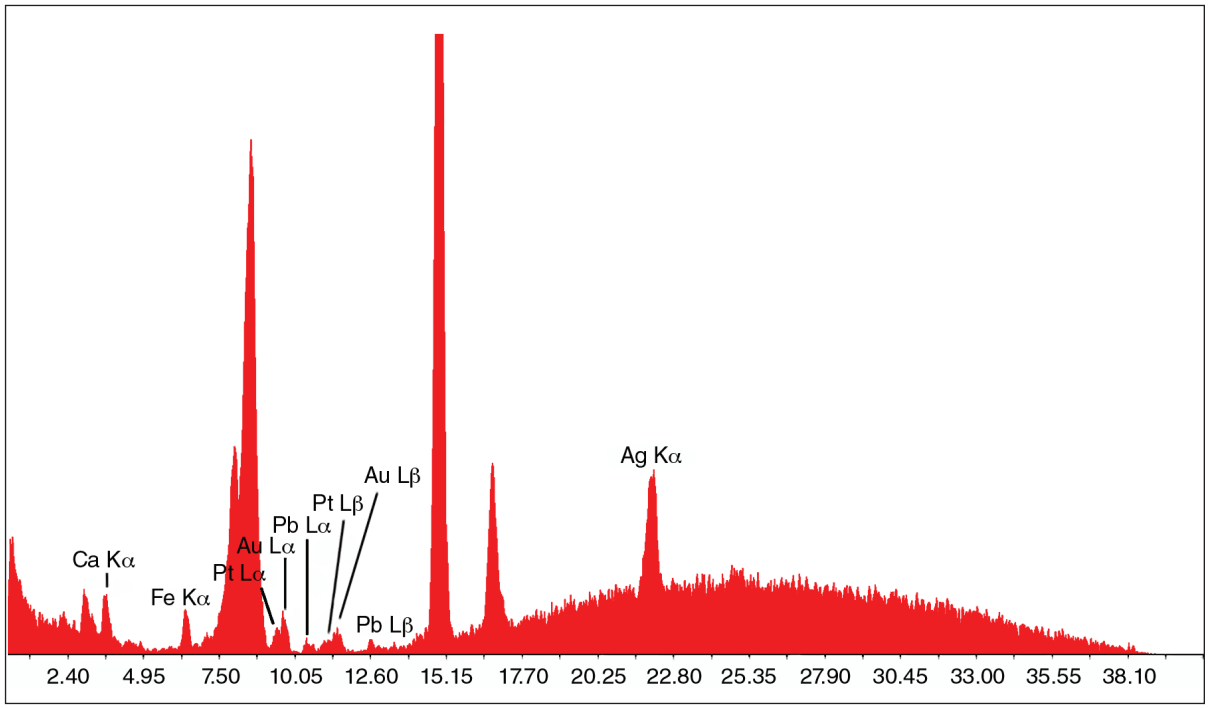


Figure 21b XRF spectrum of the photograph in fig. 21a.

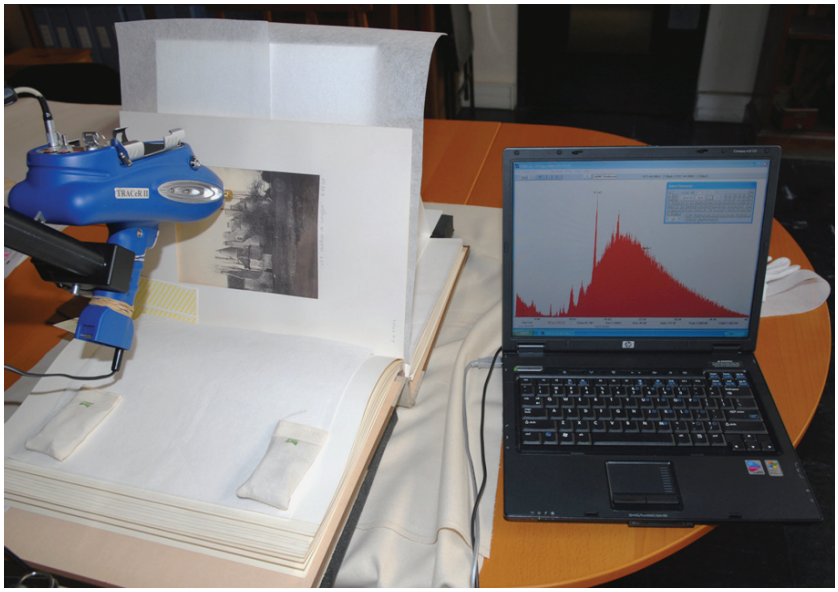


Figure 22 Materials and equipment used in XRF analysis of Brébisson's uranium-toned photograph from the collection of the Bibliothèque nationale de France, performed at the Société française de photographie, Paris. Brébisson album print reg. no. Eo 108.b V-2 no. 9. Bibliothèque nationale de France.

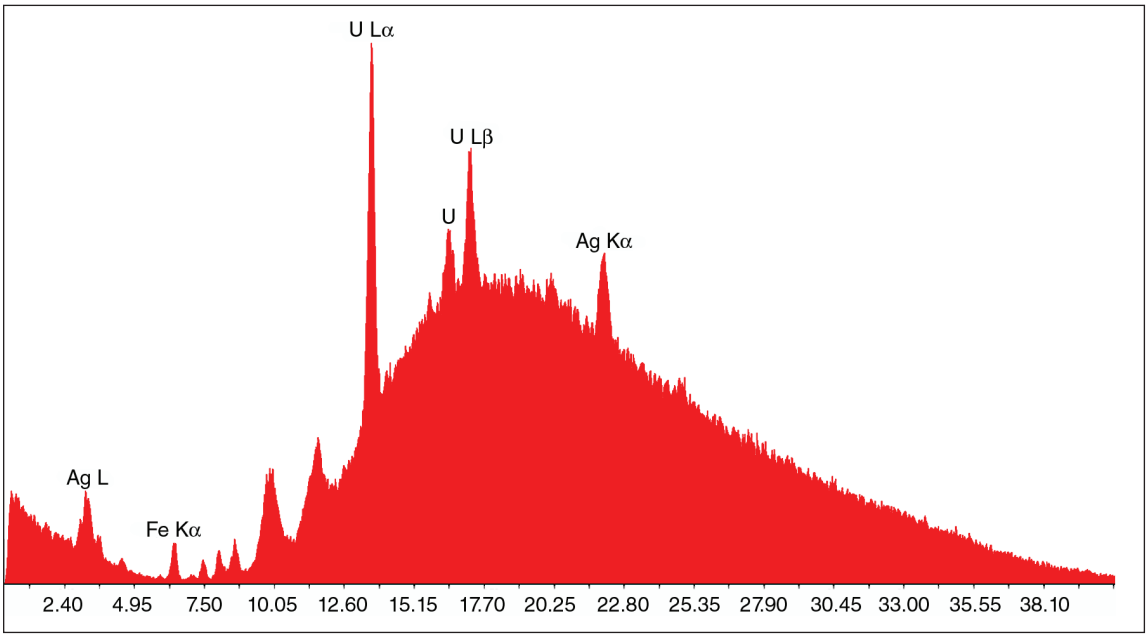


Figure 23 XRF spectrum of the uranium-toned albumen photograph in the album shown in fig. 22.

FTIR

ATR-FTIR is the most important analytical technique that can be used when identifying the albumen binder in albumen photographs. It can differentiate between albumen and gelatin, detect the presence of surface coatings, and in many instances identify major components of coating materials. Figure 24a shows a CC with a mounted albumen photograph; figure 24b shows its ATR-FTIR spectrum.

The ATR-FTIR spectrum of the photograph shows the presence of a proteinaceous binding medium that can be identified by the Amide I spectral peak at about 1626 cm^{-1} and the Amide II

Figure 24a Late 19th-century albumen photograph mounted on a CC.

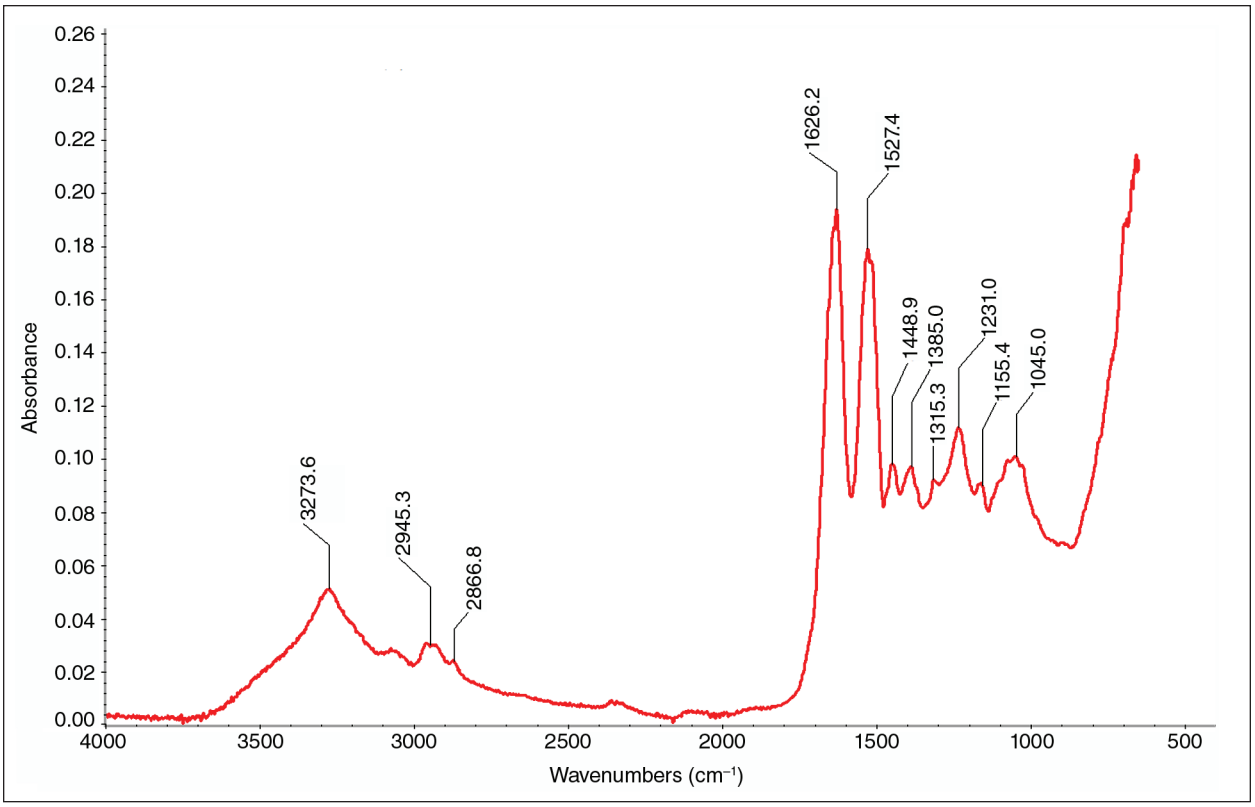


Figure 24b ATR-FTIR spectrum of the albumen photograph in fig. 24a.

spectral peak around 1527 cm^{-1}. These two spectral peaks are typical for a number of different proteins (albumen, gelatin, casein, etc.). A detailed inspection of the spectral region between 1470 and 1250 cm^{-1} is needed when trying to differentiate between albumen and gelatin photographs.

Figure 25a shows an example of a nineteenth-century gelatin POP photograph mounted on a CC; figure 25b shows its ATR-FTIR spectrum. The spectrum shows the presence of both the Amide I and Amide II spectral peaks but slightly different spectral features between 1470 and 1250 cm^{-1}.

Figure 25a Late 19th-century gelatin POP photograph mounted on a CC.

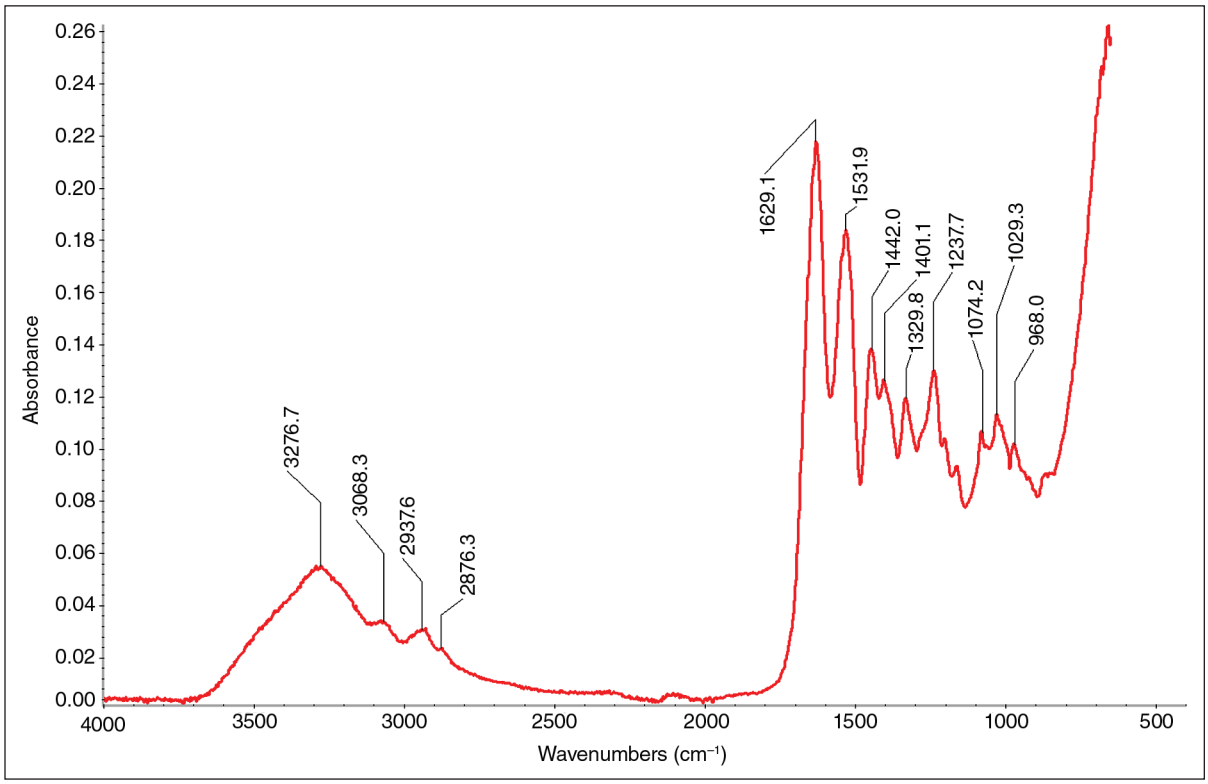


Figure 25b ATR-FTIR spectrum of the gelatin photograph in fig. 25a.

Figures 26a and 26b show close-ups of the spectral region between 1470 and 1250 cm^{-1} for the photos in figures 24a and 25a.

The ATR-FTIR spectrum of the albumen photograph shows two spectral peaks of about the same intensity at 1448 and 1385 cm^{-1}. The spectrum of the gelatin photograph shows not two but three spectral peaks at 1442, 1401, and 1329 cm^{-1}. The intensity of the spectral peaks at 1442 and 1401 cm^{-1} are also not the same. The first spectral peak of the region is usually larger than the second one. There may be a slight shift between the recorded positions of these spectral peaks and a slight difference between peak ratios, but this spectral "trend" holds rather well when analyzing uncoated albumen and gelatin photographs with relatively high concentrations of proteinaceous binders. The analysis of photographs with low concentrations of albumen and gelatin (albumen paper prepared using a highly diluted albumen, matte albumen, or gelatin) might show both the Amide I and Amide II spectral peaks, but the intensity of the peaks in the critical 1470 to 1250 cm^{-1} region of the spectrum might be too low to allow for clear identification of the binder in the photograph.

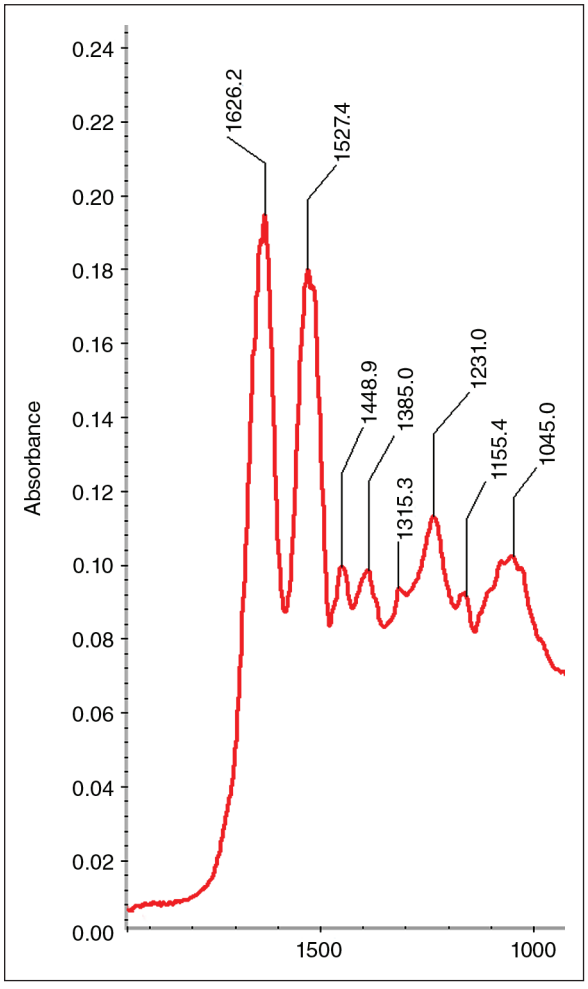


Figure 26a Detail of the 1470 to 1250 cm^{-1} spectral region for fig. 24a.

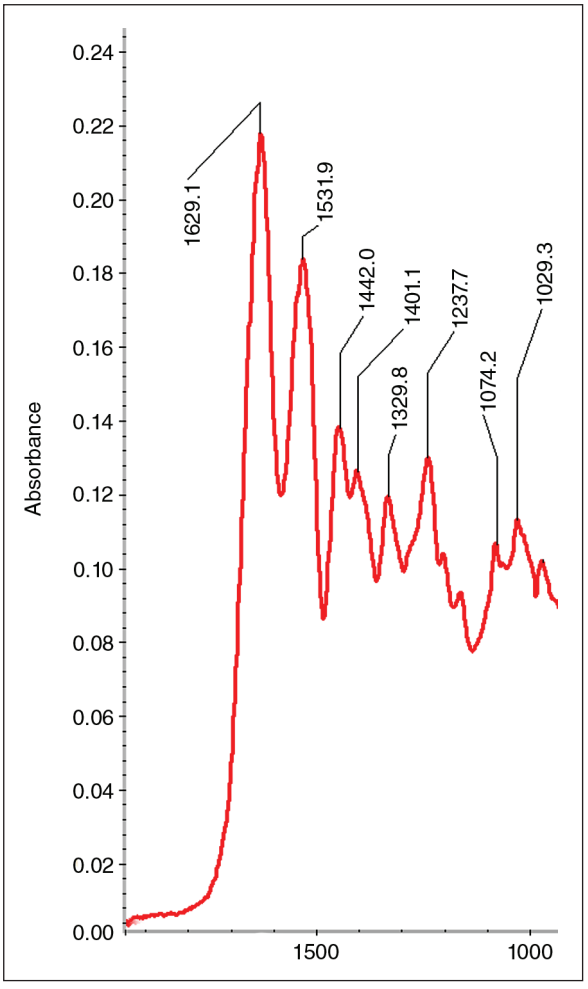


Figure 26b Detail of the 1470 to 1250 cm^{-1} spectral region for fig. 25a.

As stated above, after about 1870 the preference of the public and customers of photographic studios turned toward glossy albumen photographs. In response, photographers and the photographic materials industry introduced double-coated albumen photographic paper that was known to yield high-gloss albumen photographs.

ATR-FTIR analyses of an 1867 albumen photograph and an 1878 albumen photograph (fig. 27) show that the analysis is able to allow for assessment of the thickness of the albumen layer in the photographs. The ATR-FTIR spectra of both photographs can be compared in figures 28a and 28b.

The relative thickness of the albumen layer can be assessed by measuring the ratio between the Amide I (~1630 cm^{-1}) spectral peak, representing albumen, and the spectral envelope of the cellulose substrate around 1020 cm^{-1} of the albumen print. The thicker albumen layer attenuates the signal of cellulose and makes it less intense. Even a visual comparison of the two spectra (see figs. 28a, 28b) allows one to assess which photograph has a thicker albumen layer.

Figure 27 Two albumen CDV photographs, produced in 1867 (left) and 1878.

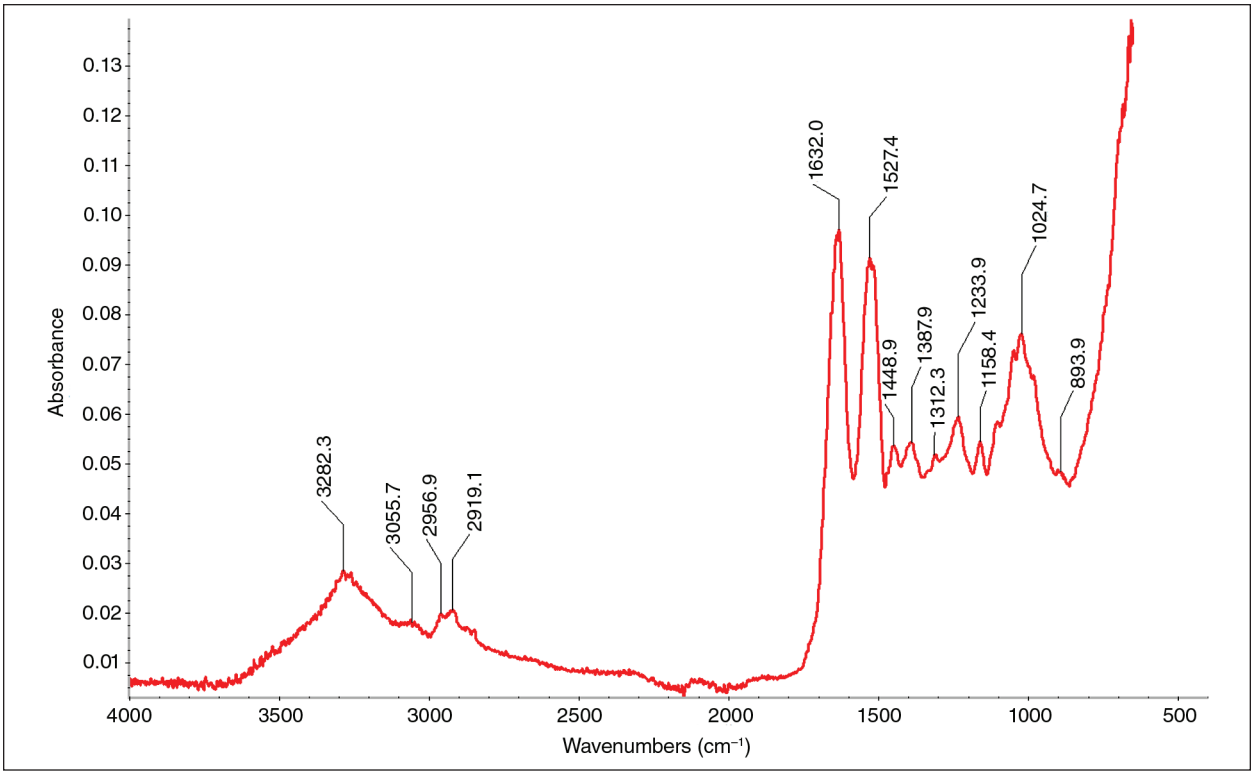


Figure 28a ATR-FTIR spectrum of the 1867 albumen photograph in fig. 27.

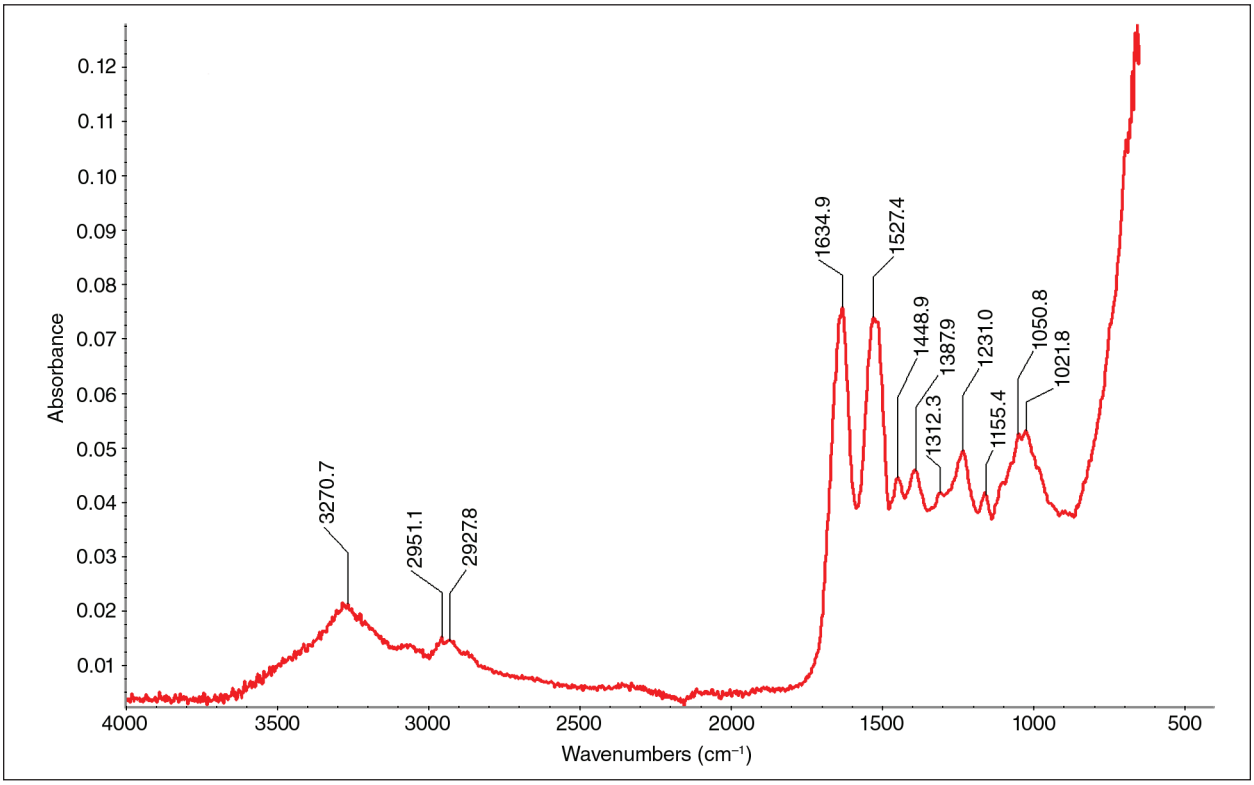


Figure 28b ATR-FTIR spectrum of the 1878 albumen photograph in fig. 27.

Most unmounted albumen photographs consist of a thin paper substrate coated with a thin or very thin layer of albumen containing the imaging and toning metals. The albumen layer is so thin that the infrared beam of the ATR-FTIR spectrometer, in most cases, penetrates it and also interacts with the paper substrate of the photograph. The presence of the cellulose-based paper substrate shows up in the spectra of albumen photographs as a more or less pronounced spectral envelope of cellulose between 1250 and 850 cm^{-1}.

The thicker albumen layer of the 1878 photograph attenuates more of the signal of the cellulose than the thinner albumen layer of the 1867 albumen photograph (see fig. 27). As a result, the spectral envelope of the cellulose around 1020 cm^{-1} is less intense for older, single-coated albumen photographs.

Early albumen printers experimented with diluted albumen when preparing the paper as a way to avoid the glossy appearance that was not agreeable at that time to the public and to customers who were accustomed to the matte surface appearance of widely used salt prints. Floating paper on a bath of salted, diluted albumen produced albumen paper lean on albumen. When used for printing, such a photographic paper produced less glossy or almost matte photographs that closely resembled previously common salt prints. This greatly complicated the situation for photograph curators, photograph conservators, and conservation scientists when trying to identify and categorize a large set of nineteenth-century albumen-based photographs. Further complicating matters was the fact that in many types of nineteenth-century writing and photographic papers, gelatin was also used as an internal binder in the paper (fig. 29). This represents an extreme case for 1840s paper. Most other analyzed papers show only a very low intensity Amide I peak. In some cases the concentration of the internal binder was so low that even the Amide I, otherwise a very intense spectral peak, was almost invisible.

The ATR-FTIR analysis of a large number of different salt paper, albumenized, and albumen photographs led to the development of an objective, ATR-FTIR-based criteria for naming and categorizing different types of albumen-based photographs. The ATR-FTIR spectrum in figure 30 is typical of single-coated albumen photographs produced between 1855 and 1870.

The spectral intensities of the Amide I spectral peak at 1640 cm^{-1} and the peak at the shoulder of the spectral envelope of cellulose at 1100 cm^{-1} are similar. When analyzed using the ATR-FTIR spectrometer, the albumen photographs produce similar ratios of both peaks and can be categorized as single-coated albumen photographs.

The ATR-FTIR spectrum in figure 31 represents a set of later (after about 1870) albumen photographs containing a larger concentration of albumen binder than can usually be produced using just a single albumen coating. The ATR-FTIR spectra of these types of albumen photographs have a shoulder peak from the cellulose spectral peaks at 1109 cm^{-1} of lower or much lower intensity than the corresponding Amide I peak at 1646 cm^{-1}. Albumen photographs yielding similar spectra can be described as albumen-rich or double-coated albumen photographs.

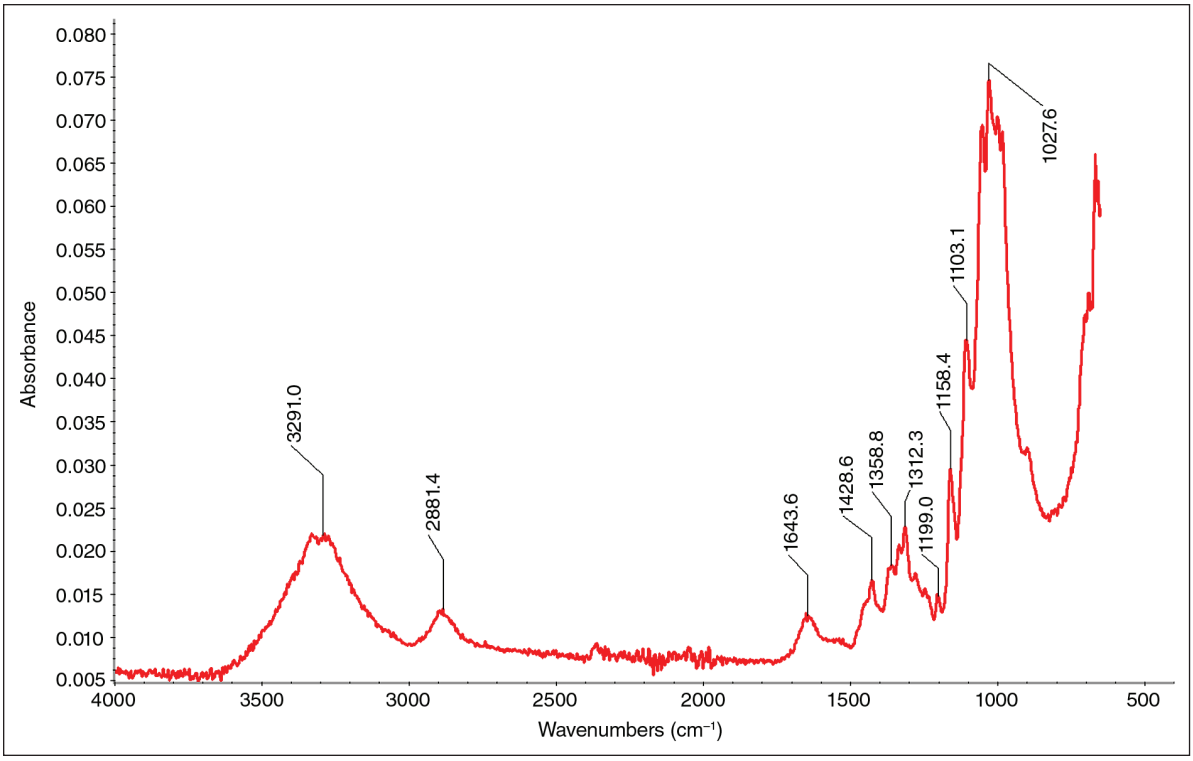


Figure 29 ATR-FTIR spectrum of 1840s Talbotype paper showing a weak spectral signal of gelatin used as an internal binder.

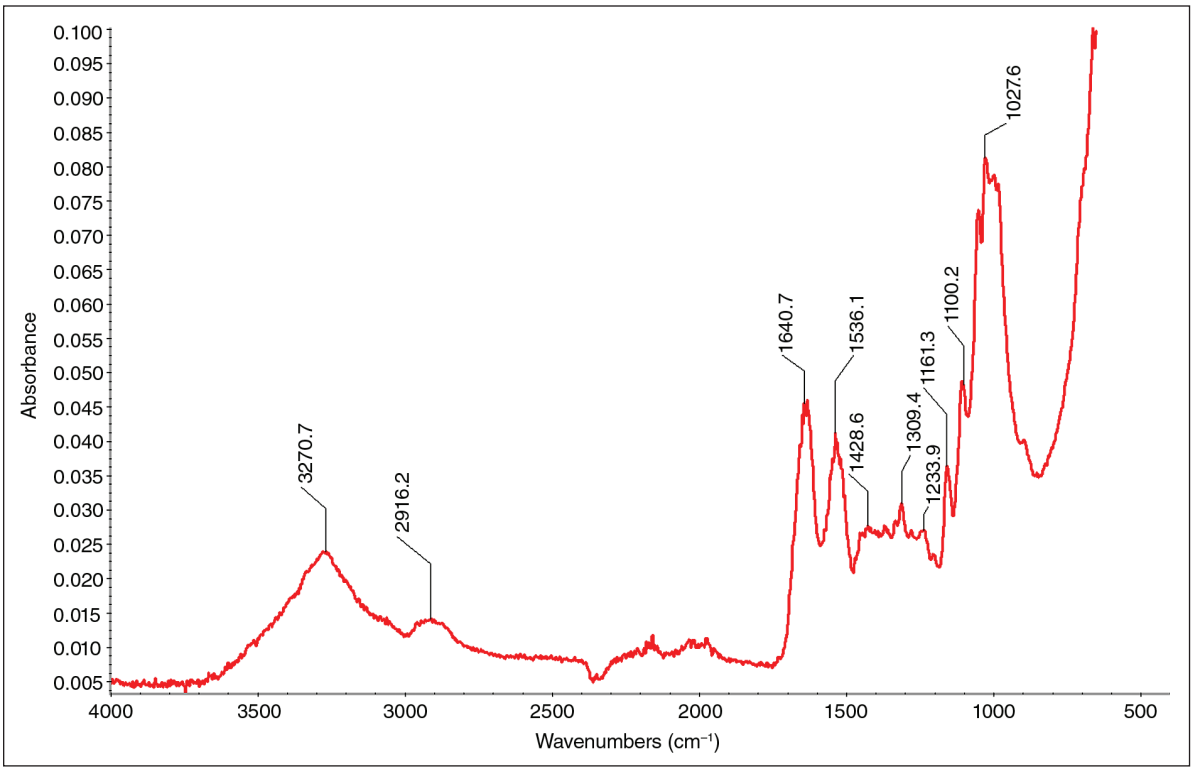


Figure 30 ATR-FTIR spectrum of a typical single-coated albumen photograph.

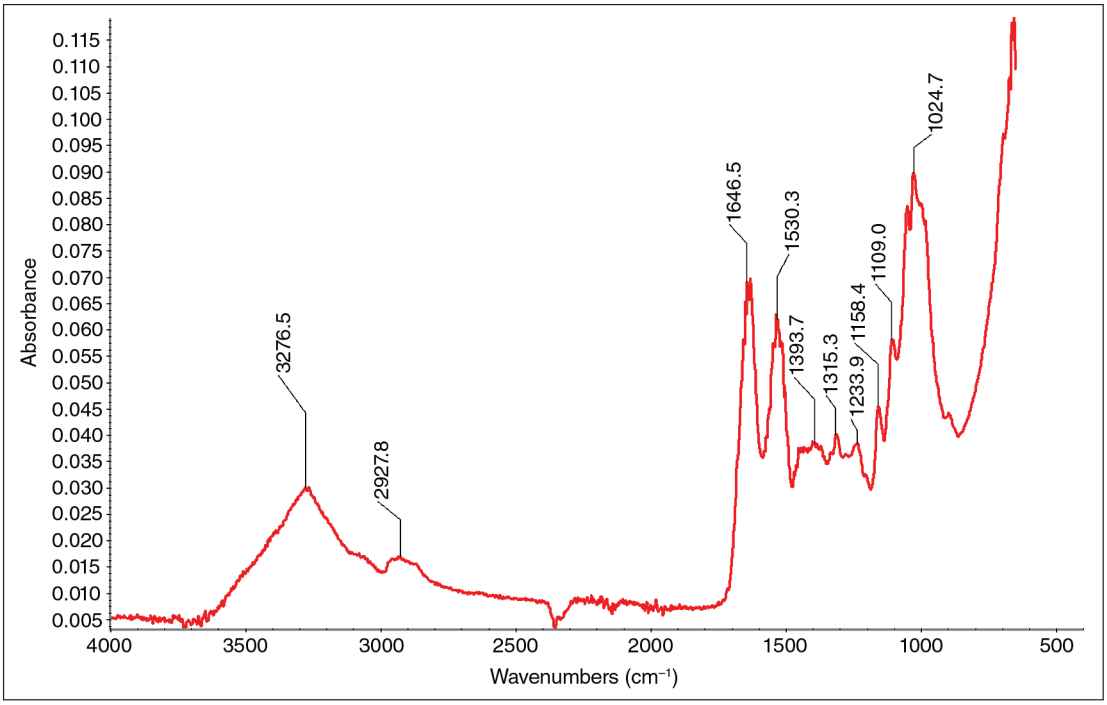


Figure 31 ATR-FTIR spectrum of a typical double-coated albumen photograph.

All albumen-based photographs that contain a much lower concentration of albumen were probably produced using diluted albumen and can be called albumenized photographs. The ATR-FTIR spectra of these photographs (figs. 32a–32c) exhibit smaller but still clearly identifiable Amide I peaks (at 1640 cm^{-1}) together with a pronounced shoulder peak of the cellulose envelope at ~1100 cm^{-1}.

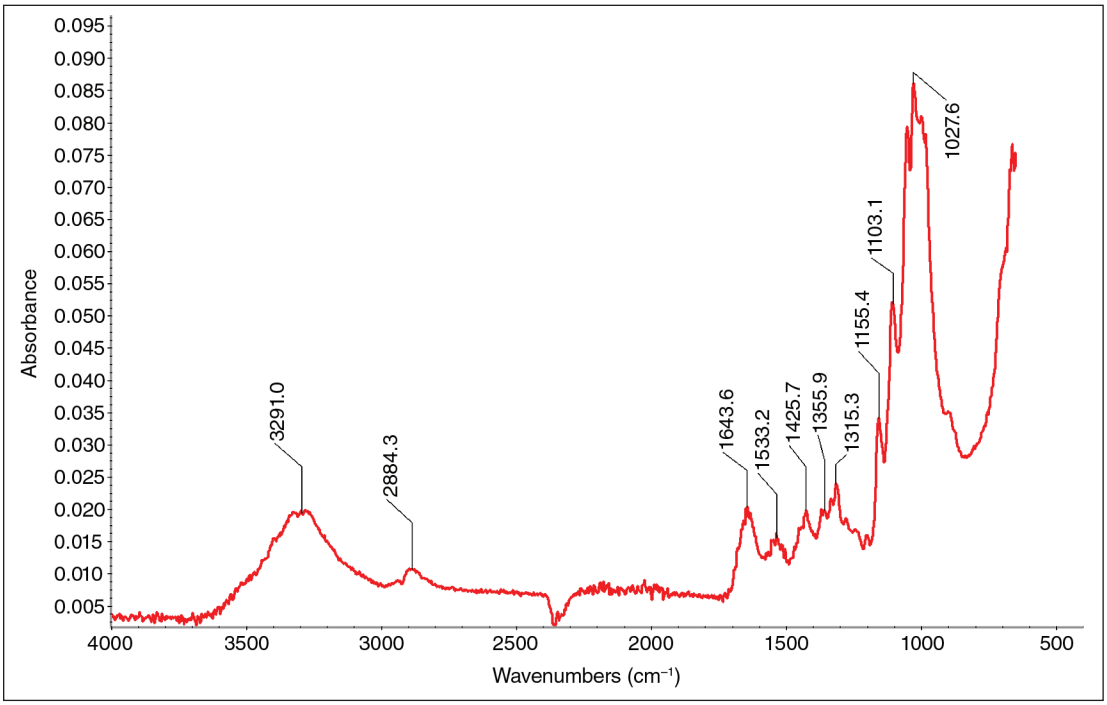


Figure 32a ATR-FTIR spectrum of an albumenized photograph.

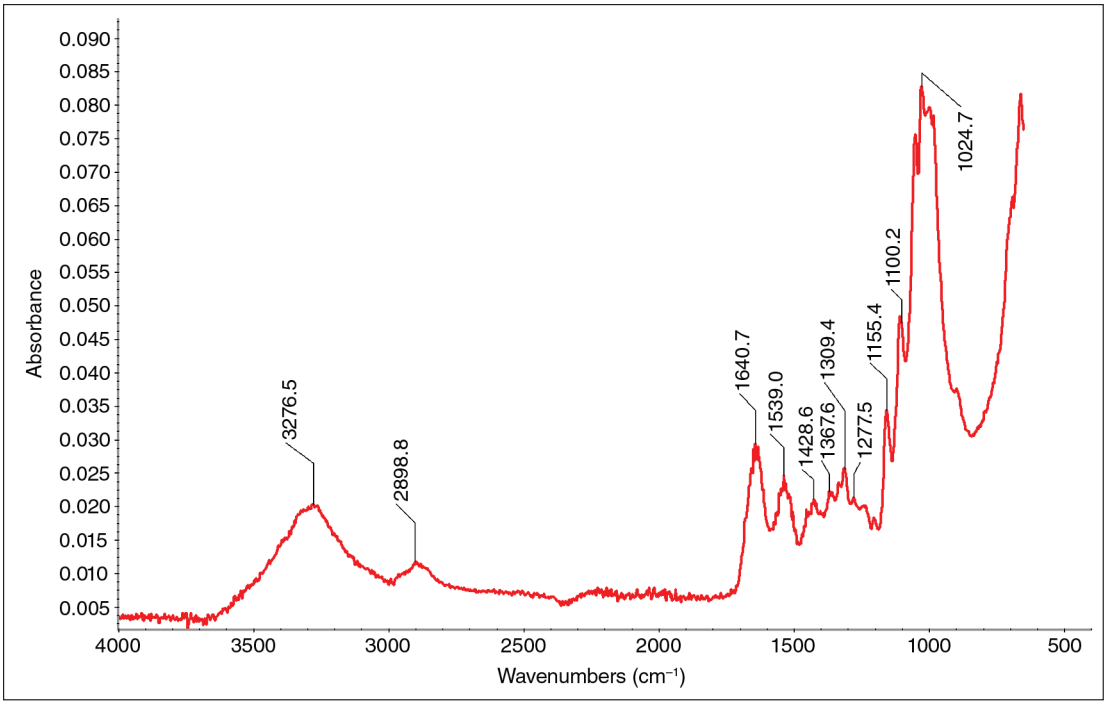


Figure 32b ATR-FTIR spectrum of an albumenized photograph.

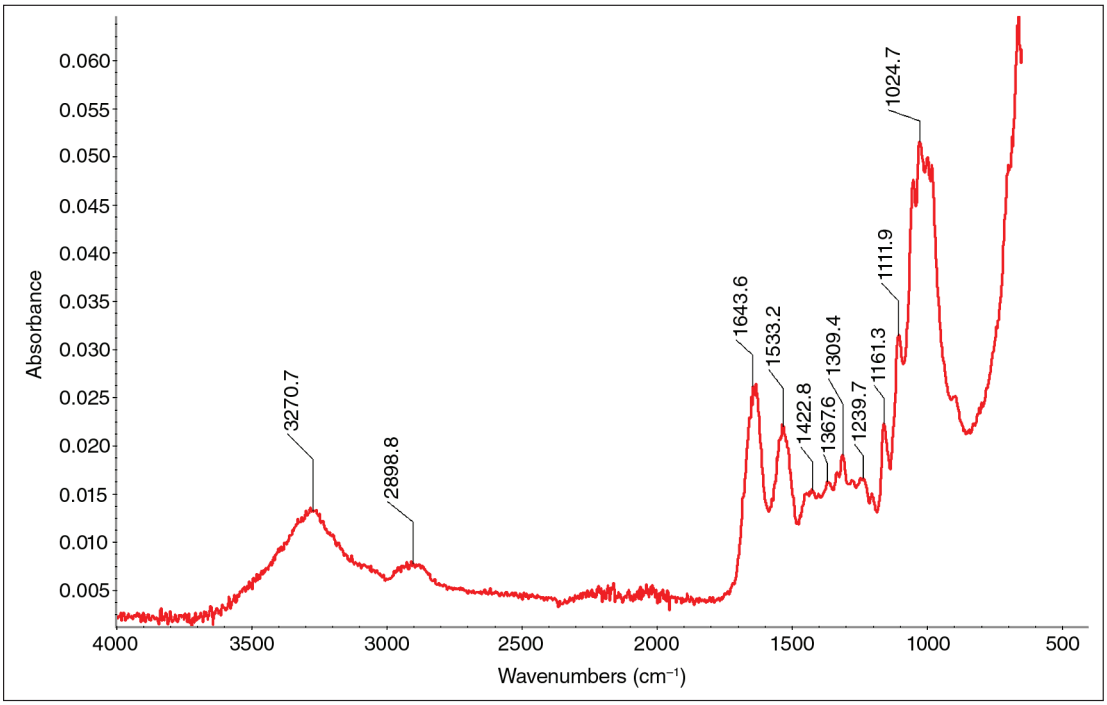


Figure 32c ATR-FTIR spectrum of an albumenized photograph.

The methodology described above for identifying different categories of albumen-based photographic images is powerful and objective, but caution must be exercised when dealing with images that have analytical signatures on boundaries of different categories of photographs. Unlike XRF spectrometry, ATR-FTIR spectrometry is not a technique that allows for simple quantitative interpretation of analytical results. The method of albumen preparation (fresh/

putrefied), the presence of internal sizing, and the problem of porosity of the paper substrate—to name the most important factors—might modify the apparent thickness of the albumen layer and the intensity of the observed spectral peaks.

Other Analytical Signatures

Enzyme-Linked Immunosorbent Assay

Another technique that can aid in and help confirm the presence of albumen in photographs is enzyme-linked immunosorbent assay (ELISA). ELISA is an assay technique used for detecting and quantifying the amount of various substances (proteins, antibodies, hormones, etc.) in a sample. For the detection of albumen, the technique uses antibodies specific to ovalbumen, the albumen protein in chicken eggs, which are bound in the wells of a microplate (fig. 33). Albumen, if present in the sample of interest, will bind to the antibodies on the plate. Either the bound albumen-antibody complex will directly cause a color change in the solution, or an additional substance will be added that binds to the albumen-antibody complex, causing a color change. The absorbance of the solution is then measured at an appropriate wavelength using a spectrophotometer. The color change is compared to a series of standard albumen solutions to determine if the solution contains albumen. The amount of albumen can be determined based on the absorbance of the solution as compared to the absorbance of the standard solutions.

To determine the presence of albumen in a photograph, a dry cotton applicator is used to swab the surface of the photograph (fig. 34). The typical surface of an albumen photograph has cracking, which results in raised and broken portions of the emulsion layer on the surface that are then picked up by the dry swab (fig. 35).

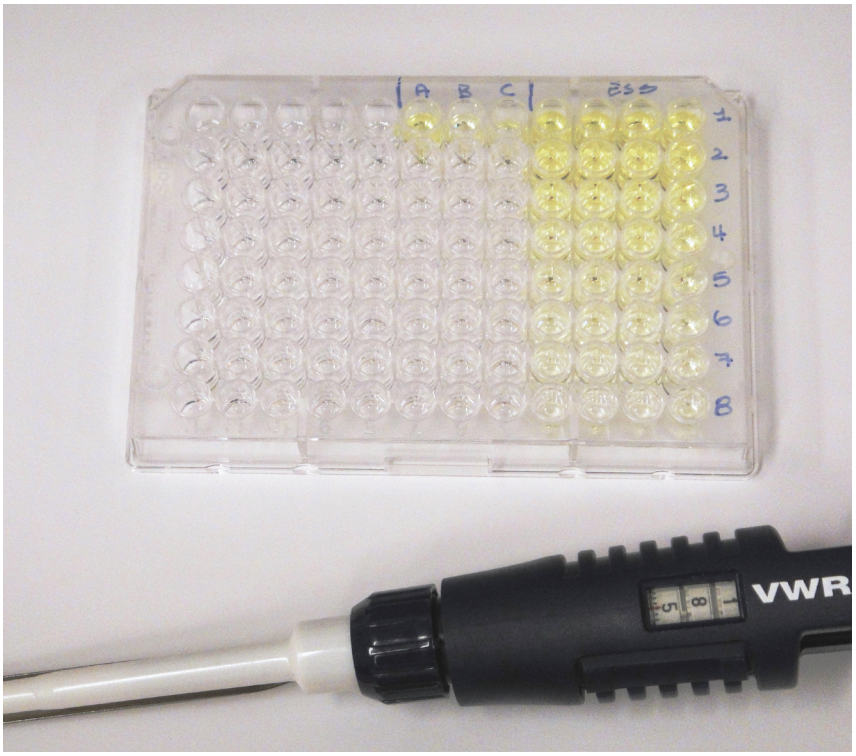


Figure 33 Microplate and autopipette used for the preparation of albumen samples for ELISA assays.

Figure 34 Dry swabbing of the surface of a photograph to determine the presence of albumen using ELISA.

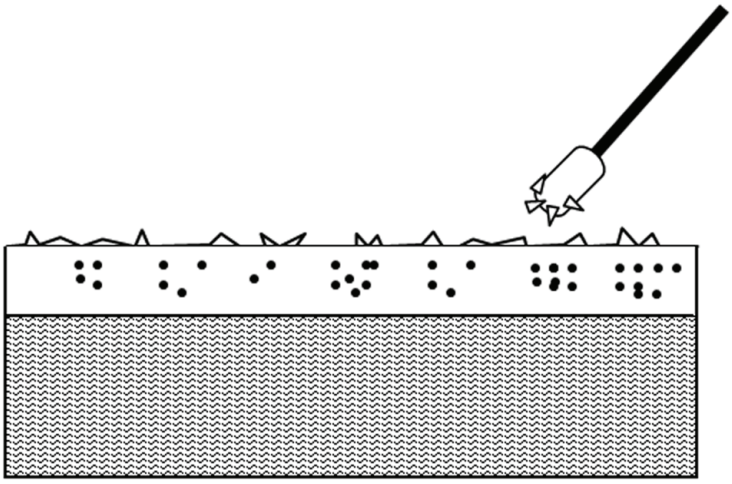


Figure 35 Schematic representation of the effectiveness of dry swabbing on the cracked surface of an albumen photograph.

Swabbing the surface using very light pressure, similar to dusting, can remove enough material from some of these raised surfaces for the test without causing any visible damage to the photograph. The swabbed sample is then prepared and analyzed using ELISA. The detection limits for albumen are typically in the range of ~1 ng/ml but vary based on the manufacturer of the product. Because the amount of material removed from the surface varies based on several factors (pressure applied during swabbing, surface condition, albumen concentration, etc.), quantitative results are not possible unless the amount of material removed can be standardized. A negative result is not a confirmation that there is no albumen in the photograph; rather, the amount of material removed during the dry swab procedure may not contain enough albumen to obtain a positive result.

Identification Problems

Post-Process-Treated Albumen Photographs

Albumen photographs were toned before fixing, so the toning step was an integral part of the darkroom processing of albumen photographs. The albumen process was introduced during the early 1850s, when a number of photographers discussed, researched, and experimented with different chemical procedures that could be used to protect the photogenically developed silver of albumen photographs against environmental effects, pollutants, and moisture that were considered potential sources of many instances of photograph fading.

Varnishing and surface coating of processed albumen photographs was one of the procedures recommended for increasing the photographs' longevity. A number of different varnishes and coatings were published in nineteenth-century photographic literature and can be found in various types of photographic collections.

Figure 36 shows a nineteenth-century CC photograph coated using a beeswax-based varnish. The ATR-FTIR spectrum (fig. 37) of this photograph shows the presence of both albumen and cellulose. Besides all of the usual spectral features of a single-coated albumen photograph, the spectrum also shows unusually intense CH spectral peaks (CH, CH2, and CH3 bonds around 2913 cm^{-1}). The comparison of these spectral peaks in the albumen photographs shown and discussed above reveals that these peaks are much more intense and well separated. The presence of these spectral peaks in the spectra of albumen photographs indicates the presence of organic molecules other than those belonging to the albumen layer. A detailed inspection of the spectrum also identifies the 1739 cm^{-1} spectral peak that is, in this case, rather weak but still identifiable as a shoulder on the left side of the intense Amide I peak. This spectral peak is typical for many organic materials containing so-called ester bonds (-CO-O-). These chemical bonds are part of the internal chemical structure of beeswax, which is an ester of fatty alcohols and fatty acid. Beeswax-based varnishes were used to protect albumen photographs. It is quite reasonable, based on the ATR-FTIR analysis, to interpret this spectrum as one of a beeswax-coated albumen photograph.

Some photographers objected to the slightly yellow tonality of unbleached beeswax and instead used bleached beeswax or a varnish made of paraffin wax. Typical recipes called for dissolving white paraffin wax in kerosene (a mixture of aliphatic hydrocarbons). When a slightly matted photograph (fig. 38) was analyzed, ATR-FTIR spectrometry detected the presence of spectral features similar to those observed in the spectrum of a beeswax-coated albumen photograph (see fig. 37). The ATR-FTIR spectrum (fig. 39) of the matte photograph shows the well-developed and sharp groups of C-H spectral peaks that are typical for coating with long and straight chains of hydrocarbons.

The only difference in the spectrum of the beeswax-coated photograph is the total absence of the ester bonds that would be present around 1739 cm^{-1}. Because there are no other prominent spectral features in the spectrum, it is possible to say that the photograph may have been coated using a paraffin-based varnish. This was confirmed by preparing and analyzing test albumen photographs coated by laboratory-prepared paraffin varnishes.

A number of authors in nineteenth-century photographic literature recommended varnishing albumen photographs with collodion (fig. 40), a reasonable recommendation. During the second half of the nineteenth century and before photographers began to accept newly developed dry

Figure 36 Albumen photograph treated with a beeswax-based varnish.

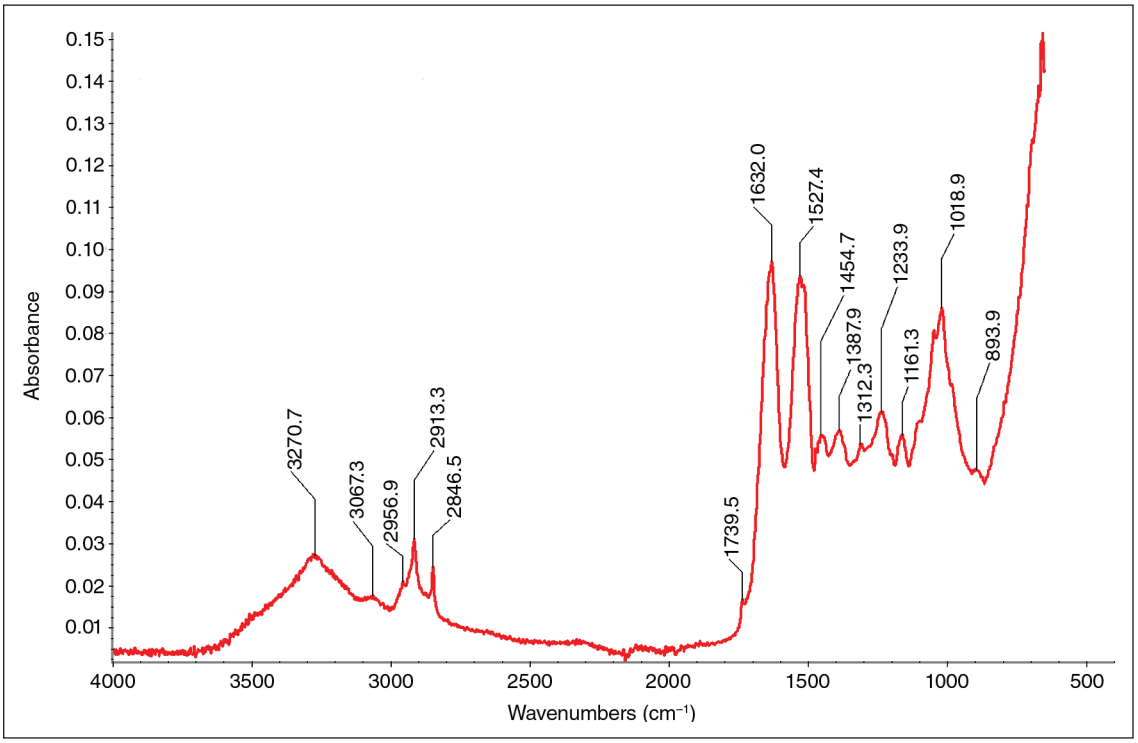


Figure 37 ATR-FTIR spectrum of the beeswax-varnished albumen photograph in fig. 36.

(silver gelatin emulsion) plates, the wet and dry collodion processes were the major processes used to produce photographic negatives. Many photographers had collodion readily available in their laboratories. Having a low permeability for moisture, collodion varnishes promised to provide protection against moisture pollutants in the air and against mechanical damage when handled.

The ATR-FTIR spectrum (fig. 41) of the photograph in figure 40 is almost identical to the ATR-FTIR spectrum of glossy collodion photographs (see Collodion on Paper section). In this case

Figure 38 Semi-matte albumen photograph.

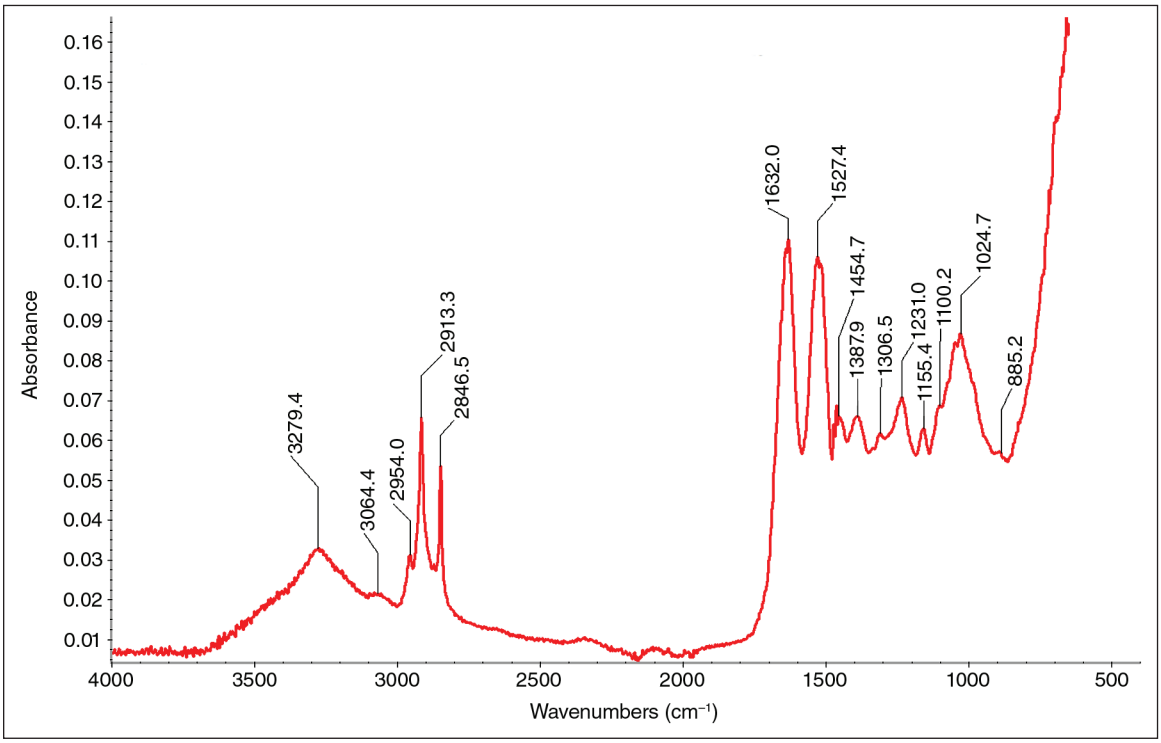


Figure 39 ATR-FTIR spectrum of the albumen photograph in fig. 38 coated with a paraffin varnish.

Figure 40 Nineteenth-century photograph heavily coated with a collodion-based varnish.

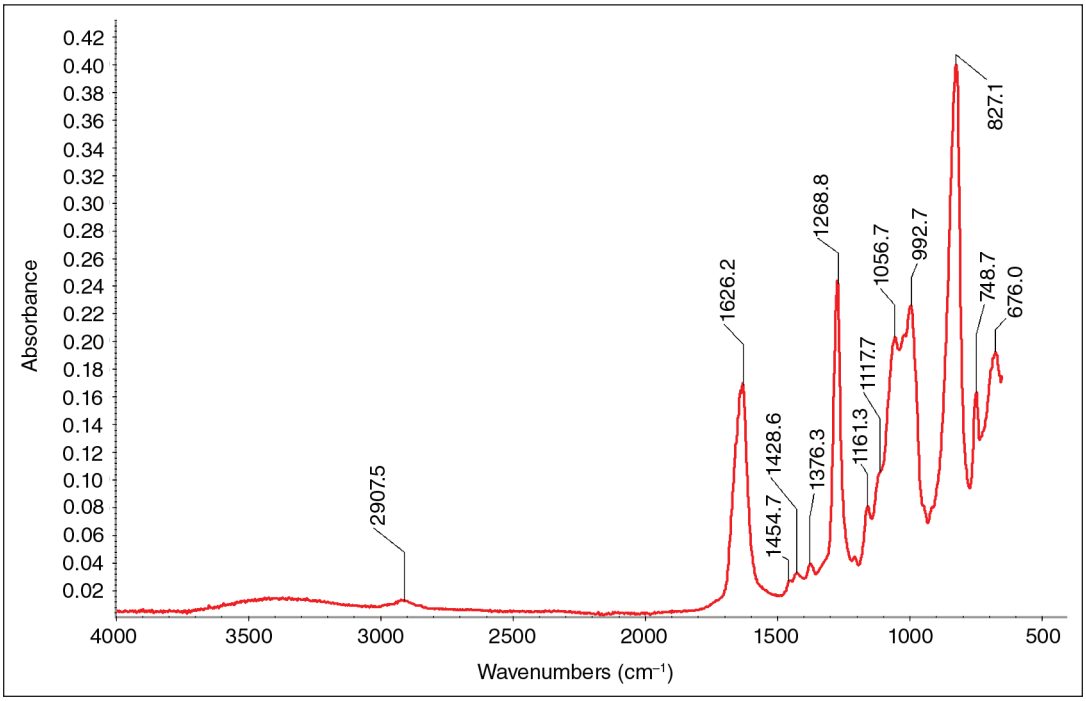


Figure 41 ATR-FTIR spectrum of the collodion-coated albumen photograph in fig. 40.

the collodion layer is so thick that the IR beam of the ATR-FTIR spectrometer does not penetrate below the collodion layer. The resulting spectrum does not contain any spectral information that would allow for the spectral identification of the albumen. The major spectral peaks are of collodion at 1626, 1268, and 827 cm^{-1}. A potential Amide I peak of albumen overlaps with the 1626 peak of collodion. The spectrum does not show any presence of the Amide II spectral peak of albumen that would be visible under a thinner layer of collodion.

The albumen photograph under the collodion layer can be identified only under a stereomicroscope. The clear and highly transparent collodion layer allows the observation of not only the paper fibers under the albumen layer but also cracks in the albumen layer. This is due to slightly different refractive indices of both the albumen and collodion layers. Figures 42a–42c show these features of the heavily collodion-coated albumen photograph at different magnifications.

Albumen photographs coated with thick layers of collodion varnish are very glossy. The thick collodion layer makes unmounted photographs very stiff. When applied to mounted photographs (CDV, CC, etc.), the collodion layer of old photographs has a tendency to curl the edges of the photograph and in many instances partially separate the photograph from the mount substrate.

Lightly collodion varnished photographs (fig. 43) are usually less glossy, and the presence of a thin collodion layer can be detected by its iridescence and by using an ATR-FTIR spectrometer. The ATR-FTIR spectrum (fig. 44) of the photograph in figure 43 contains spectral signals of both the thin collodion layer and the albumen

Figure 42a Paper fibers and cracks visible in the albumen layer under a thick coating of collodion varnish at 10× magnification.

Figure 42b Paper fibers and cracks visible in the albumen layer under a thick coating of collodion varnish at 25× magnification.

Figure 42c Paper fibers and cracks visible in the albumen layer under a thick coating of collodion varnish at 40× magnification.

Figure 43 Albumen photograph lightly varnished with collodion.

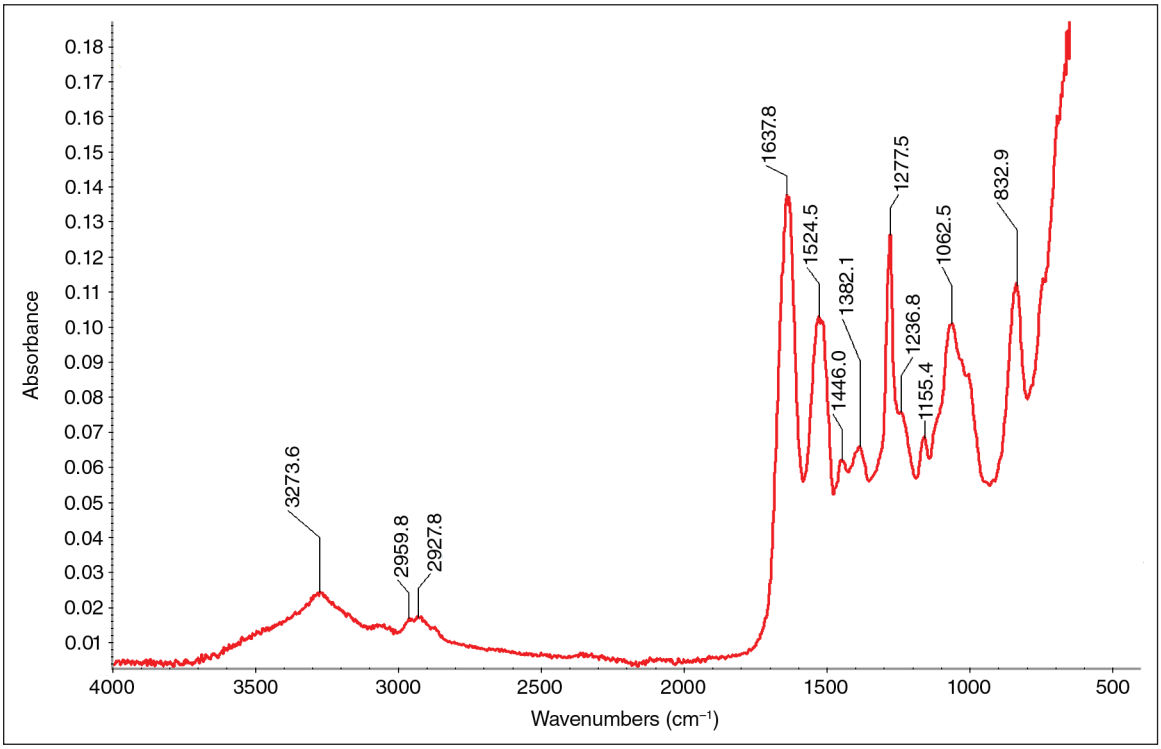


Figure 44 ATR-FTIR spectrum of the albumen photograph lightly varnished with collodion in fig. 43.

layer underneath. The spectrum exhibits well-developed Amide I and Amide II spectral peaks of albumen at 1637 and 1524 cm^{-1}, respectively. The main spectral peak of collodion at 1637 cm^{-1} overlaps with the Amide I peak of the albumen. The presence of the collodion coating can be identified by the presence of its two other main spectral peaks at 1277 and 832 cm^{-1}. When viewed under a microscope, no traces of the surface coating can be seen.

Shellac-based varnishes were and still are used in arts and crafts. Shellac was the most important furniture varnish of the nineteenth century and was used as a fixative for drawings and pastels. In photography, shellac varnish was used to coat tintypes, some glass negatives, and some salt prints and albumen photographs, such as the one in figure 45.

The ATR-FTIR spectrum (fig. 46) of this analyzed photograph shows very intense and well-developed spectral peaks of shellac. The spectrum of albumen overlaps with many of the spectral peaks of shellac, but the presence of peaks such as the main shellac peak at 1710 cm^{-1} and the secondary spectral peak of shellac at 943 cm^{-1} is free of albumen peak interferences and can be used to identify the presence of the shellac resin. For a thick shellac layer, the main spectral peak that indicates the presence of the protein layer (albumen or gelatin) is the Amide II peak at 1521 cm^{-1}.

Our laboratory experiments show that very thin shellac layers on albumen photographs do not provide spectral features that would allow for the determination of the presence of a shellac coating with a high level of certainty. The presence of a shellac coating can be assessed only by the presence of a spectral shoulder on the left side of the Amide I peak of albumen around 1629 cm^{-1} and has a characteristic shoulder at about 1710 cm^{-1} (fig. 47).

Figure 45 Mounted albumen CC varnished with shellac.

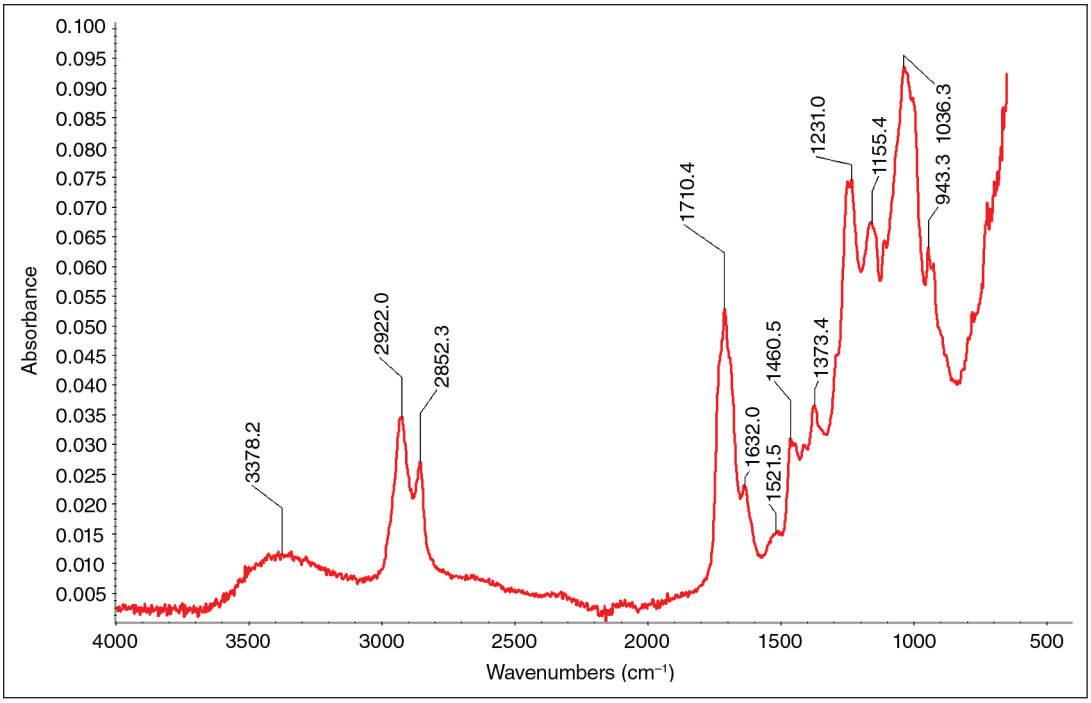


Figure 46 ATR-FTIR spectrum of the shellac-coated albumen photograph in fig. 45.

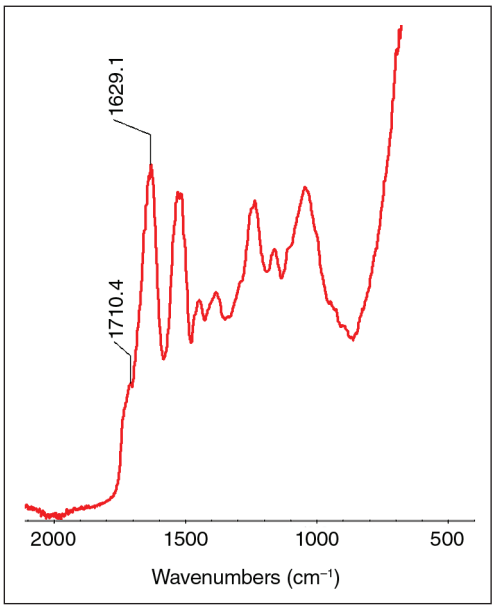


Figure 47 Detail of the ATR-FTIR spectrum of a thin shellac layer on an albumen photograph.

IMPORTANT VARIANTS OF THE ALBUMEN PROCESS

Protalbin process
Matte-albumen process

Protalbin Process

Process-Related Information

The protalbin process was a variant of the albumen process developed and patented in 1897 by Dr. Leon Lilienfeld in Vienna. Protalbin-based photographic paper was manufactured and sold by the Wiener Chemische Werke in Vienna until about 1900 and then by the Protalbin Werke, A.G. Dresden. Protalbin photographic paper was manufactured using alcohol soluble vegetable proteins. The vegetable albumen "emulsion layer" containing silver halides was machine coated on a baryta paper substrate.

The most important clue that allows for the identification of protalbin photographs is the indication of the paper type imprinted on the matting boards of many professionally produced photographs. The process was discussed in the photographic literature stating that advantages of the process included image quality and image stability, which could have made printing photographs on protalbin paper more desirable (figs. 48, 49).

Figure 48 Hermann Krone, *Seated Woman*. Protalbin process cabinet card (CC). Historical Didactic Museum of Photography, Plate 63. Hermann Krone Collection, Institute for Applied Photophysics, Technical University Dresden.

Figure 49 Detail of fig. 48 showing the printed label on the CC indicating the use of protalbin paper.

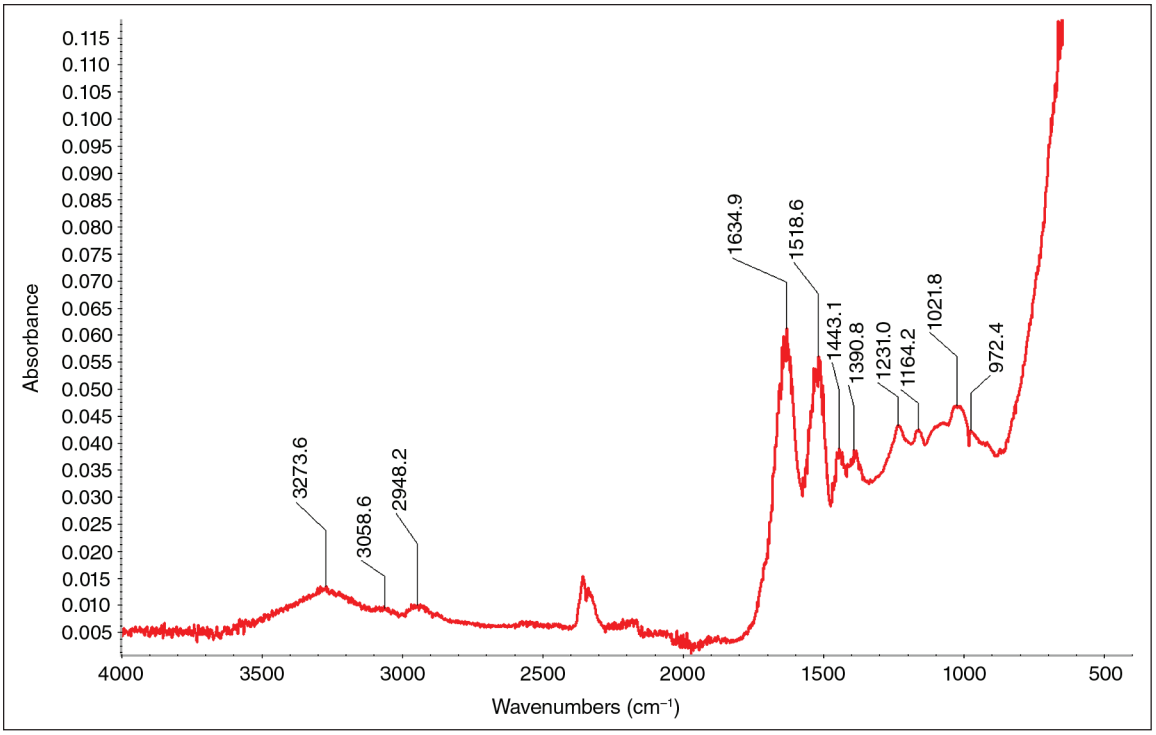


Figure 50 ATR-FTIR spectrum of the protalbin photograph in fig. 48.

Visually, protalbin process photographs (which are very rare) look like well-processed and gold-toned albumen or collodion photographs. Microscopic examination shows the presence of a baryta layer under the image layer. The baryta layer was sometimes slightly colored (blue).

XRF analysis of the mounted protalbin photograph shows the presence of silver (Ag), the main image-forming metal of the protalbin process. The dark-violet color of the image is due to gold toning, which was confirmed by XRF analysis. The presence of both barium (Ba) and strontium (Sr) confirms the microscopic identification of the baryta layer. Other chemical elements identified by XRF analysis were iron (Fe), manganese (Mn), and chromium (Cr). These chemical elements were also identified in the gray CC mounting board substrate, confirming that they were in the mount, not the photograph.

The ATR-FTIR spectrum of the protalbin process photograph (fig. 50) shows all of the major spectral peaks of albumen (there are not enough spectral differences in the recorded spectrum that would allow for identification of the vegetable albumen). Spectral peaks at 1021 and 972 cm^{-1} are typical for the baryta layer of the photograph.

Matte-Albumen Process

(Matt Albumin, Albumat, Albumon, Albumatpapier, Alboidin)

Process-Related Information

The most common way to produce matte-albumen photographs was to use diluted or highly diluted albumen. A number of experiments were carried out, and a number of recipes for making

matte-albumen photographic papers were published in the nineteenth-century photographic literature. The most important variant of the matte-albumen process was introduced in 1895 by the German photochemist A. F. Hubl (1853–1932). His matte-albumen formula was also used by several manufacturers when producing matte photographic material that could compete in appearance with the much more expensive platinum papers that started to be produced commercially in the late 1870s. Matte-albumen photographic papers were produced mainly in Europe, particularly Germany, and their commercial production ended in the late 1920s, when they were replaced by a number of matte silver gelatin photographic papers capable of yielding similar visual effects.

Matte-albumen photographic paper was prepared by mixing albumen stock with a salted solution of starch and coating the resulting mixture on a usually rough paper substrate. The resulting photographic paper was then exposed, toned, and fixed as any other albumen photograph. Toning using gold, platinum, or a combination of both produced an entire range of image colors and tonalities from reddish brown to violet black.

A matte-albumen photograph is shown in figure 51. Information on the type and manufacturer of the paper used for printing the photograph is embossed in the lower right corner of the photo (fig. 52).

Figure 51 Photograph printed on T & M matte-albumen paper.

Figure 52 Detail of fig. 51 showing the product information embossed in the lower right corner of the photograph.

Visual inspection of the photograph indicates a rather pleasing rough matte surface. The unmounted matte-albumen photographs are not as thin as unmounted glossy albumen prints, and the verso of the print shows the same surface quality as the recto. Microscopic examination shows a rough surface to the print. Consulting period product catalogs reveals that paper manufacturers offered a wide range of different matte-albumen photographic papers with different surface qualities and paper stock colors (off-white, beige, light brown, etc.). Figures 53a–53c show microscopic details of the photograph at different magnifications.

XRF analysis of an unmounted matte-albumen photograph (fig. 54) shows the very strong spectral peak of silver (Ag), typical for many POP photographs, the presence of gold (Au) toner, and a small concentration of lead that is contained uniformly within the paper substrate.

Identification of the organic binder in matte-albumen photographs using ATR-FTIR spectrometry is rather complicated and often does not produce a clear process identification on its own. The ATR-FTIR spectrum (fig. 55) of a matte-albumen print shows weak spectral peaks of Amide I and Amide II at 1649 and 1536 cm^{-1}, respectively. However, because of the low surface concentration of albumen due to absorption into the paper substrate and its dilution with a starch solution,

Figure 53a Microscopic detail of the matte-albumen photograph in fig. 51 at 10× magnification.

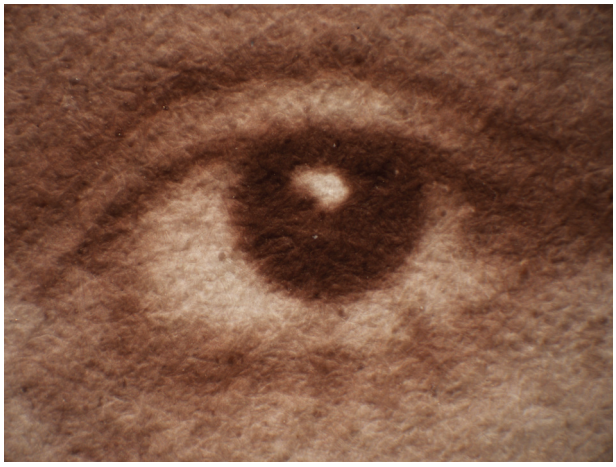
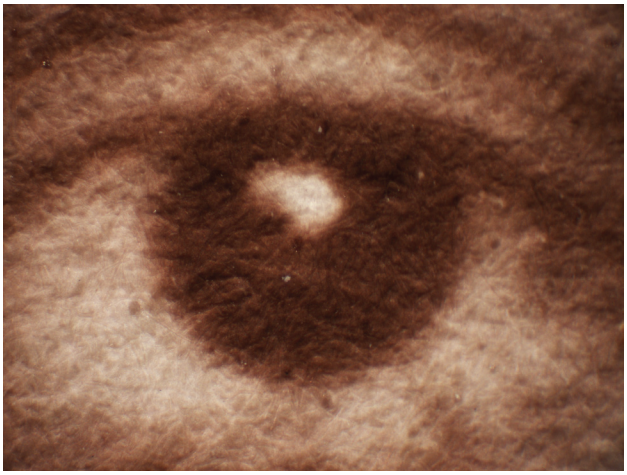


Figure 53b Microscopic detail of fig. 51 at 25× magnification.

Figure 53c Microscopic detail of fig. 51 at 40× magnification.



the well-developed spectral peaks that can be used to differentiate between albumen and gelatin are not evident. When compared with the ATR-FTIR spectra of previously covered albumenized prints, the matte-albumen prints fall into a category of very weakly albumenized prints.

It is quite possible that the analysis of some matte barytaless silver gelatin photographs may produce similar analytical results. If there is a necessity for precise identification of the nature of the organic binder, the previously described ELISA antibody test may provide information on the presence or absence of ovalbumen in the photograph.

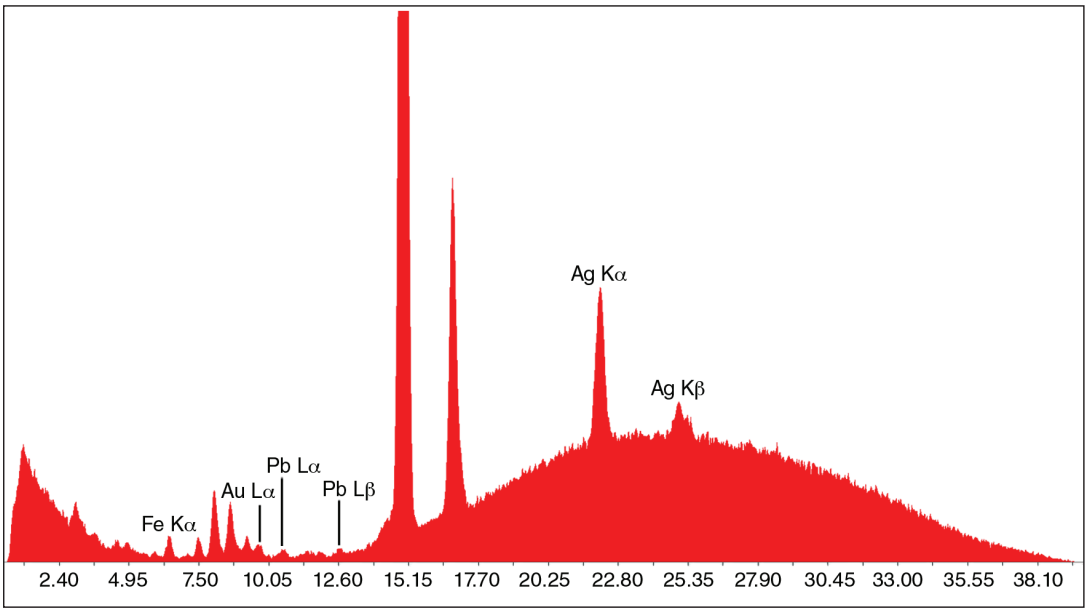


Figure 54 XRF spectrum of a matte-albumen photograph.

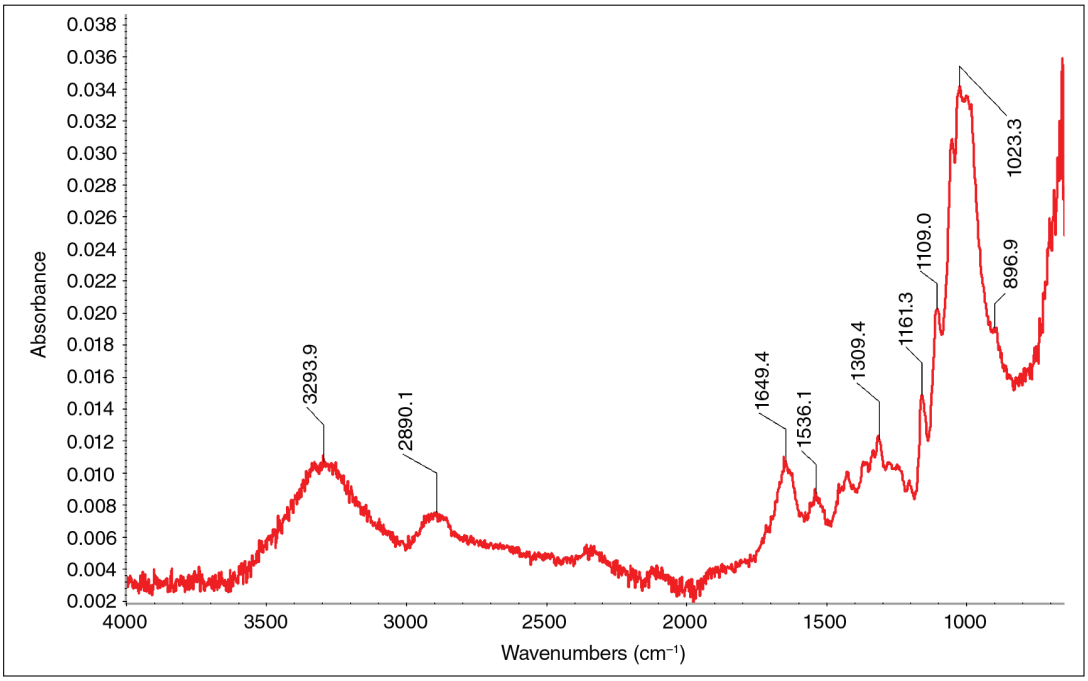


Figure 55 ATR-FTIR spectrum of a matte-albumen print.

INTERPRETATION GUIDE

Table 1 Summary of the main microscopic and analytical signatures of albumen photographs and some processes commonly misidentified as albumen. The information below is for typical versions of each process. Exceptions to each entry may exist but are rare.

Albumen Prints													
Process	**Surface Coating**	**Paper Fibers**	**Ag**	**Au**	**Pt**	**Ba**	**Other Inorganics**	**Celluose**	**Albumen**	**Collodion**	**Gelatin**	**Other Organics**	**Tonality**
Albumen	(X)	X !	X !	(X)	(X)	–	(Ti)*	X !	X !	–	–	(coatings)	Brown-purple
Collodion	–	–	X	(X)	(X)	X	Sr	–	–	X	–	–	Brown-black
Gelatin	(X)	–	X	(X)	–	X	Sr	–	–	–	X	(coatings)	Range depending on toning
Salt print	(X)**	X	X	(X)	–	–	(Ti)*	X	(X)	–	(X)	–	Brown-black

X Present
– Absent
( ) May be present
! Key signature

(X)** Beeswax, albumen, or gelatin (very rare)
(Ti)* Some modern prints on 20th- and 21st-century substrates containing TiO_2

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