The Atlas of Analytical Signatures of Photographic Processes

COLLODION ON PAPER

Dusan C. Stulik | Art Kaplan

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The Getty Conservation Institute
1200 Getty Center Drive, Suite 700
Los Angeles, CA 90049-1684
United States
Telephone: 310 440-7325
Fax: 310 440-7702
Email: gciweb@getty.edu
www.getty.edu/conservation

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: A. C. Vroman, *An Arizona Sky and Twin Buttes*, 1895, gold-toned, silver collodion photograph. Private collection.

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COLLODION ON PAPER

English: collodion
French: *collodion*
German: Kollodiumverfahren

HISTORICAL BACKGROUND

There is no clear inventor of collodion-on-paper photography. Instead, a series of inventors was responsible for the development and introduction of the process, from early tests and experiments to practical, industrially produced photographic material. Among them are Marc Gaudin (1853), William Henry Fox Talbot (1854), G. W. Simpson (1865), Jean Laurent and José Martinez-Sanchez (c. 1866), and J. B. Obernetter (1867–68).

The collodion-on-paper photographic process (see sample photograph in fig. 1) had a long and interesting history of development, from an early idea to the industrial production of different variants of glossy and matte-collodion photographic papers widely used by both amateur and commercial photographers between about 1870 and 1930. After 1930, it was almost entirely replaced by many different forms of both POP and DOP silver gelatin photographic papers.

Figure 1 A. C. Vroman, *An Arizona Sky and Twin Buttes*, 1895, gold-toned, silver collodion photograph. Private collection.

Figure 2 shows a historical timeline for the collodion-on-paper photographic process.

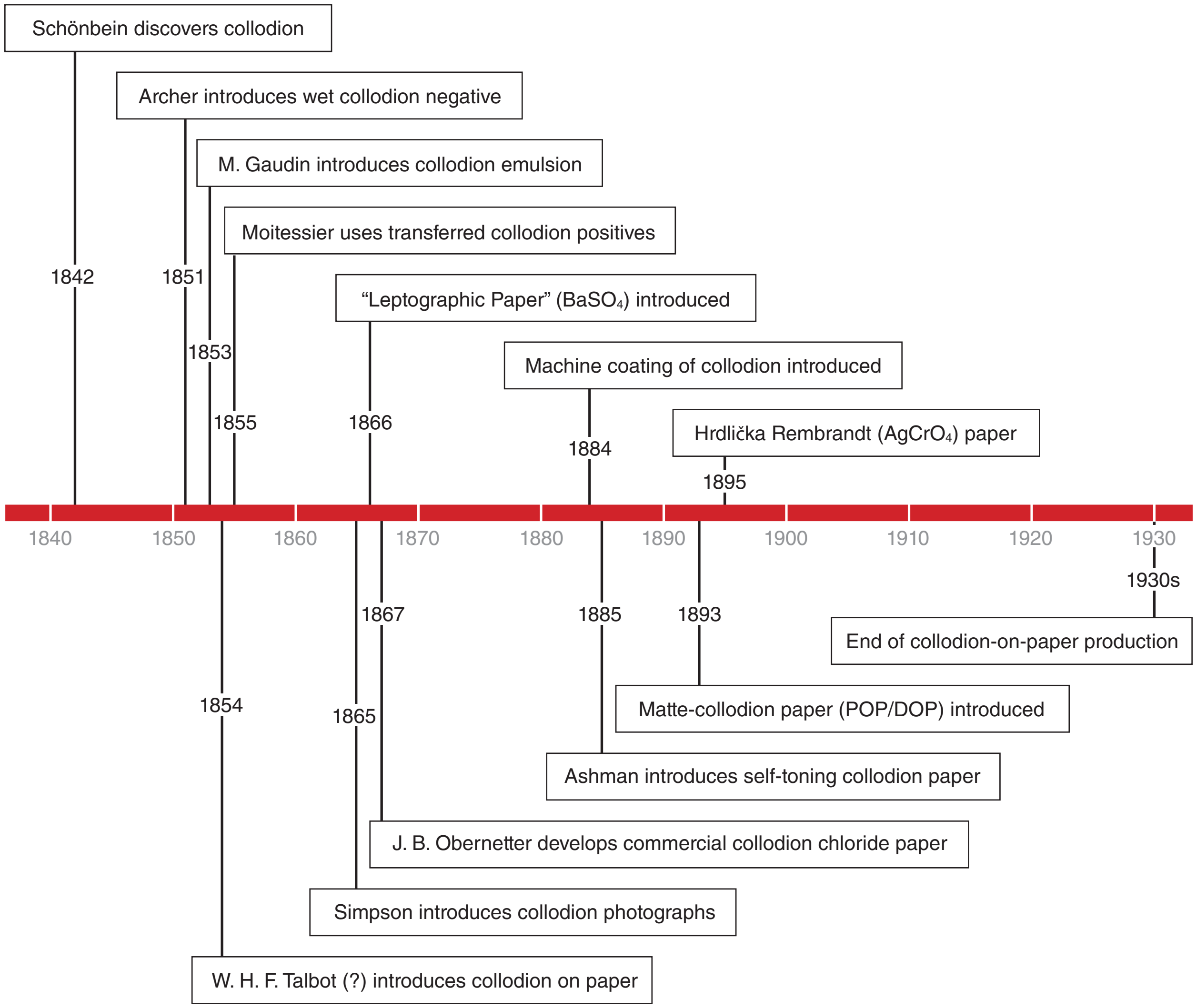


Figure 2 Timeline for the collodion-on-paper photographic process.

Process Description

Early experiments conducted with collodion on paper relied on the use of a heavily sized paper that was needed to prevent deep penetration of the collodion emulsion into the paper. (Though it is not technically correct, the term *emulsion* was widely used in the nineteenth-century photographic literature on the process.) Photographs created using this early version of the process still exist and can be found in a number of museum collections with holdings of historical photographic materials. Most of the still existing collodion-on-paper photographs were produced on baryta paper—usually industrially made—supplied by merchants of photographic materials and supplies.

Preparation of the Collodion-Silver Halide Emulsion

The first step in the preparation of collodion photographic paper was to prepare the collodion-silver chloride photographic emulsion. The collodion needed for the preparation of the emulsion was produced industrially by nitrating cotton and dissolving the resulting cellulose nitrate in a mixture of ethyl alcohol and diethyl ether. This solution was available from photography or pharmaceutical supply houses and was called collodion. Relatively early on, the quality of collodion paper was found to benefit greatly from using well-aged collodion, which produced a more uniform collodion-silver halide emulsion and adhered better to the paper substrate.

The collodion emulsion was prepared by mixing collodion with silver nitrate and small amounts of citric or tartaric acid and by mixing another portion of collodion with alcohol-ether soluble halides (usually calcium, strontium, or lithium chlorides). Both solutions were then combined under nonactinic light. The silver nitrate reacted with alkali or alkaline earth chlorides, forming microcrystals of silver chloride that were well dispersed in the collodion solution. Some recipes also called for the use of bromide compounds or chloride and bromide mixtures, resulting in less frequenty used collodion-bromide or collodion-chlorobromide emulsions.

As described here, the process of making the collodion emulsion sounds simple, but it was a demanding technological operation that required very strict conditions (concentrations of individual chemicals, temperatures, stirring, and adding individual materials in a precisely specified order). Small amounts of glycerin or castor oil often were added to make the final emulsion more pliable and less prone to cracking when dry, and to facilitate more uniform toning of processed photographs. Baryta-coated paper substrates were then hand coated (before 1889) or machine coated (after 1889) with the collodion emulsion.

Hand Coating of Collodion Photographic Paper

The collodion-on-paper photographic process was introduced at a time when most amateur and commercial photographers were well acquainted with the preparation and manipulation of wet collodion negatives. The hand coating of the collodion emulsion was similar to the coating of wet collodion negatives. The baryta-coated paper substrate was laid on a glass plate and held in place with the photographer's fingers. The collodion emulsion was poured onto the middle of the paper, and by rotating and tilting the glass plate, the photographer was able to produce a uniform emulsion layer across the paper. If a slightly larger piece of paper was used, the less uniformly coated edges were trimmed from the final photograph. Special coating frames were available for less experienced photographers.

Early manuals describing the preparation of collodion paper usually called for treating the substrate with a very thin coat of emulsion to yield a more uniform coating and a more consistent quality of the final photograph.

Machine Coating of Collodion Photographic Paper

After A. Kurtz in Germany introduced, in 1889, a machine for the large-scale mechanical production of collodion paper, most papers used from that point on were machine coated. Industrially produced collodion papers were available from a number of manufacturers in different formats, packed in boxes with the emulsions face-to-face and special “straw paper” to regulate moisture content of the paper base and to reduce the paper curling typically found in collodion paper photographs. Large rolls of baryta paper substrate were mechanically pulled through a tub of collodion emulsion and dried in a horizontal tunnel using a stream of hot air. The collodion emulsion dried quickly, and the resulting roll of collodion paper was then cut to the desired format and packed for shipment.

A major advantage of collodion paper production was that, unlike gelatin-based photographic paper, which required a long production line and a complicated arrangement of festoons to facilitate the slow drying process of the water-rich gelatin, collodion contained organic solvents and dried quickly. The production line for the preparation of collodion paper could be rather short (~120 feet). Disadvantages included the use of highly flammable organic solvents (ether and alcohol) and the potentially explosive cellulose nitrate. Paper curling is caused by differential moisture absorption in the collodion and paper substrate. The collodion layer is virtually water free, but the substrate expands when exposed to moisture in the air. This results in extreme inward curling of collodion paper during drying.

Development, Processing, and Post-Processing Treatment of Collodion Paper

Collodion-based photographic papers were POP photographic papers that, similar to albumen or POP silver gelatin photographic papers, did not require chemical development. The prepared or purchased collodion paper was placed under a negative into a photographic copy frame and was photolytically developed by light exposure. The subsequent processing (washing and fixing) reduced the amount of developed silver, so the collodion paper had to be overprinted to achieve the desired silver density of a final photograph. When removed from a copy frame, the light-developed image was washed in water to eliminate the soluble silver salts that remained in the collodion layer.

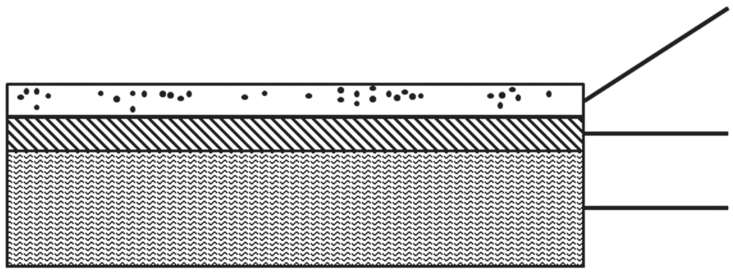
The next step is toning. A number of different toning formulas were prescribed in the nineteenth-century photographic literature. Most of these recipes called for a borax-gold chloride solution, and some substituted sodium phosphate or sodium tungstanate for the borax. Manuals also stressed that the toning solution be kept slightly alkaline. The toning operation of collodion emulsion photographs seems to be more delicate than the toning of albumen photographs, and shorter toning times are often recommended to achieve more uniform results.

Toned collodion photographs need thorough washing before fixing. Some manuals recommended a hardening bath of chromium alum or formaldehyde to restrict swelling of the gelatin in the baryta layer, which may later cause adhesion problems of the collodion layer. Fixing of toned collodion photographs is done using a simple solution of sodium thiosulfate in water, and most published procedures call for longer fixing times (up to 15 minutes). This was due to the low permeability of water through the collodion layer. Fixed photographs are again washed before drying or mounting.

Post-Processing Treatment of Collodion Photographs

Due to curling problems, most collodion photographs can be found mounted on rigid board. After 1870, a great variety of industrially prepared mounting boards became available to both professional

Figure 3 Cross section of a typical glossy collodion photograph.



and amateur photographers (more on mount formats, styles, and dating clues can be found in the Card Photograph section [forthcoming]). Collodion photographs could be mounted when still partially wet using water-based mounting mediums or pastes. Glossy collodion photographs also benefit from surface burnishing, which produces very glossy photographs. The burnishing was done when the photo was still slightly moist. Manuals recommended applying a cold roller first, then a hot roller to produce exceptionally high-gloss photographs. A roller that was too hot, however, would usually produce a reddish image. An albumen solution mixed with color-matched pigments was recommended as a spotting medium for damaged collodion photographs.

Before the introduction of matte-collodion photographic papers in 1894, if a matte surface was needed or desired, it was prepared by drying the wet surface of the collodion photograph and squeegeeing it on a high-quality ground glass plate. A semi-matte finish was also produced by coating the photograph with a solution of beeswax and kerosene.

Figure 3 shows a schematic cross section of a typical glossy collodion photograph.

Main Application of the Collodion-on-Paper Process

The collodion-on-paper process was used as an alternative to albumen photographs by amateur and professional photographers. After 1870, the availability of commercially produced collodion photographic papers provided a convenient printing medium for amateur photographers who were working with smaller cameras and commercially made silver glass plate negatives and wanted to reduce the number of processing steps in the darkroom. Commercial photographers used collodion papers when producing smaller prints, namely card photographs of various formats. Because of their severe curling, collodion photographic papers were rarely used for producing large-format photographs. This is why museum collections usually do not have large holdings of collodion photographs in larger formats.

Noted Photographers Using the Collodion-on-Paper Process

A. C. Vroman

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Wentzel, F. 1960. *Memoirs of a Photochemist*. Philadelphia: American Museum of Photography.

Penichon, S. 1999. “Differences in Image Tonality Produced by Different Toning Protocols for Matte Collodion Photographs.” *Journal of the American Institute for Conservation* 38(2): 124–43.

IDENTIFICATION: GLOSSY COLLODION PAPER PHOTOGRAPHS

Visual Signatures

Visual Characteristics

Because of their strong tendency to curl, most glossy collodion photographs were mounted on solid matte board (fig. 4). These photographs may have an entire range of colors, from light brown to dark black-violet, based on whether they were toned (figs. 5, 6). Depending on atmospheric conditions—the amount of moisture in the air, for example—many glossy and semi-glossy collodion photographs show a typical interference color pattern when viewed at an angle against a light source (fig. 7).

Many glossy collodion photographs show signs of mechanical damage from frequent handling. Because the collodion layer is often very thin, mechanical scratches penetrate through the entire layer of collodion into the white baryta layer. Most of the damage manifests as thin scratch lines in the image that can be examined under a microscope.

Microscopic Characteristics

Microscopic investigation of glossy collodion photographs does not allow the observation of individual particles of silver. Photogenically formed silver particles, which are typical for most glossy collodion photographs, are too small to be detected (figs. 8a–8c). The thin layer of collodion might show mechanical scratches reaching into the baryta layer (figs. 9a, 9b).

Figure 4 Three glossy collodion photographs mounted on solid matte board.

Figure 5 Unmounted, untoned glossy collodion photograph.

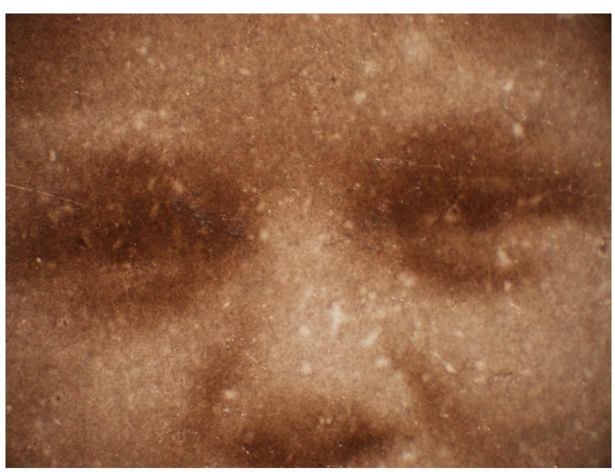
Figure 6 Mounted, gold-toned semi-glossy collodion photograph.

Figure 7 Glossy collodion photograph displaying a typical interference color pattern when held up to a light source.

Figure 8a Detail of the photograph in fig. 7 at 10× magnification.

Figure 8b Detail of the photograph in fig. 7 at 25× magnification.

Figure 8c Detail of the photograph in fig. 7 at 40× magnification.



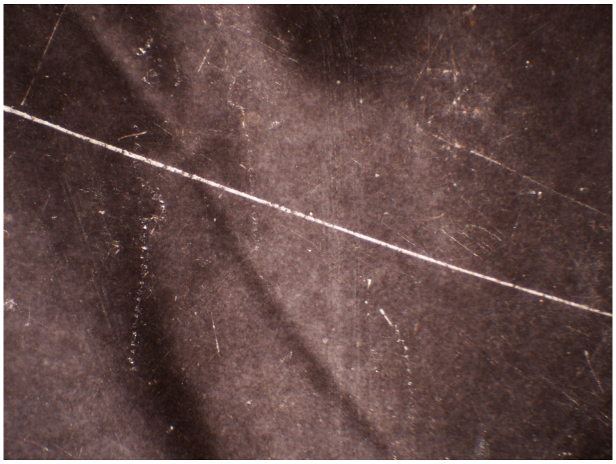


Figure 9a Detail of the photograph in fig. 6 at 25× magnification, showing a slight scratch into the baryta layer.

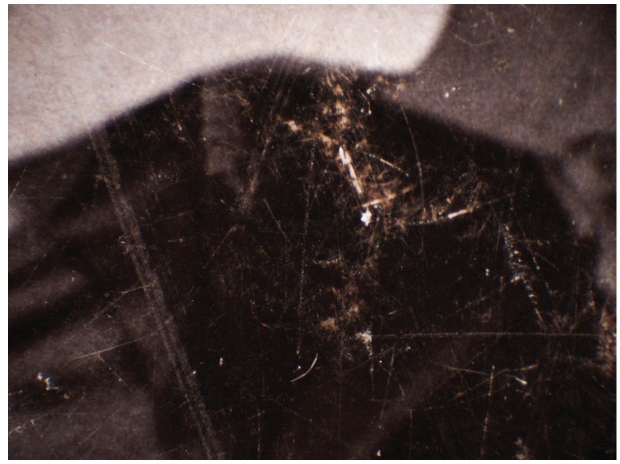


Figure 9b Detail of the photograph in fig. 6 at 25x magnification, showing another scratch into the baryta layer.

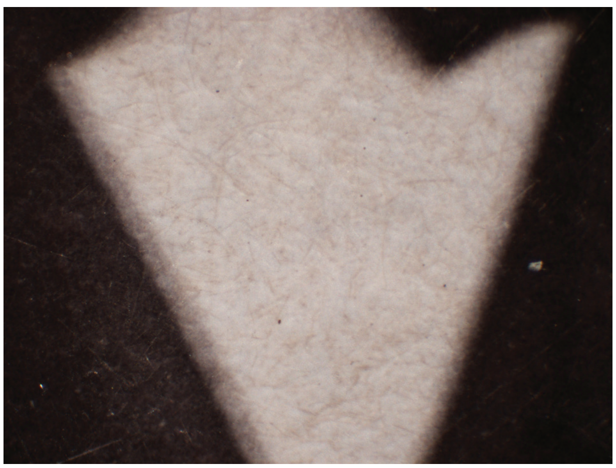


Figure 10a Detail of the Dmin area of the photograph in fig. 6 at 40× magnification, showing fibers in the paper substrate.

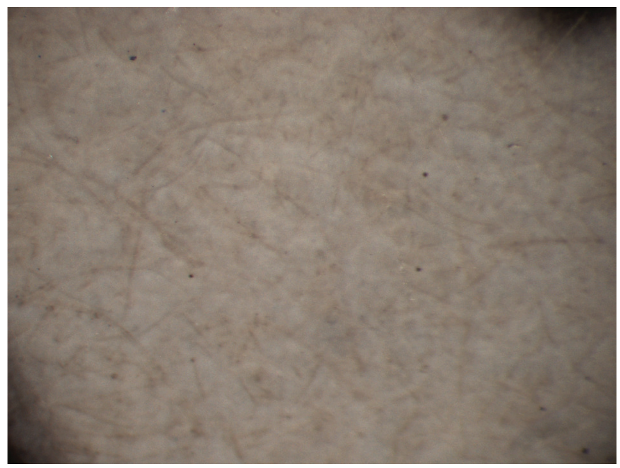


Figure 10b Detail of the Dmin area of the photograph in fig. 6 at 80× magnification, showing fibers in the paper substrate.

Fibers of the paper substrate are almost undetectable during microscopic inspection of the Dmin areas of glossy collodion photographs. Only careful observation of these image areas at relatively high magnification (40× and 80×) allows for the detection of some fibers that are covered by baryta or appear to be embedded in the baryta layer (figs. 10a, 10b).

Analytical Signatures

XRF

XRF analysis allows the detection of silver and toning elements in glossy collodion photographs and the confirmation of the presence of the baryta layer under microscopic inspection. Most professionally produced glossy collodion photographs were toned, but those done by some amateurs were not. Figure 11 shows an XRF spectrum of the untoned glossy collodion photograph

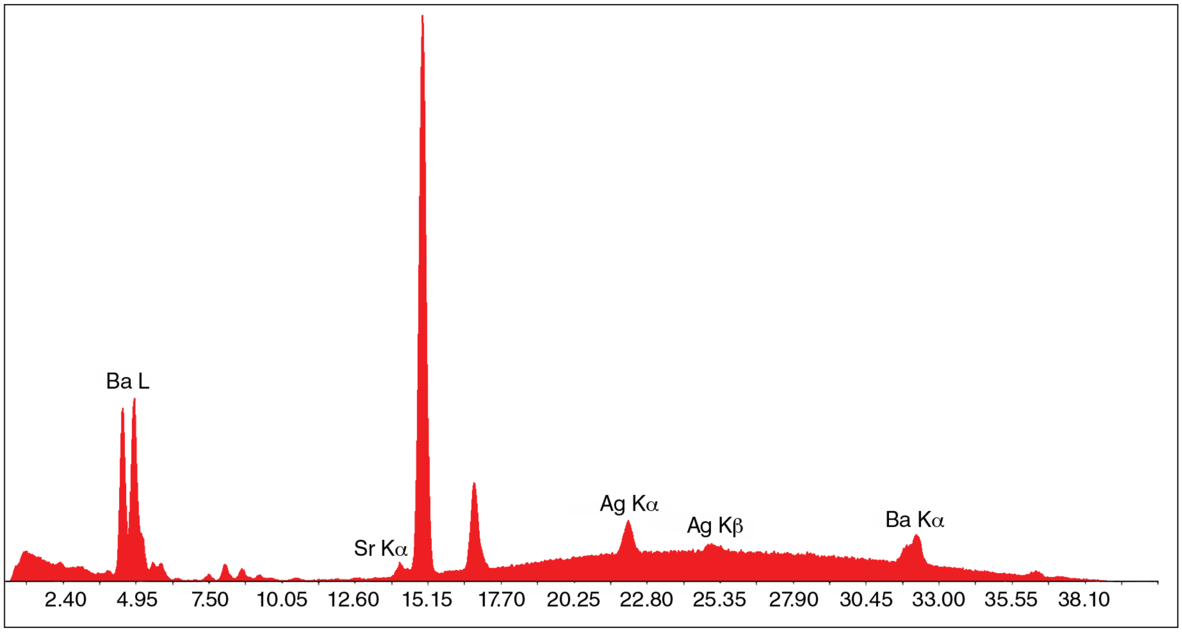


Figure 11 XRF spectrum of the unmounted, untoned glossy collodion photograph in fig. 5.

in figure 5. The spectrum shows the presence of silver (Ag) in the image layer and the presence of both barium (Ba) and strontium (Sr) in the baryta layer.

Two professionally made, cabinet card (CC)–mounted glossy collodion portraits were produced from the same negative but toned to produce images of different tonalities: violet black (fig. 12a) and dark gray (fig. 12b). XRF analysis of the violet-black photograph reveals that it was heavily toned using gold toner (fig. 13).

The XRF spectrum of the violet-black toned print shows the presence of silver (Ag) and gold (Au) from the image layer and barium (Ba) and strontium (Sr) from the baryta layer. The analytical signal of the other chemical elements detected by the XRF analysis of the Dmax area of the photograph comes from the mounting board of the photograph. The analysis of the back of the mounting board confirms that these elements are present in the mounting board alone (fig. 14).

XRF analysis of the dark-gray photograph (see fig. 12b) shows the presence of all the chemical elements detected in the violet-black version, with the addition of platinum (Pt) (fig. 15). This, together with gold toning, produces the dark-gray tonality. The concentration of gold in this image is substantially lower than in the violet-black photograph. Some experience is needed in interpreting XRF spectra of photographs toned with both gold and platinum. The spectral peak of platinum (Pt Lα) at 9.44 keV overlaps with the spectral peak of gold (Au Lα) at 9.71 keV. The two XRF Lβ spectral peaks for both elements also overlap (Pt Lβ at 11.07 keV with Au Lβ 11.44 keV). This overlap can be solved using an XRF spectrometer with a higher spectral resolution. Figure 16 documents the spectral overlap of Au and Pt recorded using a combination of two thin film standards of gold and platinum.

Figure 12a CC-mounted glossy collodion photograph with violet-black tonality.

Figure 12b CC-mounted glossy collodion photograph with dark-gray tonality.

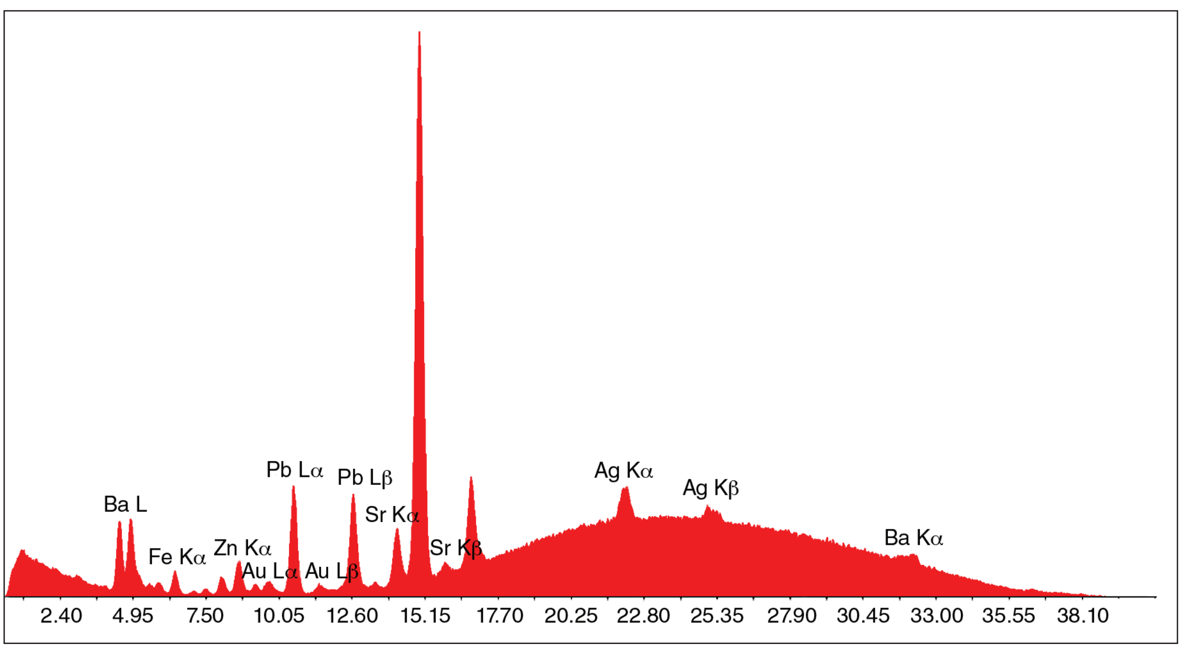


Figure 13 XRF spectrum of the violet-black collodion photograph in fig. 12a, showing the use of gold toner.

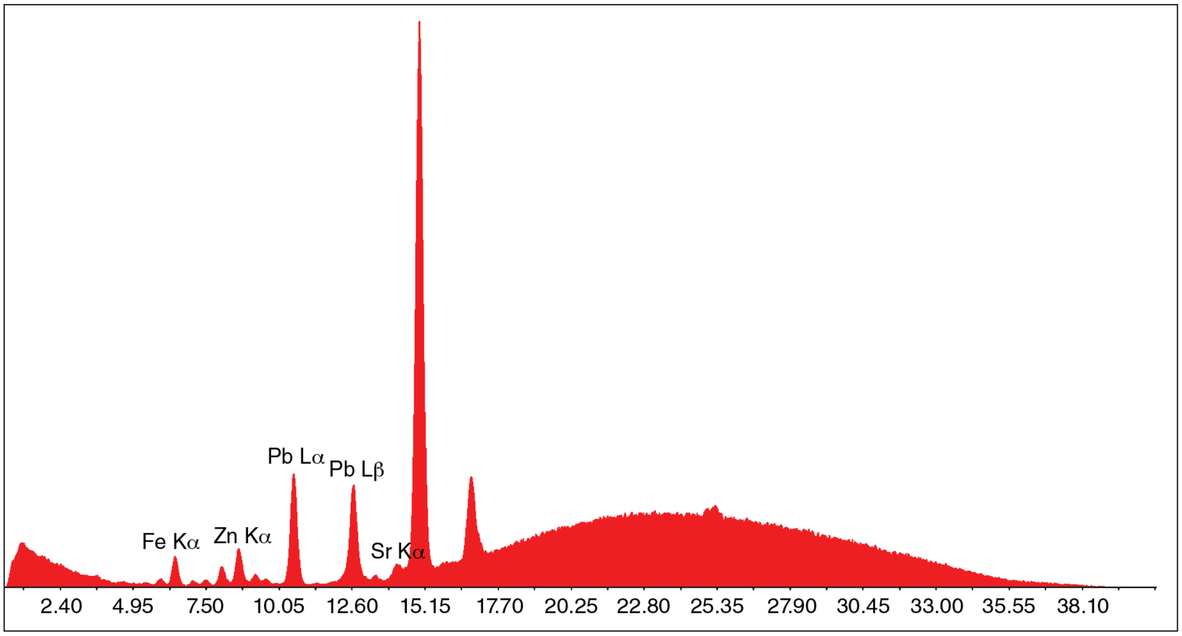


Figure 14 XRF spectrum of the mounting board of the photograph in figure 12a.

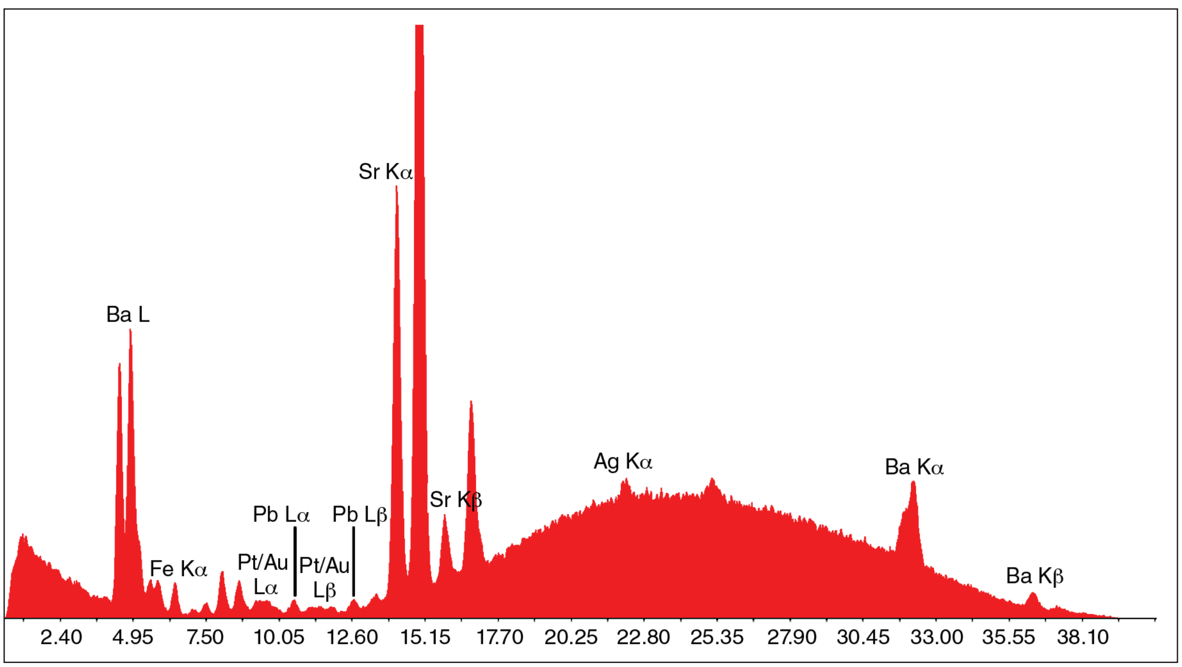


Figure 15 XRF spectrum of the photography in fig. 12b, showing the presence of all chemical elements found in fig. 12a, plus platinum (Pt).

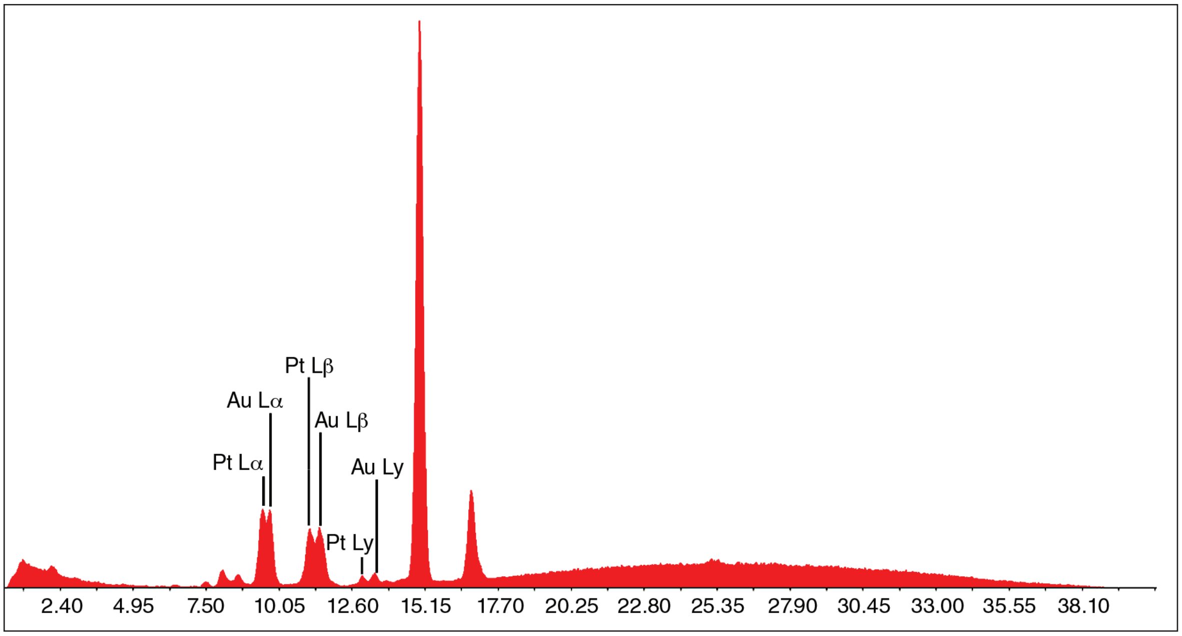


Figure 16 Spectral overlap of Au and Pt using gold and platinum thin film standards, each containing approximately 50 micrograms per square centimeter of the element.

There is a strong overlap of both the Lα and Lβ spectral peaks. For the small concentrations of both elements, the resulting spectral peaks almost completely overlap, forming a broad double spectral peak. Experience and the availability of analyzed samples with different concentrations of both elements can help interpret the analytical data if an XRF instrument with higher spectral resolution is not available.

FTIR

ATR-FTIR analysis is very effective when confirming the presence of collodion in the image layer of the photograph or when detecting and identifying any application or treatment of glossy collodion photographs with other types of organic coatings and varnishes. This method of analysis also allows differentiation between unvarnished glossy, semi-matte, and matte-collodion photographs. An example of a very glossy, nineteenth-century CC-mounted photograph appears in figure 17a. ATR-FTIR analysis of this photograph (fig. 17b) shows all the typical spectral attributes of glossy collodion photographs.

The ATR-FTIR spectrum shows very intense and well-developed spectral peaks typical of collodion (1630, 1270, and 821 cm^{-1}). The presence of C-H bonds in the spectrum, 2917 cm^{-1}, is typical for all organic materials with C-H bonds, but its relatively low intensity indicates the absence of any varnish or organic coating. A typical glossy collodion image layer is very thin, which allows the detection of a gelatin binder from the baryta layer under the collodion layer. A low-intensity Amide II spectral peak at about 1540 cm^{-1} usually indicates the presence of a gelatin-based baryta layer.

Figure 17a Nineteenth-century CC-mounted glossy collodion photograph.

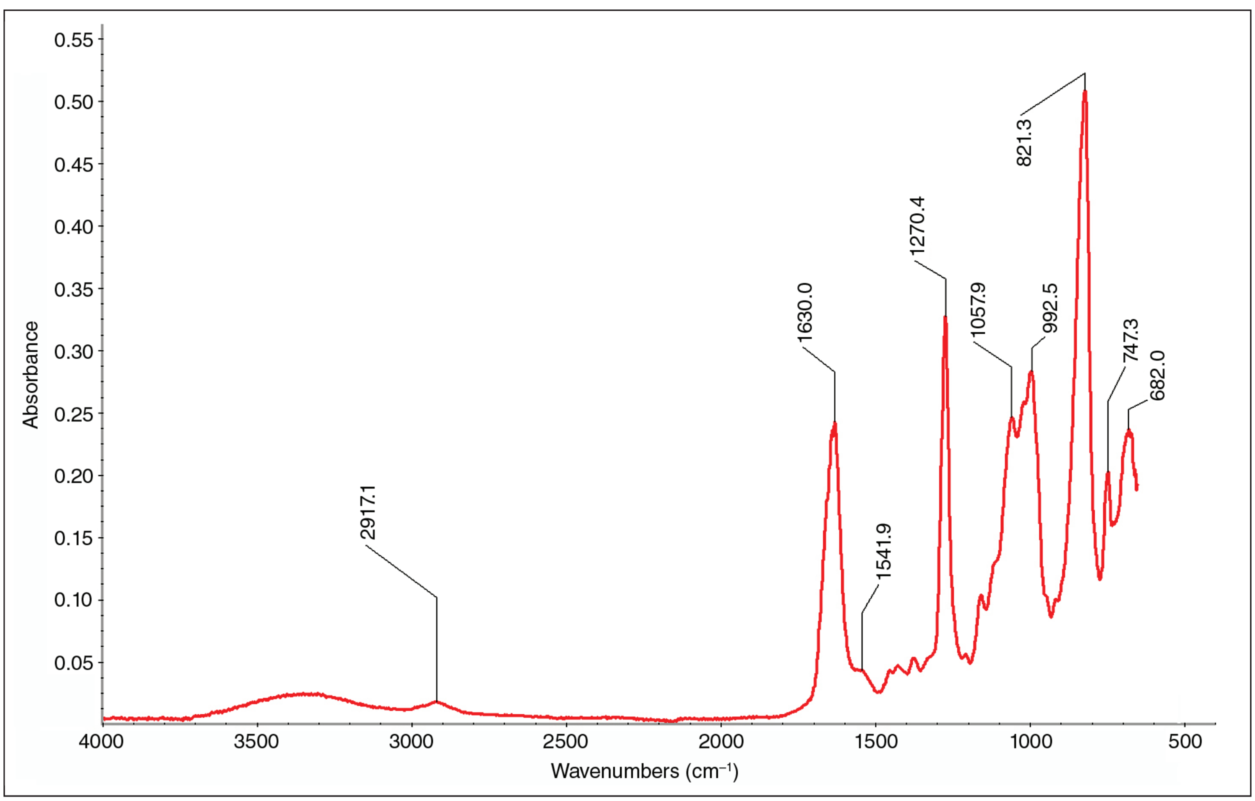


Figure 17b ATR-FTIR spectrum of the photograph in fig. 17a, showing typical spectral attributes of collodion.

Post-Process Treatment of Glossy Collodion Photographs

Before a matte variant of the collodion process was developed in the 1890s, the main procedure used in creating a matte surface on glossy collodion photographs involved drying the photo on a surface of matte glass or treating it with a beeswax-based varnish. Figure 18 shows an example of such a photograph mounted on a CC substrate.

The surface of the photograph is matte, with a slight sheen when viewed at an angle. The photograph does not exhibit the interference color pattern typical of glossy collodion photographs. No presence of surface coating is visible when examined under a microscope, but ATR-FTIR analysis clearly detects the presence of the surface varnish layer (fig. 19).

Intense, well-developed spectral peaks of C-H functional groups at 2956, 2916, and 2849 cm^{-1} indicate the presence of a varnish layer. The presence of C-H vibrations of long aliphatic chains (based on the ratio between CH, CH_2, and CH_3 peaks), together with the presence of the ester functional group at 1736 cm^{-1}, is typical for beeswax-based materials used in the nineteenth century when treating or coating photographs and photographic negatives.

Figure 18 CC-mounted glossy collodion photograph treated with a beeswax-based varnish to produce a matte surface.

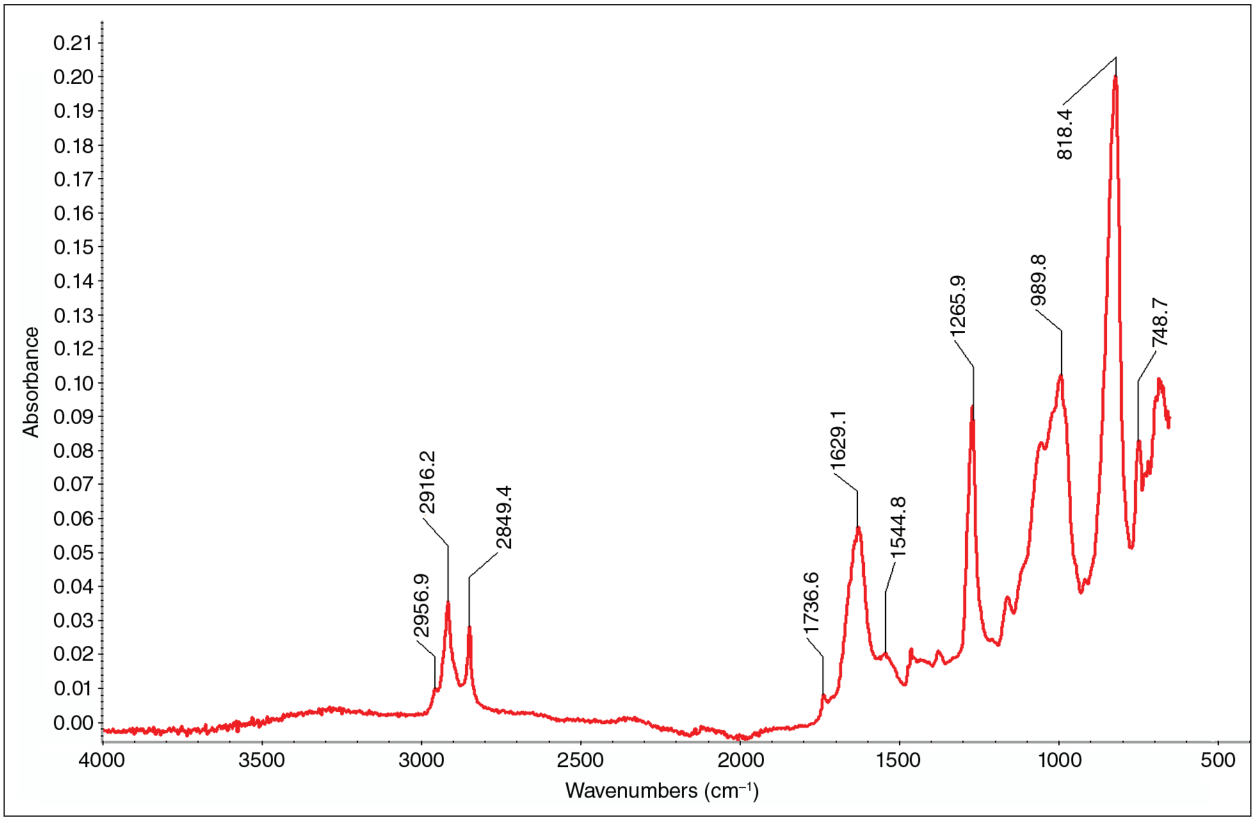


Figure 19 ATR-FTIR spectrum of the collodion photograph in fig. 18, indicating the presence of the surface varnish layer.

IMPORTANT VARIANTS OF THE COLLODION PROCESS

Self-toning collodion-on-paper photographs
Matte-collodion photographs
Tinted collodion photographs

Self-Toning Collodion-on-Paper Photographs

During the last quarter of the nineteenth century and the first decades of the twentieth century, a number of self-toning collodion papers became commercially available. After exposure and development, these types of photographic papers produced toned photographs that today cannot be easily distinguished from photographs made using regular collodion photographic papers and toned in the darkroom.

Matte-Collodion Photographs

A great number of professional portrait photographers used different kinds of commercial matte-collodion positive printing material from its introduction in the 1890s to about the late 1920s, when it was largely replaced by silver gelatin photographic material. The matte-collodion process was introduced to compete with, at that time, the highly popular platinotype photographic process famous for producing beautiful matte-black or dark brown-black photographs. Even today these photographs remain in a sound state of preservation without virtually any noticeable color shift or discoloration.

The matte surface of these photographs was produced by incorporating particles of starch into the collodion-silver halide emulsion. The standard darkroom treatment of matte-collodion photographs called for double toning using both gold and platinum. A gold toner usually was used first, and final tonality was achieved by a subsequent treatment in a platinum-toning bath. To achieve the desired tonality as shown in figures 20a–20c required a certain level of darkroom testing and calibration.

Figure 20a Matte-collodion photograph with dark-brown tonality.

Figure 20b Matte-collodion photograph with dark brownish-black tonality.

Figure 20c Matte-collodion photograph with bluish-black tonality.

XRF analyses of these three photographs appear in figures 21a–21c. A comparison of the spectra, together with a larger number of other matte-collodion photographs analyzed during our research project, shows no clear relationship between the final tonality of double-toned matte-collodion photographs and the concentration ratio between gold and platinum in the photographs. The spectrum of the dark-brown photograph (see fig. 21a) has a low concentration of gold. The two very strong dark-black photographs show different chemical compositions. XRF analysis of the dark brownish-black photograph (see fig. 21b) shows a high concentration of platinum and no gold. The bluish-black photograph spectrum (see fig. 21c) shows a very high concentration of gold and no platinum.

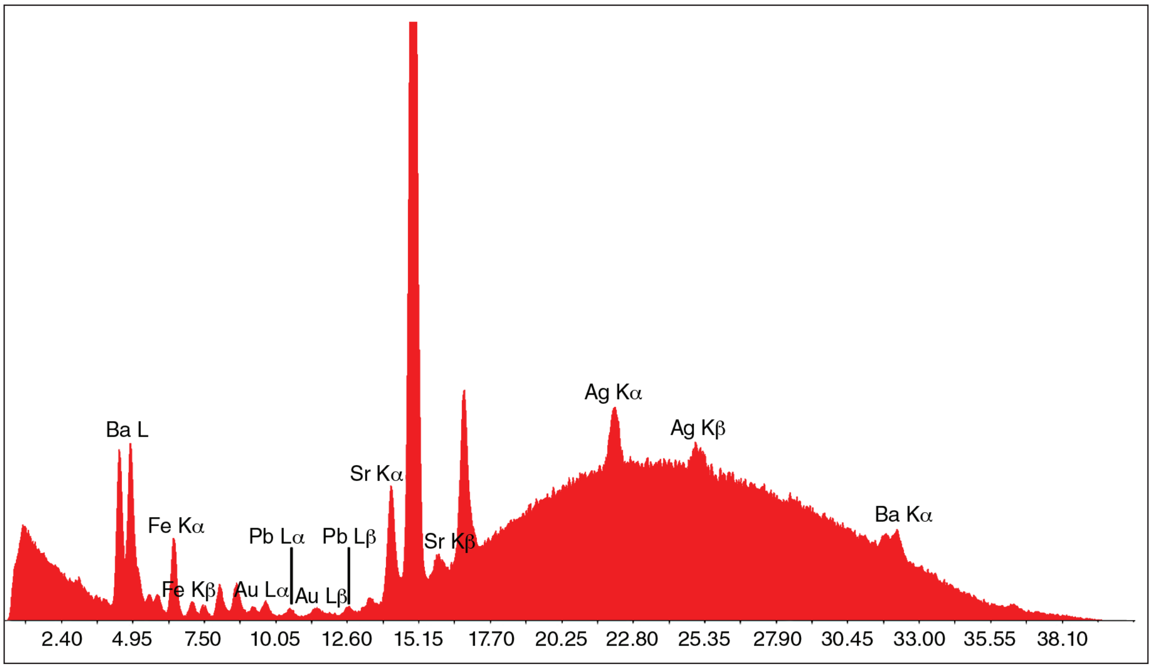


Figure 21a XRF spectrum of the dark-brown photograph in fig. 20a.

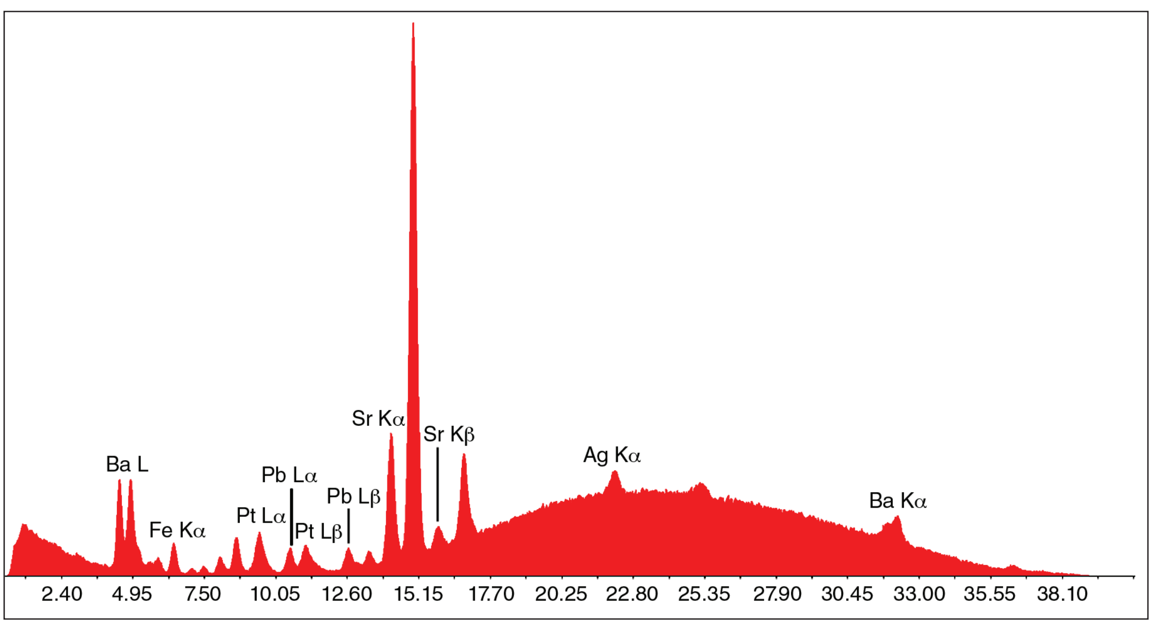


Figure 21b XRF spectrum of the dark brownish-black photograph in fig. 20b.

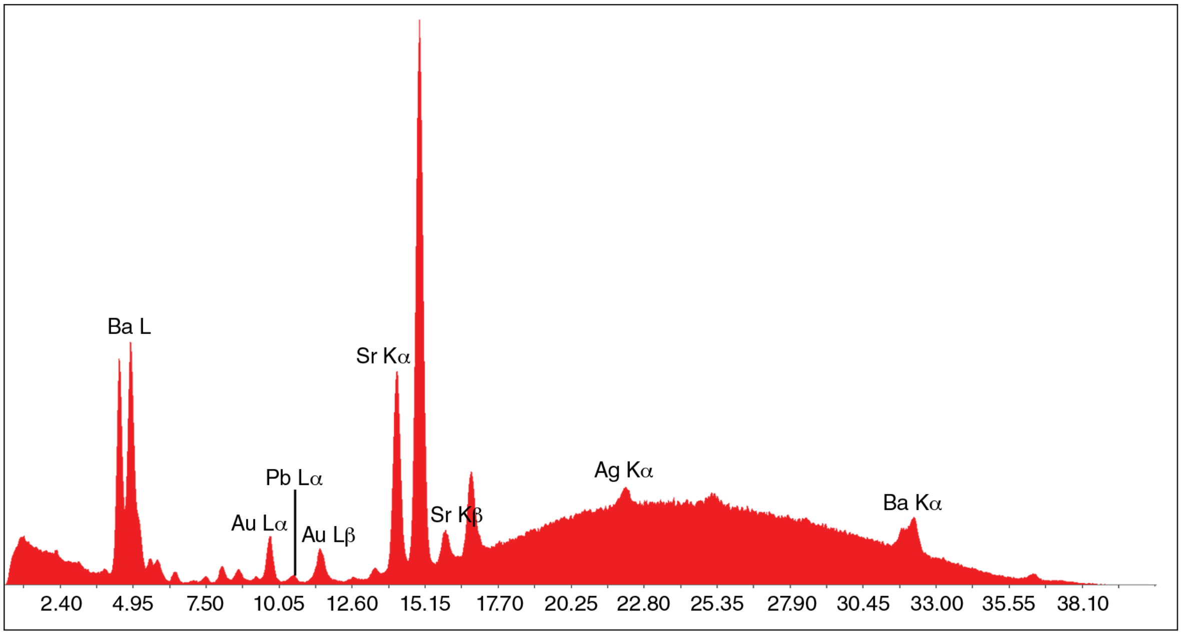


Figure 21c XRF spectrum of the bluish-black photograph in fig. 20c.

Matte-collodion photographic papers were available commercially under different names. The American Aristotype Company, for example, produced the so-called Aristo-Platino printing paper. A photograph produced using this paper is shown in figure 22a; a detail of the mount, showing the photographer's name and logo along with a description of the material used, is shown in figure 22b. XRF analysis (fig. 23) shows that the photograph is a slight variant of a regular gold- and platinum-toned matte-collodion photograph.

Figure 22a Photograph made using Aristo-Platino matte-collodion photographic paper.

Figure 22b Detail of the mount for fig. 22a, indicating the photographer's name, logo, and description of material used.

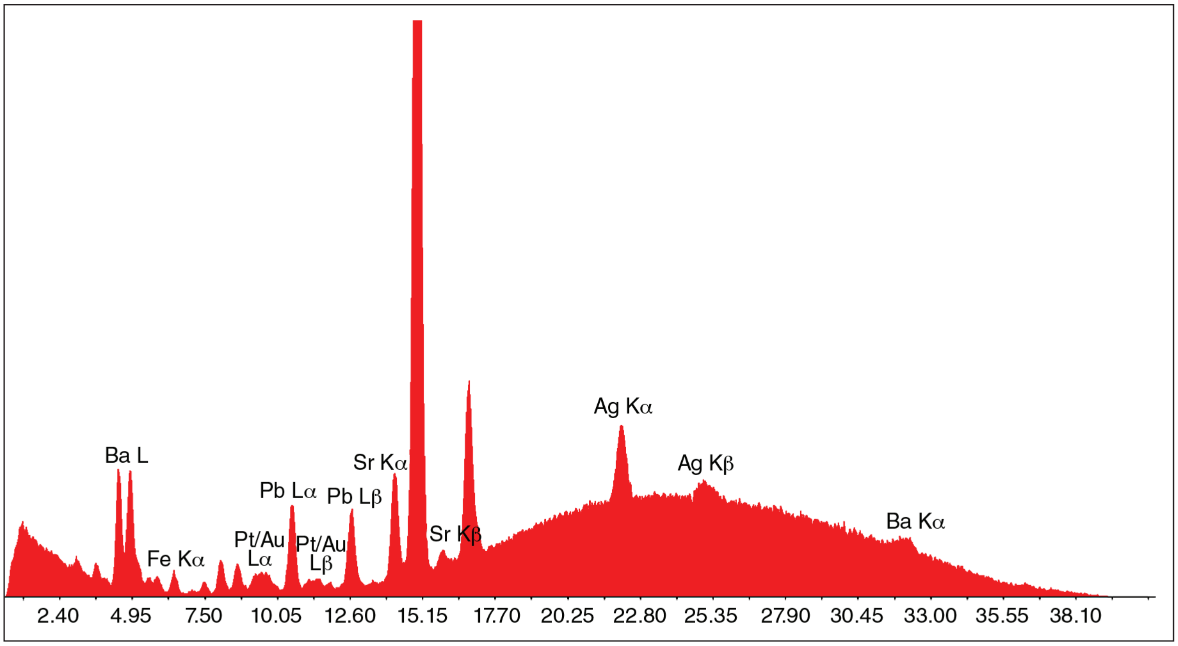


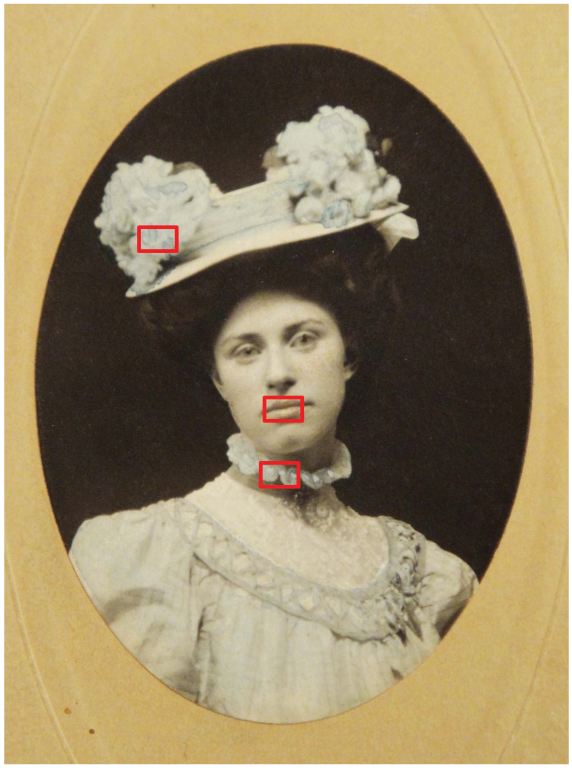
Figure 23 XRF spectrum of the Aristo-Platino photograph in fig. 22a.

Tinted Collodion Photographs

Collodion photographs were usually not tinted, but some examples indicate the application of colorants. Figure 24 shows two rare examples of untinted and tinted matte-collodion photographs. XRF analysis shows that organic colorants were used in tinting the blue area (hat), red area (lips), and white painted area of the photograph (fig. 25).

Figure 24 Untinted (left) and tinted versions of a matte-collodion photograph.

Figure 25 Analytical spots highlighting the use of colorants in the blue area (hat), red area (lips), and white painted area (collar).



Only the dots of thick white paint indicate the presence of a very high concentration of zinc (Zn). The pigment used can be clearly identified as zinc oxide (fig. 26). The concentration of organic dye material is too low for ATR-FTIR identification of the individual dyes used for tinting of the image.

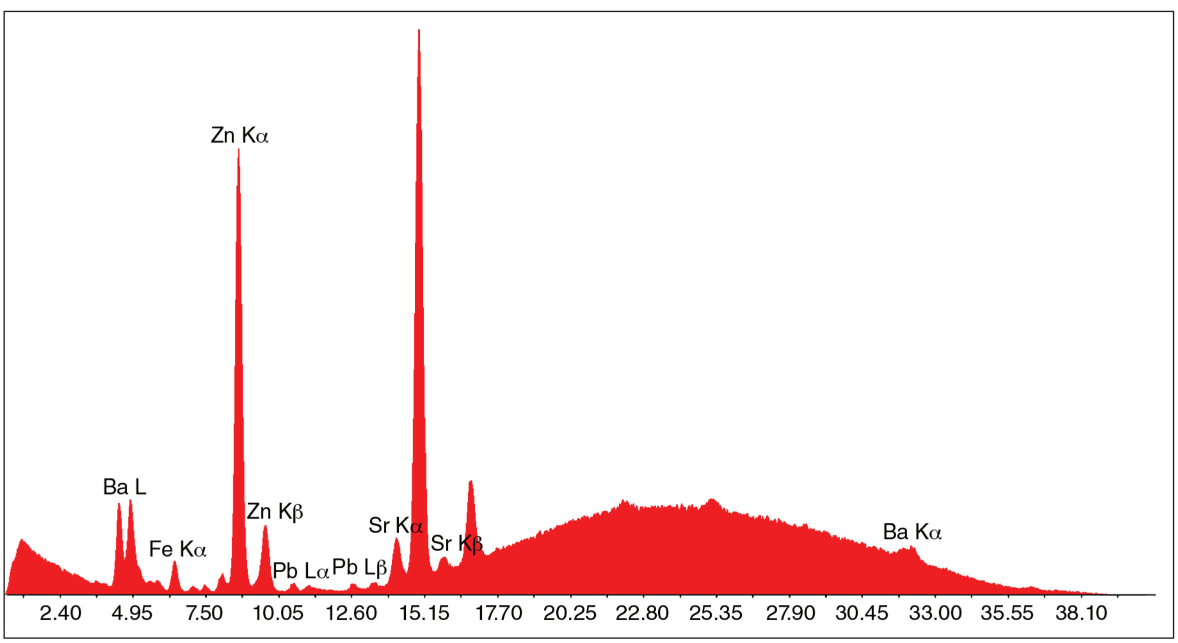


Figure 26 XRF analysis of white paint used in the decoration of the photograph in fig. 25.

INTERPRETATION GUIDE

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

Collodion Prints

Process	Surface Coating	Paper Fibers	Ag	Au	Pt	Ba	Other Inorganics	Cellulose	Albumen	Collodion	Gelatin	Other Organics	Surface/Tonality
Glossy collodion	–	–	X !	(X !)	(X)	X !	Sr !	–	–	X !	–		Brown
Matte collodion	–	–	X !	(X !)	(X !)	X !	Sr !	–	–	X !	–		Black (matte surface)
Wothlytype	(X)	X	X	–	–	–	U	X	–	X	–	–	Brown
Albumen	(X)	X	X	(X)	(X)	–	(Ti)*	X	X	–	–	(coatings)	Brown-purple
Gelatin	(X)	–	X	(X)	–	X	Sr, (Ti)*	–	–	–	X	(coatings)	Brown
Carbon	(X)**	(X)	–	–	–	–	Cr, (X)***	–	–	(X)**	X	–	Brown (glossy)
Woodburytype	(X)**	(X)	–	–	–	–	(Cr), (Fe)	–	–	(X)**	X	–	Brown-black (shellac in D-min)

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

(X)** Carbon and Woodburytype prints were sometimes coated with collodion
(X)*** Range of colors can be achieved depending on pigments/dyes used
(Ti)* Some modern prints on 20th- and 21st-century substrates containing TiO_2

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