The Atlas of Analytical Signatures of Photographic Processes

SILVER GELATIN

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: Henri Cartier-Bresson, *Gare Saint Lazare*, 1932. Printed 1979. Silver gelatin print. © Henri Cartier-Bresson/Magnum Photos.

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SILVER GELATIN

English: silver gelatin
French: *gélatino d'argent* (*tirage au*)
German: Silbergelatineabzug

HISTORICAL BACKGROUND

No single figure can be credited with the invention of the silver gelatin photographic process, which gradually became the most important photographic printing process of the twentieth century. Several inventors, including Peter Mawdsley, Josef Marie Eder, Giuseppe Pizzighelli, and Sir William de Wiveleslie Abney, can be credited with the most important contributions to its development and research of several key types of silver halide gelatin emulsions. The development of the baryta layer, even when not directly related to silver gelatin photography, goes back to its introduction by José Martinez-Sanchez and Jean Laurent in 1866.

A silver gelatin print by Henri Cartier-Bresson appears in figure 1. Figure 2 shows a historical timeline of the silver gelatin photographic process.

Silver gelatin photographic papers were available both as POP (printing-out paper) and as DOP (developing-out paper). Even though the internal chemical structure of both types is very similar, the handling and processing of each was quite different, and it is best to describe them separately.

POP SILVER GELATIN PROCESS

A number of different recipes for preparing silver gelatin printing papers were published in the photographic literature during the last quarter of the nineteenth century. The availability of commercially made silver gelatin photographic papers from photographic supply houses and catalog orders was responsible for the relatively limited preparation of photographic material by individual photographers. These photographers were still heavily involved in researching, testing, and providing recommendations for paper processing to achieve the best results or special effects for different tasks. This is well reflected in the lively discussions, idea exchanges, photographic literature, and number of photographic patents filed during that time for improvements in silver gelatin photography.

Figure 1 Henri Cartier-Bresson, *Gare Saint Lazare*, 1932. Printed 1979. Silver gelatin print. © Henri Cartier-Bresson/ Magnum Photos.

Process Description

The POP silver gelatin process involves the following steps:

1. POP photographic paper is placed under a negative into a special copy frame.
2. The copy frame assembly is exposed to daylight or artificial light until the image is developed to the desired image intensity. Guides for approximate exposure times were usually available from paper manufacturers for different lighting conditions, but some tests were needed to find good exposure conditions for a given light and negative combination. POP requires some level of overprinting because the image intensity is decreased during processing.
3. The exposed POP is washed in a water bath to remove any excess of soluble silver salts.
4. The washed POP is toned using different types of gold and platinum toners or using first a gold, then a platinum toner. Some toning formulas found in early nineteenth-century photographic literature also recommend using palladium or iridium toning. However, even after analyzing thousands of POP silver gelatin photographs, we still have not identified any existing photograph toned in that manner.
5. The toned POP photograph is washed again to remove toning chemicals and fixed using the standard hypo (sodium thiosulfate) fixer.
6. The toned and fixed photograph is thoroughly washed in running water or in multiple water changes in a water tray.
7. The washed photograph is air dried or surface polished by squeegeeing the print on a clean, polished glass and letting it dry. The fully dried photograph usually separates from the glass surface on its own.

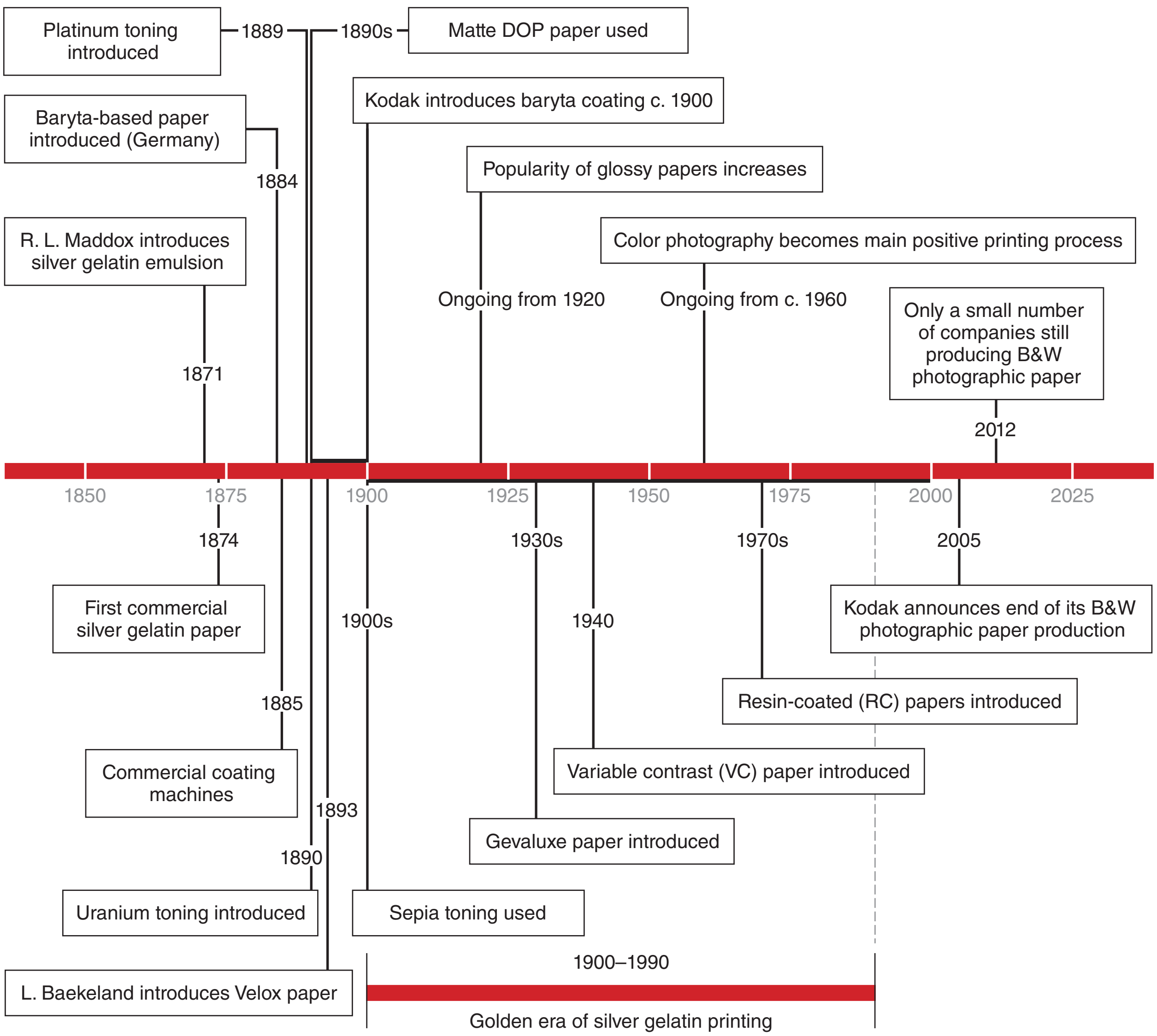

Figure 2 Timeline of the silver gelatin photographic process.

8. Many dried POP photographs are then retouched and mounted on a more rigid paper or paper board support.
9. Some photographs are varnished or surface coated to modify their appearance or to protect them from physical and environmental damage.

Figure 3 shows a schematic cross section of a typical silver gelatin print.

Main Application of the POP Silver Gelatin Process

The POP silver gelatin process answered the need for easy printing of photographs from both large-format and, at that time, new small-format cameras. Some processes called for standard sun exposure, but many so-called gaslight photographic papers could be exposed in-house using gas lights or special photographic gas burners. Kerosene lamps or early electrical lightbulbs could

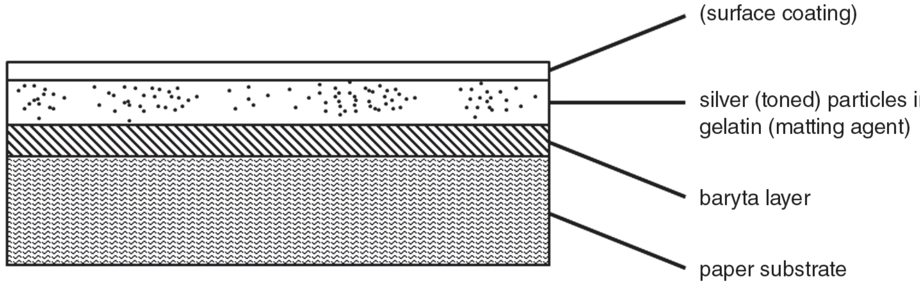

Figure 3 Schematic cross section of a typical POP silver gelatin photograph.

also be used. POP was sensitive enough so that this type of light exposure could be performed within several minutes, but it did not require the complete darkness of a darkroom as later, more sensitive photographic papers did. Some hybrid POP photographic papers called for exposure followed—after some level of image was formed photogenically—by chemical development. POP photographic papers were also used as image-proofing materials to assess the quality of produced negatives.

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Silver Gelatin–Related Patents

Joseph Swan, English Patent 2,968 (July 22, 1879), silver bromide printing paper

IDENTIFICATION: POP SILVER GELATIN PHOTOGRAPHS

Visual Signatures

Visual Characteristics

The silver image of POP photographs is developed photogenically during light exposure. Photogenically developed silver particles are much smaller than chemically developed silver particles. The color of the silver image of a POP silver chloride photograph relates to the size of the silver particles and usually ranges from light yellow-brown to red and darker brown (fig. 4).

Figure 4 Antique POP silver gelatin photographs in a range of colors.

The color of silver bromide POP images is usually cooler and grayer. These visual clues hold only for POP photographs that have not been toned. Most silver gelatin POP photographs were gold toned. The toning process increases the size of silver particles; however, the growth of image particles is not straightforward (there is some deposition of gold onto the silver particles, but our analysis of POP photographs during toning and of the gold bath after toning shows a growing concentration of silver in the gold bath during toning). Toning usually shifts the image color to red-violet or dark black-violet.

Some POP photographic papers were available with tinted (usually pink or blue) baryta layers (fig. 5). This is not a good visual clue because many albumen and silver collodion photographs produced during that time had a similar type of coloration.

Silver gelatin POP was produced in several surface-texture qualities. At first only glossy or matte surfaces were available, but after the turn of the twentieth century the number of available textures increased. Later some specialized POP papers became available. Some POP papers tried to mimic the visual appearance of more expensive and very fashionable carbon or platinum photographs. POP photographs with unusual sheen or high gloss, unusual thicknesses, or a tendency to curl may indicate the presence of a surface varnish or coating (fig. 6).

Microscopic Characteristics

Even when toned, silver-gold image particles of POP silver gelatin photographs are too small to be visible even with a powerful optical microscope. When observed under a stereomicroscope at high magnification, the particles are not visible. A detailed inspection of the boundary between dark and light areas reveals a darker "cloud" of imaging material that looks almost three dimensional, "floating" above the underlying white surface of the baryta layer (fig. 7).

Figure 5 POP silver gelatin photographs with pink and blue baryta layers.

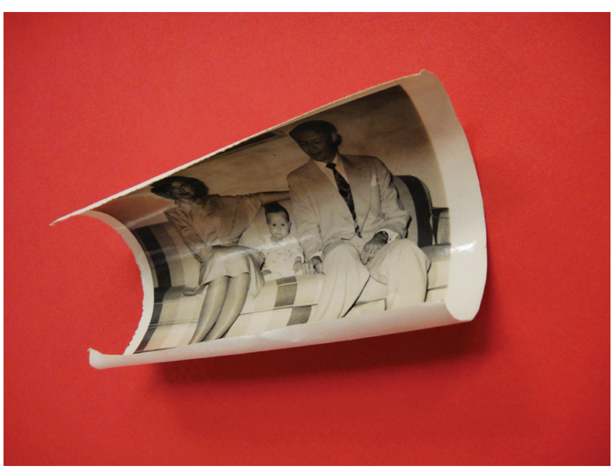


Figure 6 POP photograph showing a tendency to curl, which may indicate the presence of a surface coating.

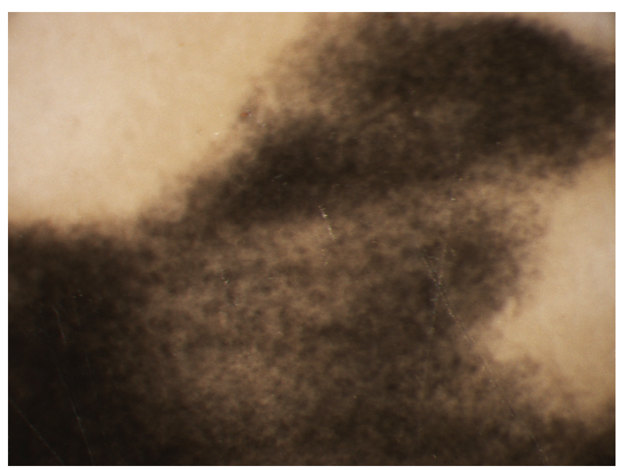


Figure 7 Detail of a POP photograph (80× magnification), showing the presence of a dark "cloud" of imaging material above the white surface.

Figure 8a Detail of a POP photograph (40× magnification), showing the presence of the baryta layer at the edge area.

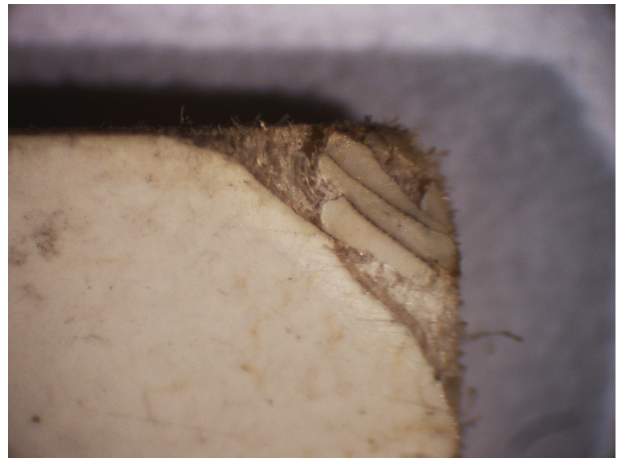


Figure 8b Detail of a POP photograph (40× magnification), showing the presence of the baryta layer at a damaged corner area.

With the exception of very early silver gelatin POP and some later types of technical and copy POP, almost all other POP papers were produced using a baryta-coated paper stock. The presence of a baryta coating and the characteristic three-layer structure of the paper can be observed when inspecting the edges of a photograph under a microscope. Even very well preserved photographs may have slightly damaged edges or corners that show fibers of the paper substrate and some separated microplatelets of the white (more white than the paper fibers) baryta layer still embedded in the paper fibers or held by the damaged emulsion layer (figs. 8a, 8b).

When edges or corners of a photograph are not accessible for inspection, the presence of a baryta layer can often be detected within the very light areas of the photograph. Focusing on the surface layer of the image and slowly refocusing through the emulsion layer reveals an absence of paper fibers. Under high magnification, the baryta layer looks flat, solid, and almost structureless.

Early silver gelatin photographs were not protected against mechanical damage by a top or supercoat of hardened gelatin. Thus, many handled POP photographs exhibit some surface scratches to the gelatin layer. These can be observed during inspection under a stereomicroscope. The gelatin layer is usually thicker than the thin collodion layer, which may have some scratches down to the white baryta layer. An uncoated gelatin layer also does not show the presence of a microcracking pattern, which is typical for older albumen photographs (fig. 9).

Analytical Signatures

XRF

The typical XRF spectrum for the majority of POP silver gelatin photographs shows the presence of silver (Ag) and gold (Au). Both are imaging metals of toned POP silver gelatin photographs. The majority of photographs also show the presence of a baryta layer identified by the presence of barium (Ba) and strontium (Sr) in the XRF spectrum. Other elements detected—calcium (Ca) and iron (Fe)—may be present as impurities in both the paper base of the photographs and the

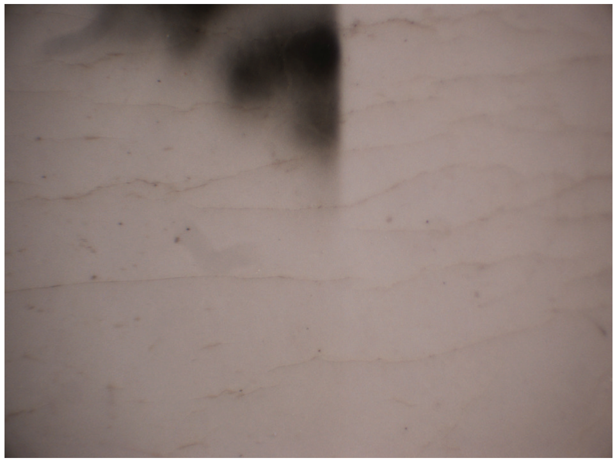


Figure 9 Detail of a typical pattern of mechanical damage to the surface of the gelatin layer (40× magnification).

baryta layer (figs. 10a, 10b). Many early silver gelatin photographic papers also exhibited the presence of lead (Pb) in the paper substrate, as indicated in the spectrum in figure 11. When detected in the XRF spectra of POP silver gelatin photographs, the presence of small amounts of chromium (Cr) can be attributed to the use of chromium alum for hardening the gelatin binder of the baryta layer.

XRF analysis of permanently mounted POP silver gelatin photographs is usually much more complicated, because the resulting spectrum represents a spectral superposition of the XRF spectra of the photograph and the card or board substrates. Figures 12a, 12b, 13a, 13b, and 14a–14c show three different mounted POP silver gelatin photographs and their corresponding XRF spectra.

Both measured XRF spectra shown in figures 12b and 13b are quite complicated due to the presence of the analytical signal from the mounting substrates. Analytical signals from mounted photographs and mounting substrates can be separated by analyzing both the Dmax area of

Figure 10a Unmounted silver gelatin photograph.

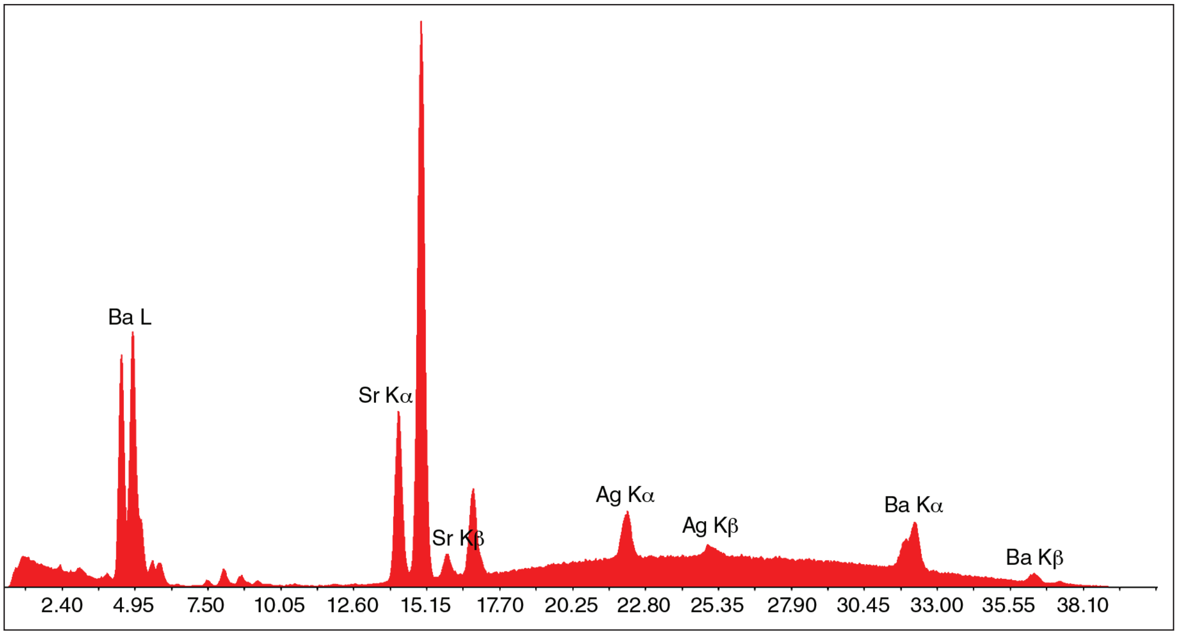


Figure 10b XRF spectrum recorded from the Dmax area of the image layer in fig.10a.

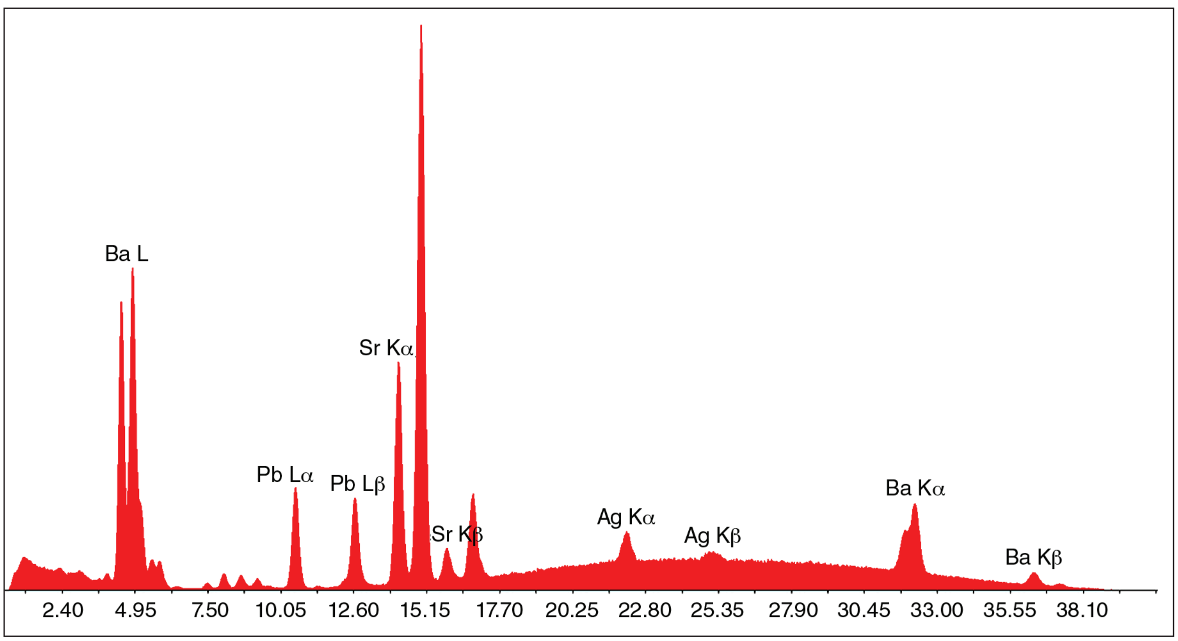


Figure 11 XRF spectrum of a POP silver gelatin photograph containing lead in its paper substrate.

Figure 12a *Cartes-de-visite* mounted POP silver gelatin photograph.

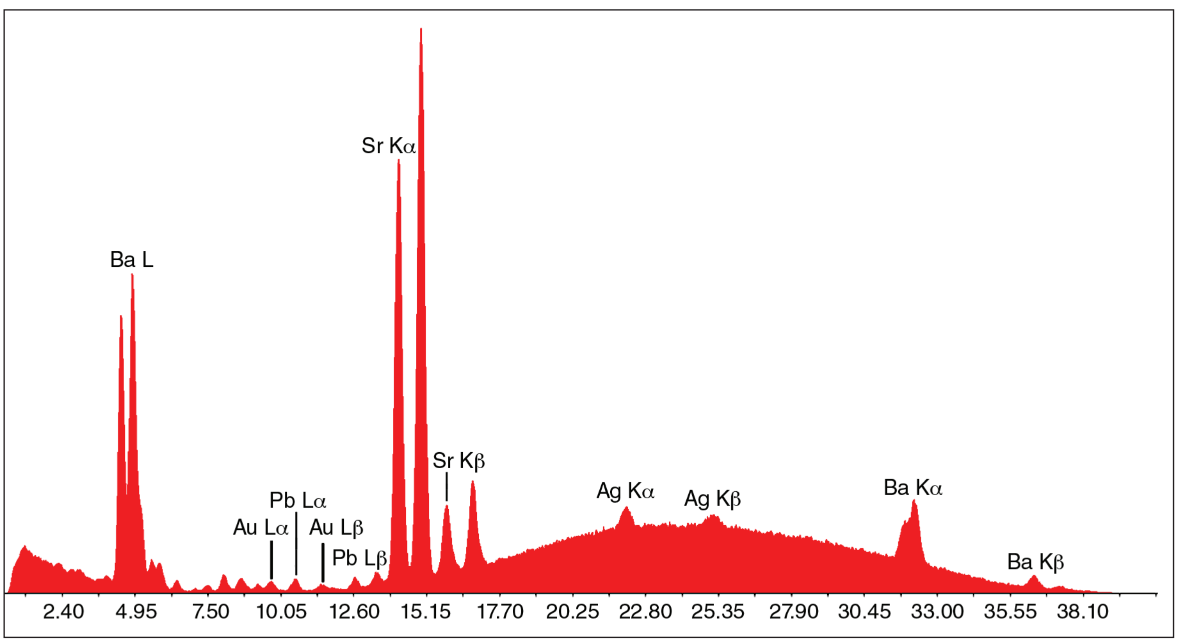


Figure 12b XRF spectrum recorded from the Dmax area of the mounted photograph in fig. 12a.

Figure 13a Album page–mounted POP silver gelatin photograph.

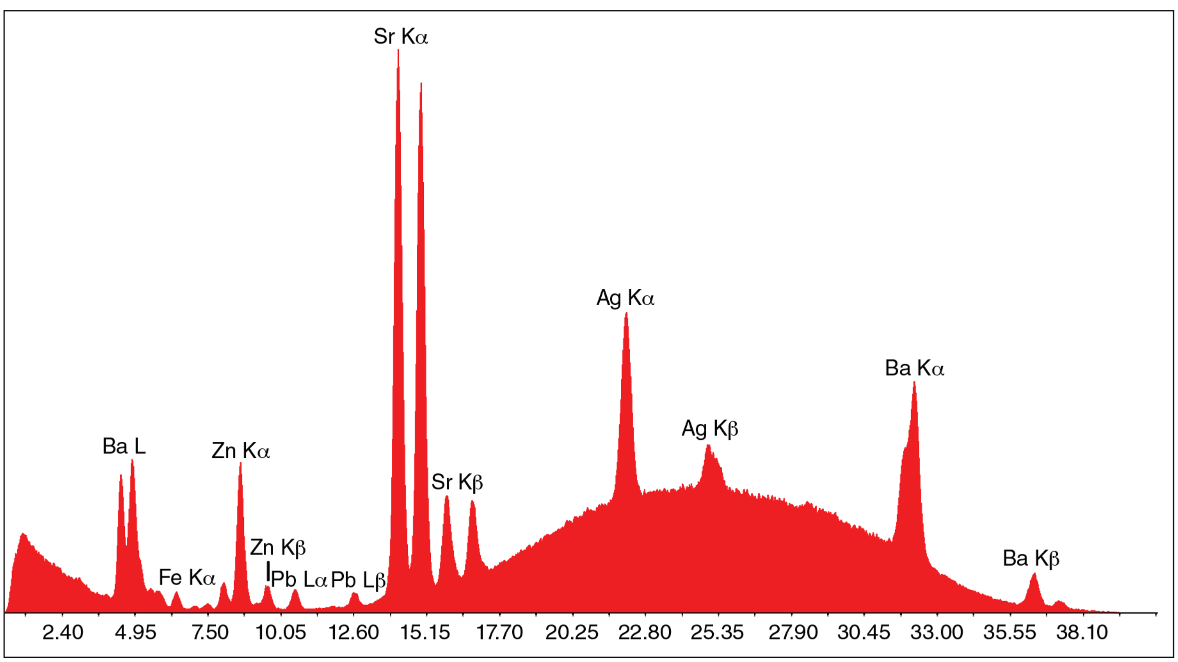


Figure 13b XRF spectrum recorded from the Dmax area of the mounted photograph in fig. 13a.

Figure 14a Cabinet card–mounted POP silver gelatin photograph indicating areas of XRF analysis.

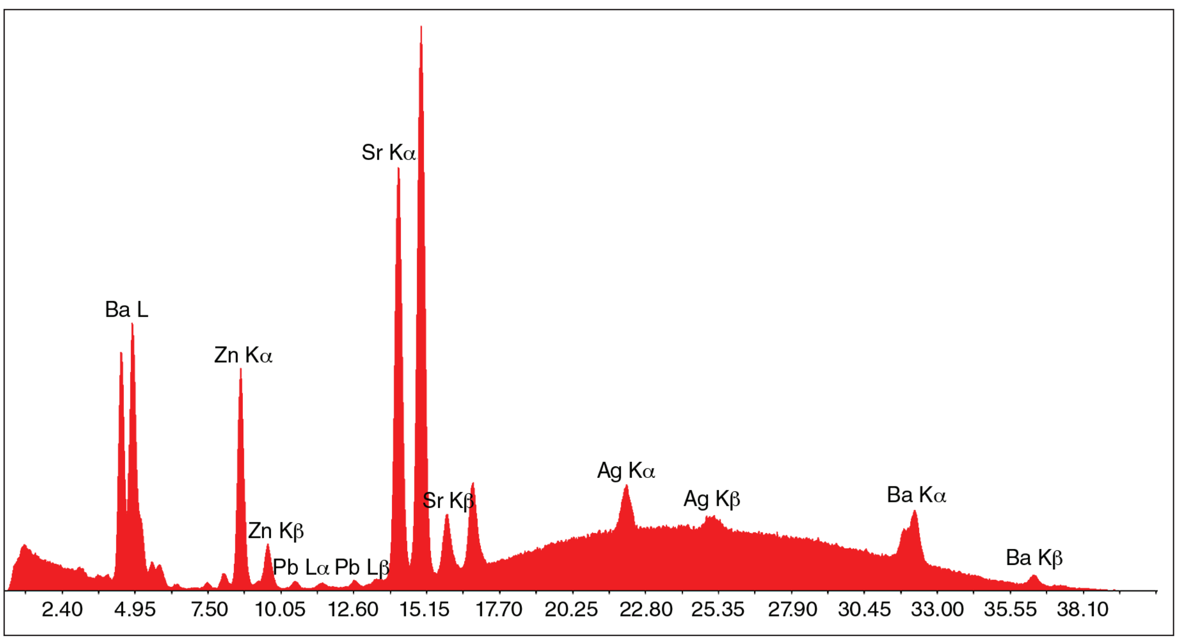


Figure 14b XRF spectra recorded from the Dmax area of the mounted photograph in fig. 14a.

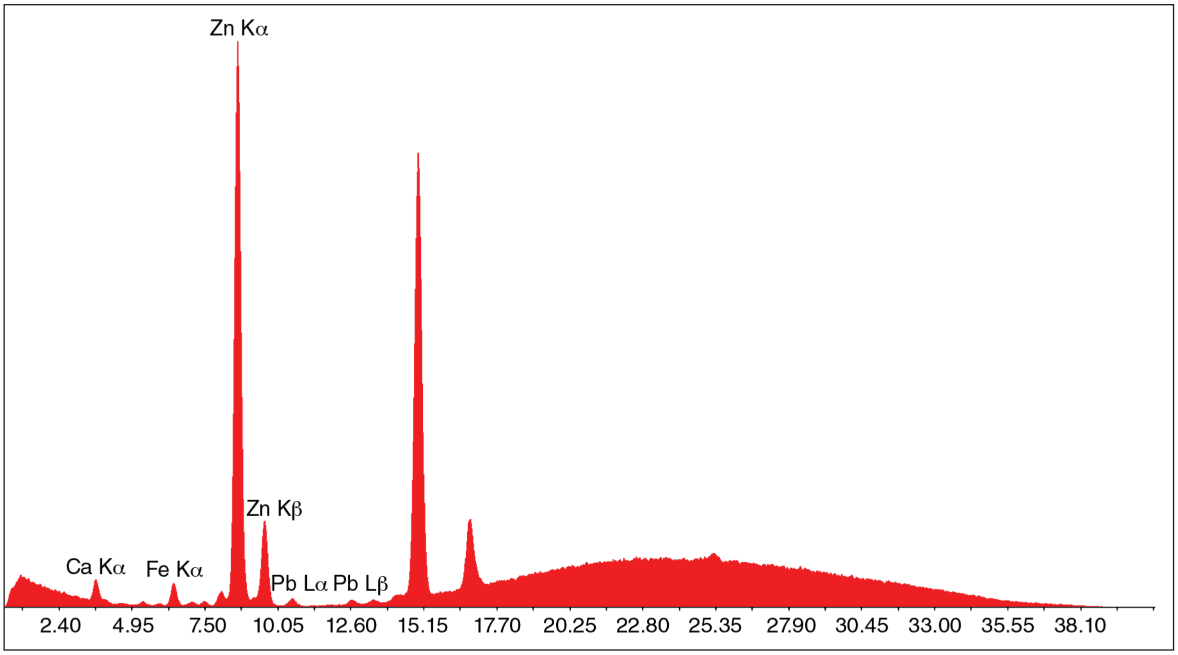


Figure 14c XRF spectrum of the mount alone from fig. 14a.

a mounted photograph and a representative area of the mounting board that does not have any decoration or embossing. The residual spectrum resulting from the subtraction usually corresponds well to the analytical signal from the photograph alone.

FTIR

ATR-FTIR analysis of POP silver gelatin photographs is usually a quick and highly reliable way to identify the gelatin binder of the photograph (fig. 15). FTIR analysis in general is not able to distinguish between POP and DOP photographs but can differentiate between gelatin and albumen photographs. Both albumen and gelatin are proteins, and the FTIR spectra of both materials are almost identical. Figures 16a and 16b show an albumen *cartes-de-visite* (CDV) photograph and its FTIR spectrum, respectively.

Figure 17 shows an FTIR spectrum for the POP silver gelatin CDV photograph in figure 12a. FTIR spectra of both photographs (see figs. 16b and 17) are almost identical. Both show Amide I and Amide II spectral peaks that indicate the presence of proteins. In the region of several smaller spectral peaks to the right of the Amide II peak, the spectral signatures between the two types of photographs differ slightly (figs. 18a, 18b).

In albumen photographs, the peaks at approximately 1451 and 1399 cm^{-1} are about the same intensity, and the peak at about 1318 cm^{-1} is very small or cannot be seen. The ATR-FTIR spectrum of gelatin-based photographs shows three peaks at about 1450, 1393, and 1312 cm^{-1}. The peaks at 1450 and 1393 cm^{-1} are not the same intensity, with the peak at 1450 cm^{-1} usually being much more intense than the peak at 1393 cm^{-1}. The peak at 1312 cm^{-1} is clearly visible for the typical concentration of gelatin.

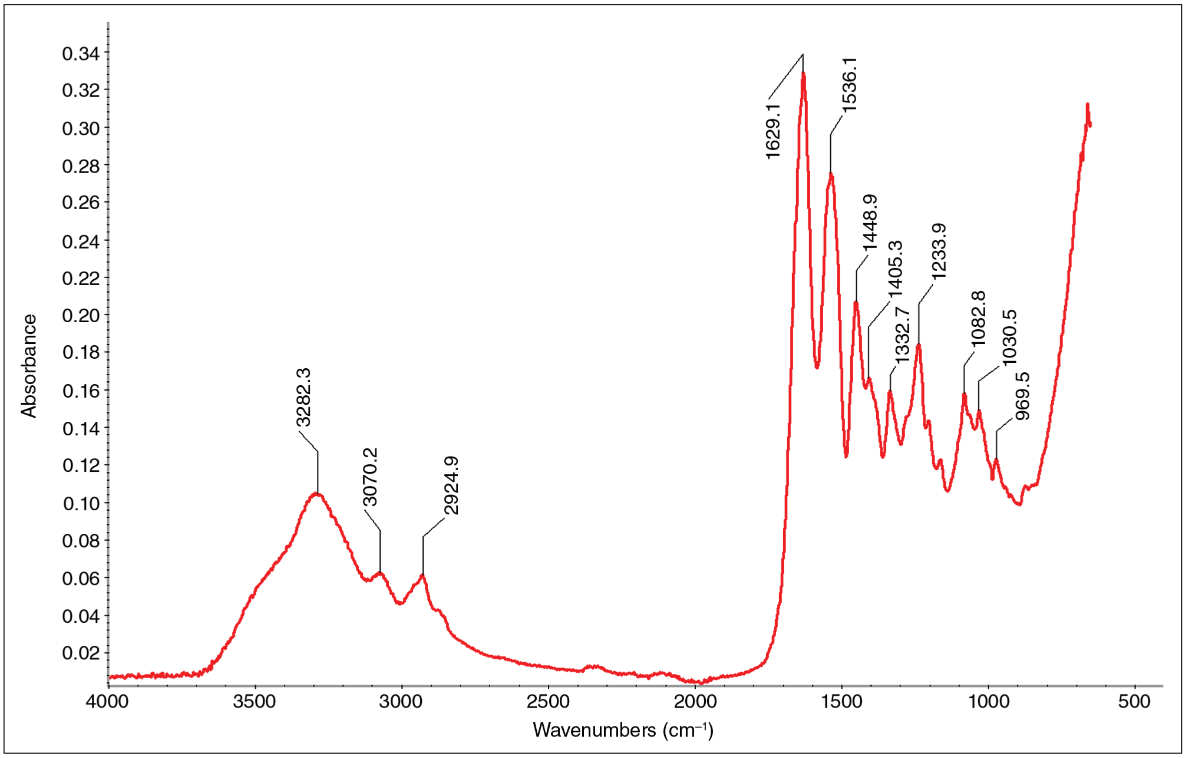


Figure 15 ATR-FTIR spectrum recorded nondestructively from the Dmin area of a POP silver gelatin photograph, identifying the gelatin binder.

Figure 16a Albumen CDV photograph.

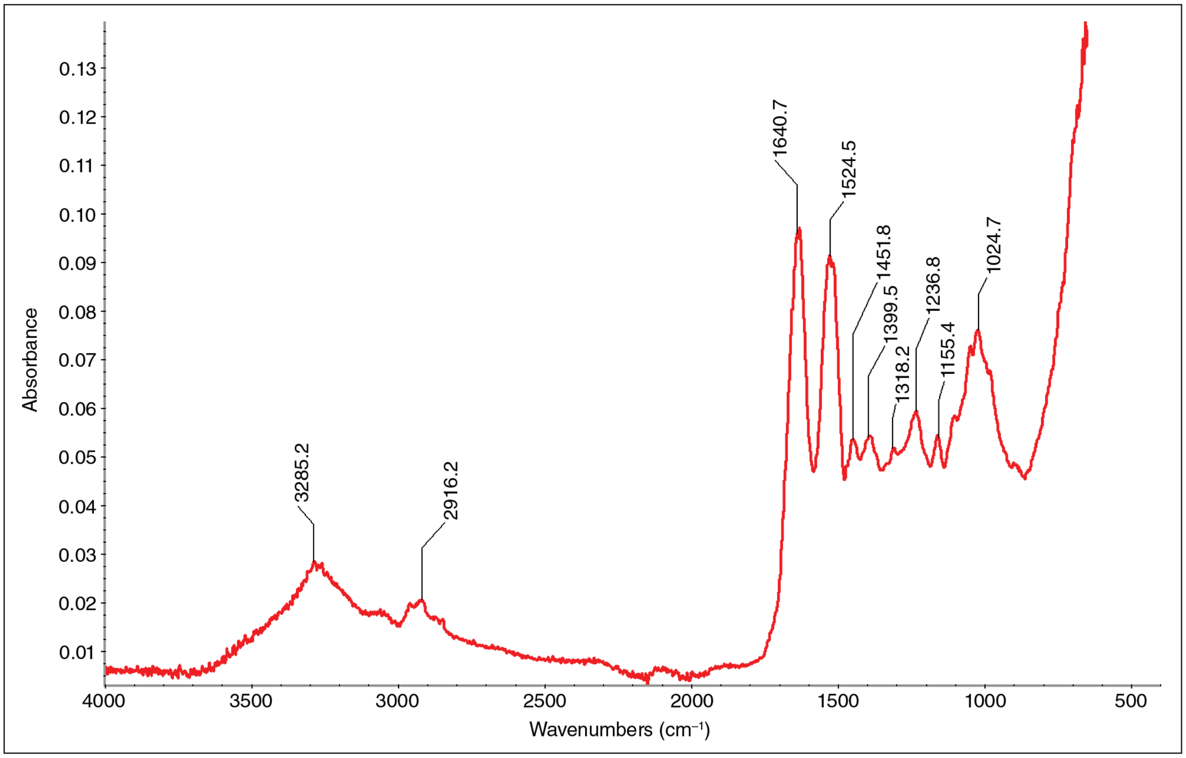


Figure 16b ATR-FTIR spectrum of the surface of the albumen CDV photograph in fig. 16a.

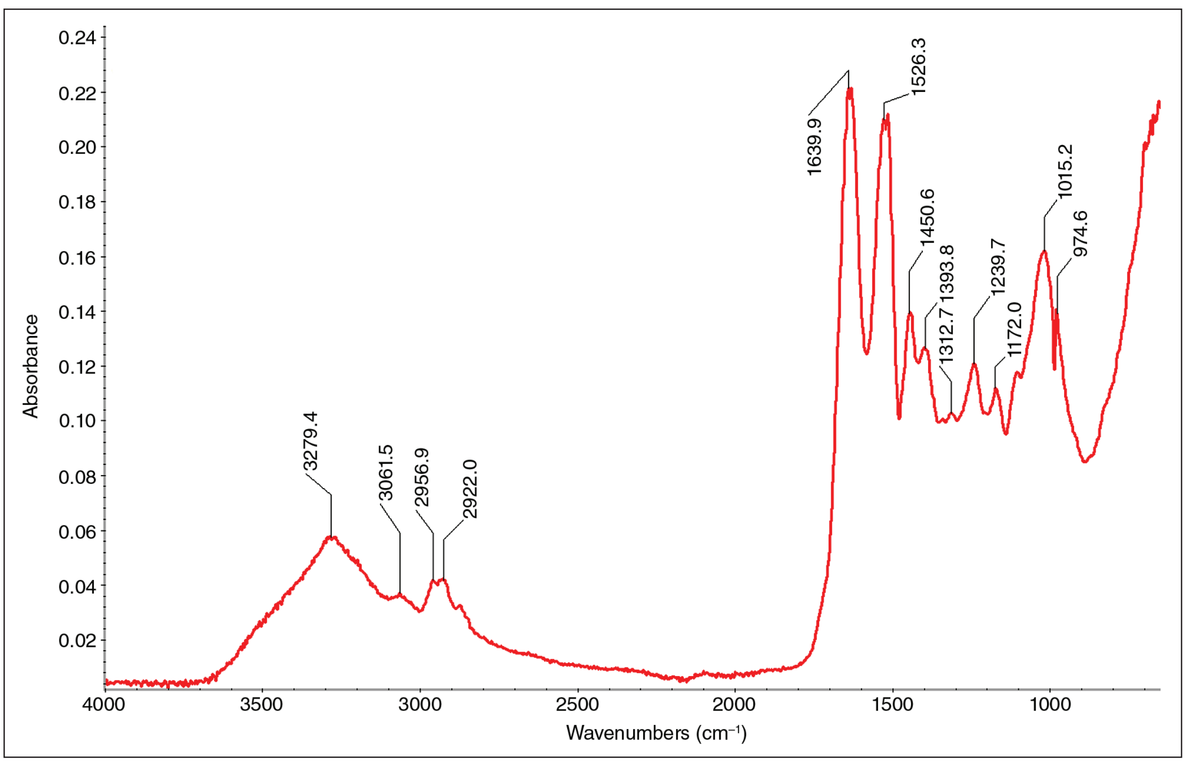


Figure 17 ATR-FTIR spectrum of the surface of the POP silver gelatin CDV photograph in fig. 12a.

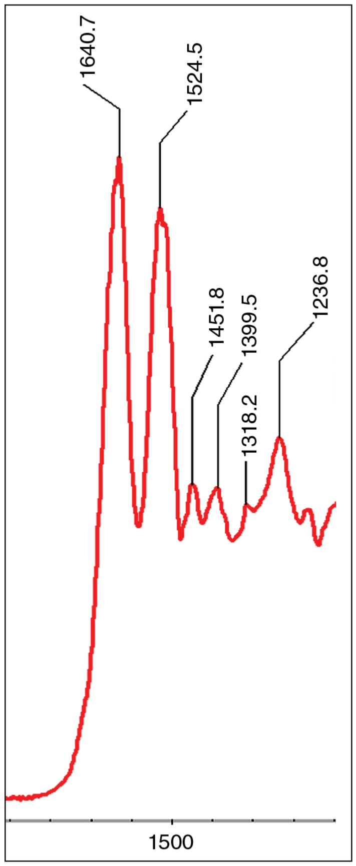


Figure 18a Detail of a typical ATR-FTIR spectral pattern of an albumen photograph.

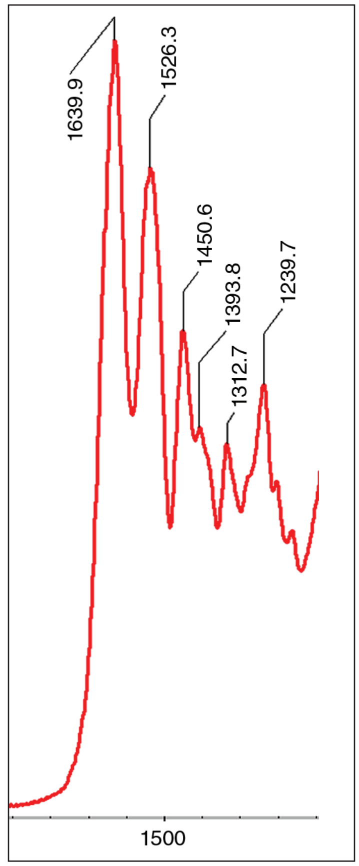


Figure 18b Detail of a typical ATR-FTIR spectral pattern of a gelatin photograph.

Other Analytical Signatures

When it is possible to remove a microscopic sample of the image layer, molecular antibody tests (ELISA assays) can confirm the presence or absence of gelatin in an analyzed photograph (see Albumen section).

Post-Process-Treated POP Silver Gelatin Photographs

Toning of POP silver gelatin photographs is usually considered to be an integral part of the process. The most important post-process modification was the application of a surface varnish or other surface coatings. Surface treatment of POP photographs was done to modify the visual appearance of the photographs (more or less gloss or sheen), to protect against mechanical damage, and/or to protect the silver image against fading due to environmental effects (air pollution, moisture, etc.). A number of varnishes and surface coatings were described in the early photographic literature, but in our analytical investigation of a large number of photographs, we were able to identify collodion-, shellac-, and beeswax-based varnishes and surface coatings as the most common.

Collodion-Based Varnishes and Coatings

Figure 19a shows an early silver gelatin POP photograph surface coated with a relatively thick collodion or collodion varnish (usually more diluted collodion).

The FTIR spectrum in figure 19b represents superposition of both the collodion coating and the lower gelatin layer. The spectrum of pure collodion is shown in figure 19c, which can be easily and reliably detected based on the presence of three peaks typical for nitrocellulose (1632, 1268, and 824 cm^{-1}).

Figure 19a Early POP silver gelatin photograph surface coated with collodion or collodion varnish.

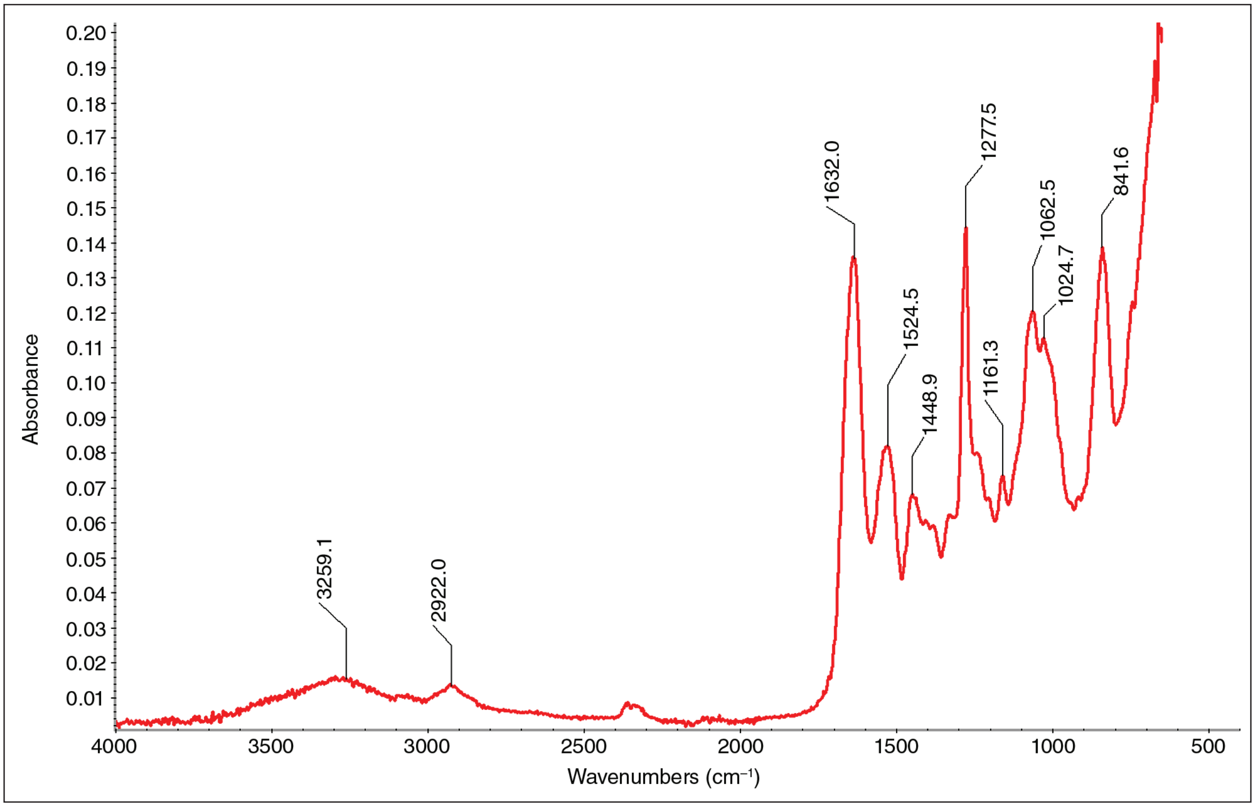


Figure 19b ATR-FTIR spectrum of the coated photograph in fig. 19a, showing superposition of the collodion coating and the gelatin layer.

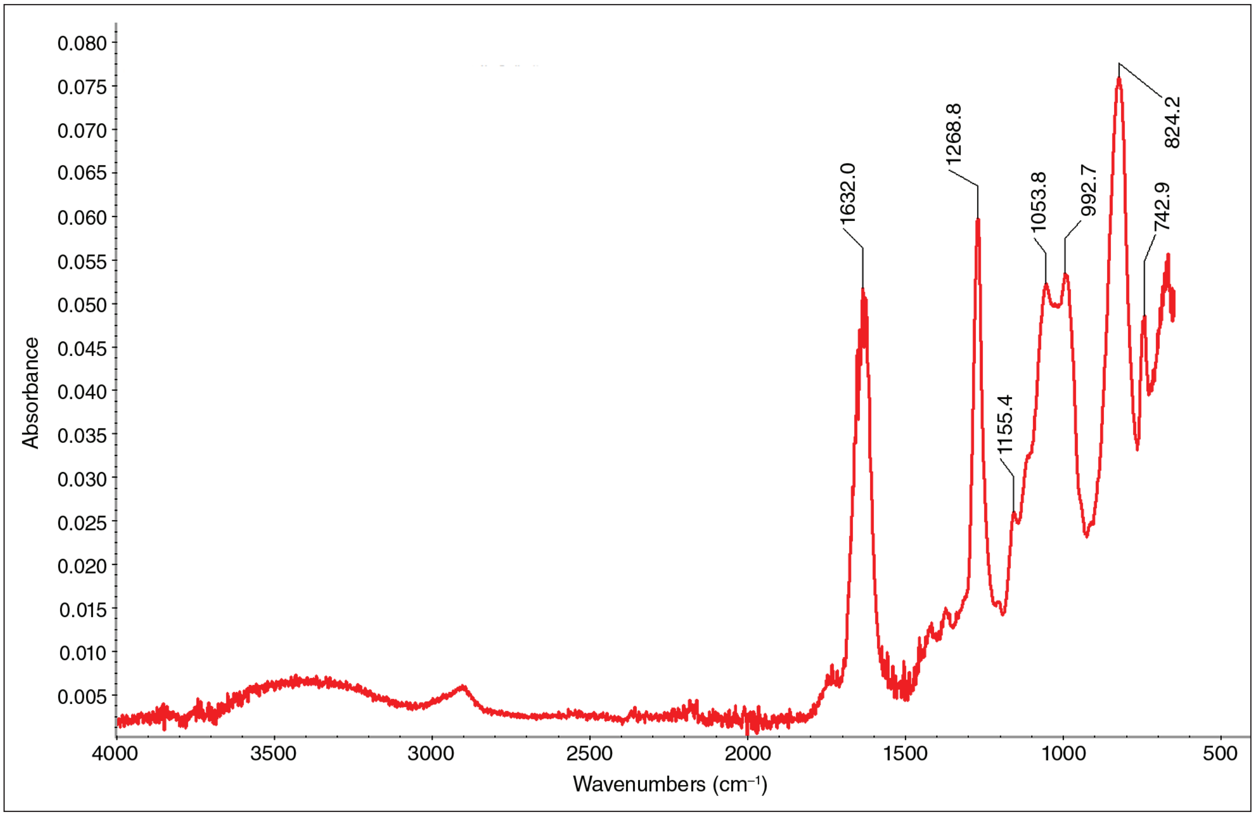


Figure 19c ATR-FTIR spectrum of pure collodion.

The presence of a gelatin layer below the collodion layer can be detected only when the collodion is very thin. The thin collodion layer allows the infrared beam of the ATR-FTIR instrument to penetrate and analyze both organic layers. The resulting FTIR spectrum shows spectral contributions from each layer. The presence of gelatin can be identified by low-intensity peaks (1524 and 1448 cm^{-1}) to the right of the collodion peak at 1632 cm^{-1} (fig. 20).

Shellac-Based Varnishes

Most shellac varnishes were so-called spirit varnishes prepared by dissolving shellac in alcohol. The same kinds of spirit varnishes were also used by artists when stabilizing, or "fixing," chalk or pastel drawings.

Shellac varnishes used by furniture makers were usually much more viscous and would have to be diluted down to fit the needs of photographers. A great number of different resins were and are commercially available (natural, orange, bleached, etc.), but the best material for photographic purposes was bleached shellac, which did not impart any additional color tint to the treated photograph. Figure 21a shows a POP silver gelatin photograph coated with a shellac-based varnish. The photograph's ATR-FTIR spectrum appears in figure 21b, and the ATR-FTIR spectrum of bleached shellac can be seen in figure 21c.

Figure 20 Detail of the ATR-FTIR spectrum in fig. 19b showing the position of gelatin peaks.

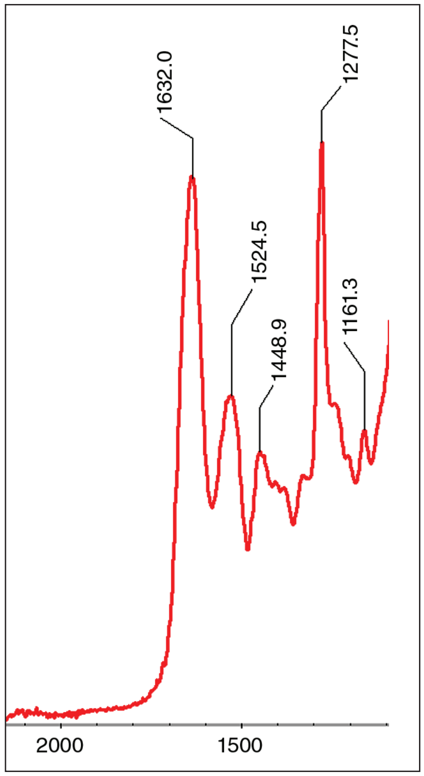


Figure 21a Shellac-varnished silver gelatin POP photograph.

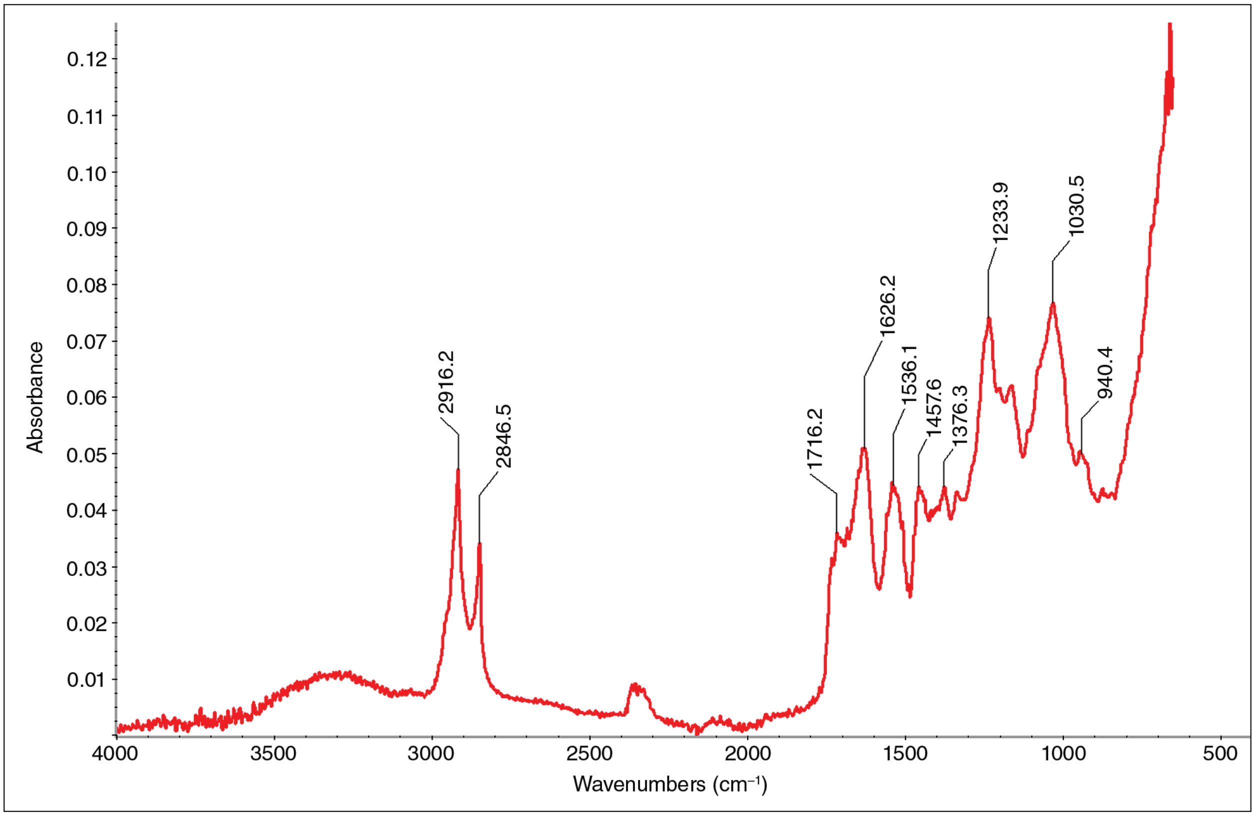


Figure 21b ATR-FTIR spectrum of the shellac-varnished photograph in fig. 21a.

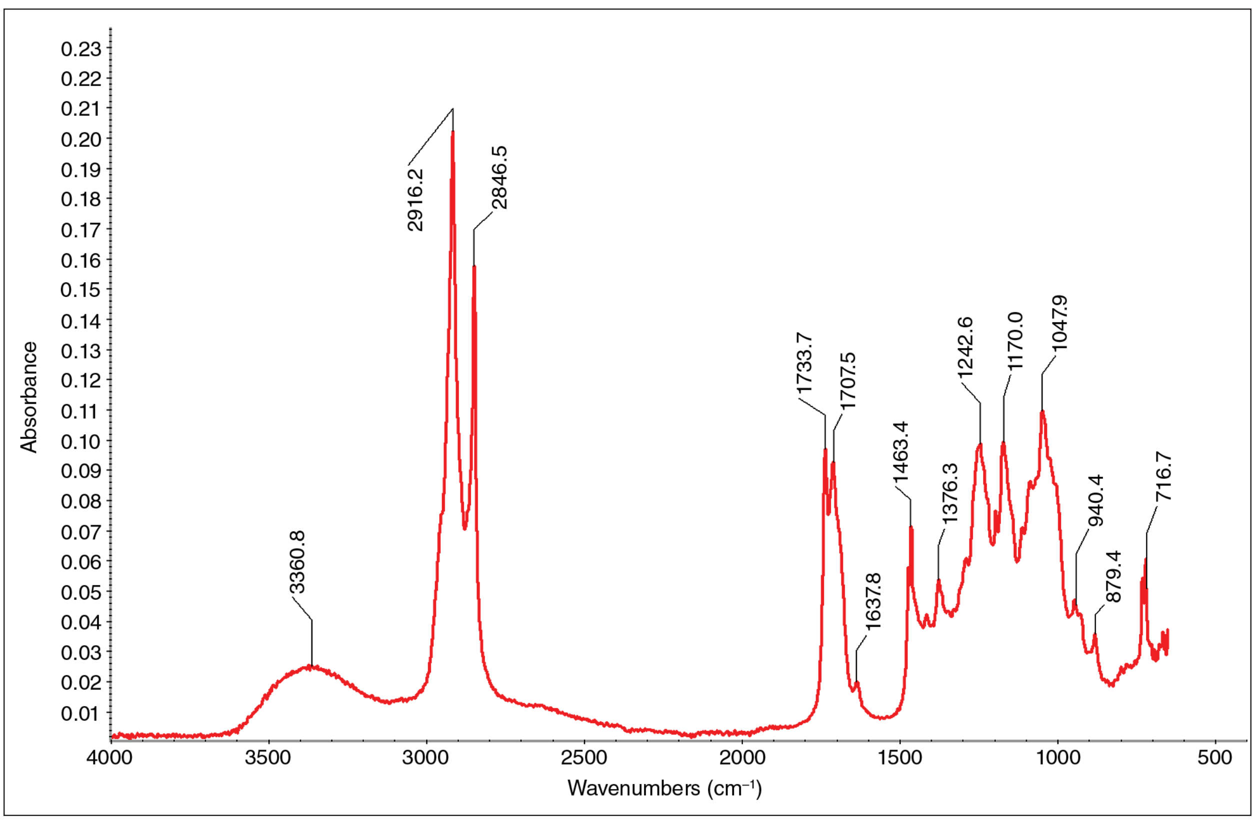
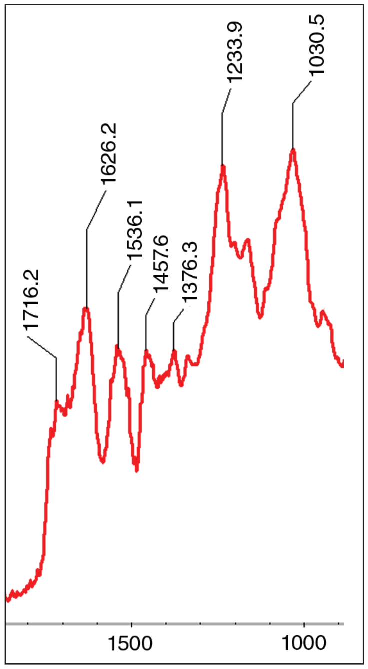


Figure 21c ATR-FTIR spectrum of the bleached shellac.

Figure 22 Detail of the ATR-FTIR spectrum of a shellac-coated photograph that identifies spectral peaks unique enough to be used in identifying shellac in a shellac-coated gelatin photograph.



Spectral peaks at 1733, 1707, 1242, 1170, and 1047 cm^{-1} are typical for shellac and do not interfere with spectral peaks of gelatin. When a thicker layer of shellac varnish is coated onto the surface of a photograph, the spectral peaks of gelatin would not be visible and the ATR-FTIR spectrum of the photograph would closely resemble the spectrum of the shellac (fig. 21c). A detail of the ATR-FTIR spectrum showing peaks that can be used to help identify the presence of shellac is seen in figure 22.

Beeswax-Based Varnishes

Beeswax-based varnishes were used frequently for varnishing, image protection, or appearance modification of almost all types of nineteenth-century photographs. After the start of the twentieth century, varnishing of photographs was used less frequently, though many photographs still exist in museum and private collections that were varnished using beeswax-based varnishes or coating formulas. Some of these materials were also available commercially. So-called encaustic paste was nothing more than beeswax dissolved in turpentine. When applied to the surface of a photograph, the turpentine slowly evaporated and the coating on the surface of the photograph today shows only the analytical signature of beeswax (figs. 23a–23c).

The presence of the beeswax can be identified in the complex spectrum of the coated gelatin photograph by the presence of the CH peaks between 2951 and 2846 cm^{-1} and the ester bond peak at 1733 cm^{-1} to the left of the Amide I peak of the gelatin (fig. 24).

DOP SILVER GELATIN PROCESS

The main difference between the POP and DOP silver gelatin processes is not in the internal structure of the photographic material but in the way the silver-based image is developed. Unlike POP photographs, which are fully developed photogenically using light, DOP silver gelatin photographic paper is exposed only for a short period of time under a negative in a copy frame or using an enlarger. The resulting invisible "latent" image is fully developed using chemical development.

Figure 23a Early POP silver gelatin photograph coated with an "encaustic paste."

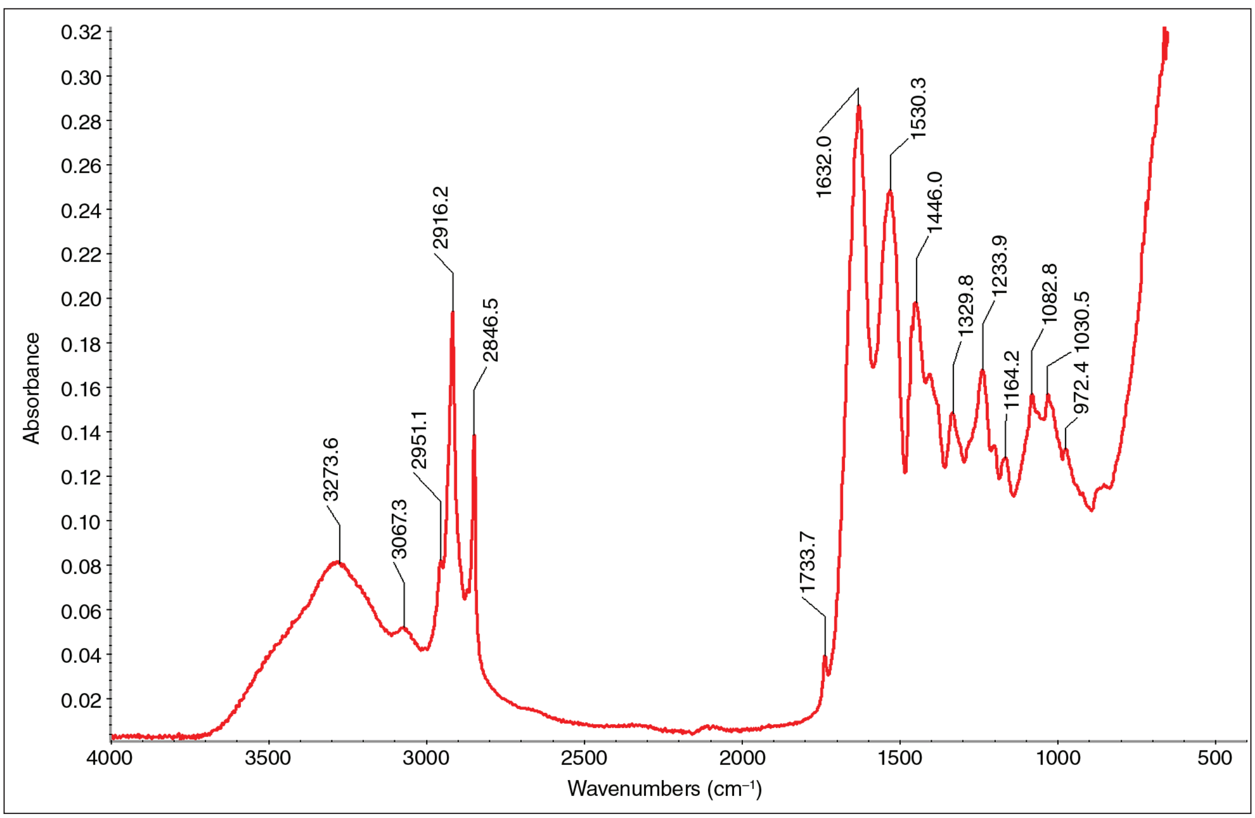


Figure 23b ATR-FTIR spectrum of the surface layer of the photograph in fig. 23a.

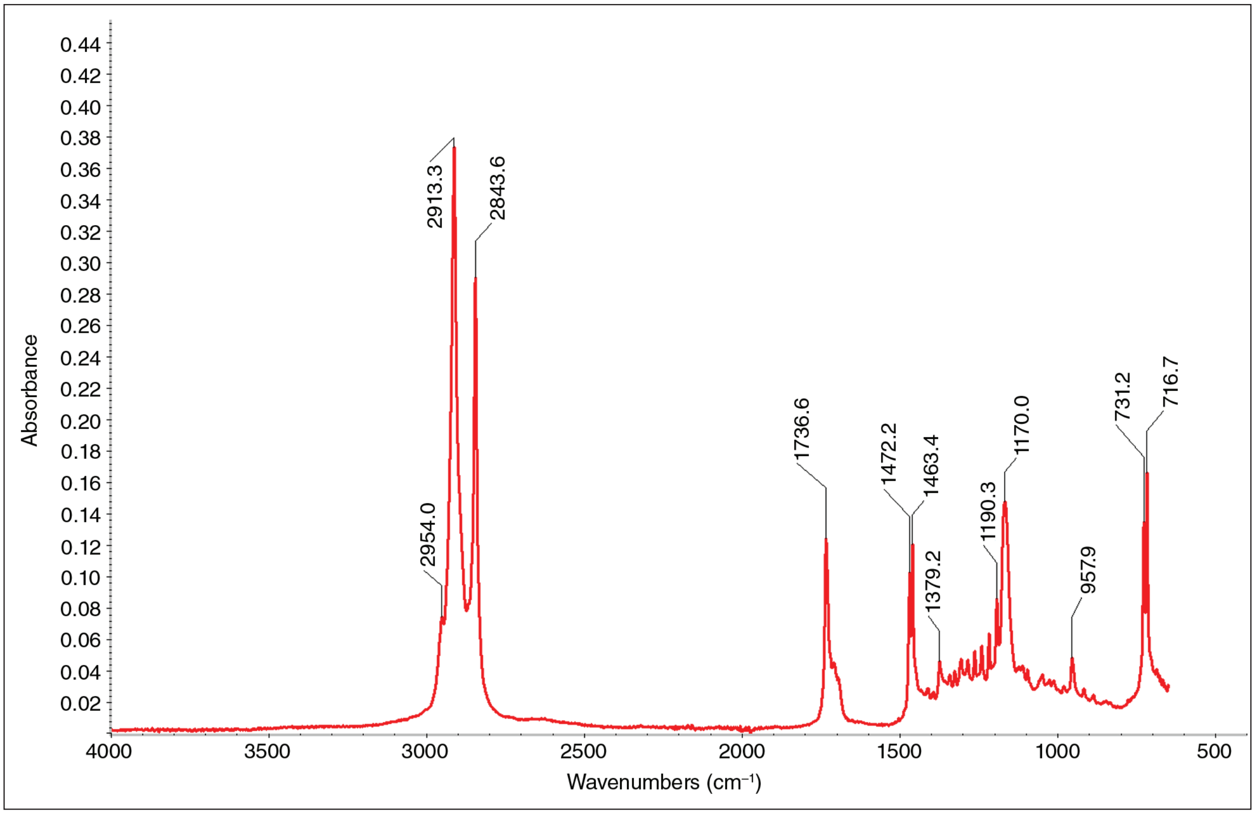
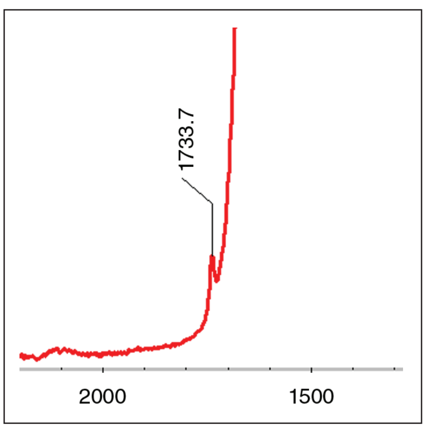


Figure 23c ATR-FTIR spectrum of the net encaustic paste formula coating after the evaporation of turpentine.

Figure 24 Detail of the ATR-FTIR spectrum of a beeswax-coated silver gelatin photograph, showing the position of the ester peak used to identify the presence of the beeswax.



Process Description

The DOP silver gelatin process involves the following steps:

1. DOP (almost 100% commercially made) is exposed for a short time in a contact exposure unit under a negative or by negative projection using an enlarger.
2. The exposed photographic paper containing the invisible "latent" image is placed into a photographic tray containing a developing solution or later into different types of

developing and processing units. Reducing chemicals in the developer results in a visible image formed of larger, filamentary silver particles.

3. The fully developed image, still containing unexposed silver halide particles, is transferred into an acid stop bath to stop the action of the developer.
4. Following the stop bath, the developed paper is transferred into a fixing bath that fully dissolves and removes any still unexposed silver halide particles.
5. The fully fixed photographic image is washed to completely remove any fixing solution and complex silver compounds produced by the fixing solution from the gelatin emulsion layer or the paper base of the fixed photograph.
6. The fully processed and washed photographs are air or hot-air dried.
7. Most silver gelatin DOP photographs were left as such, but some were chemically toned to modify the typical black or dark-brown tonality. Some photographs were also varnished or coated both for protection against environmental effects or to modify the gloss or matte appearance of the photographs. Some pre-1960 photographs were also hand tinted to mimic more expensive color photographs.

The typical cross section depicted here represents only the most important type of DOP silver gelatin photograph usually described as baryta-coated, fiber-based, black-and-white photographs (fig. 25). Silver gelatin DOP photographic papers with this general internal structure were first used in the 1890s and as of 2012 are still being produced.

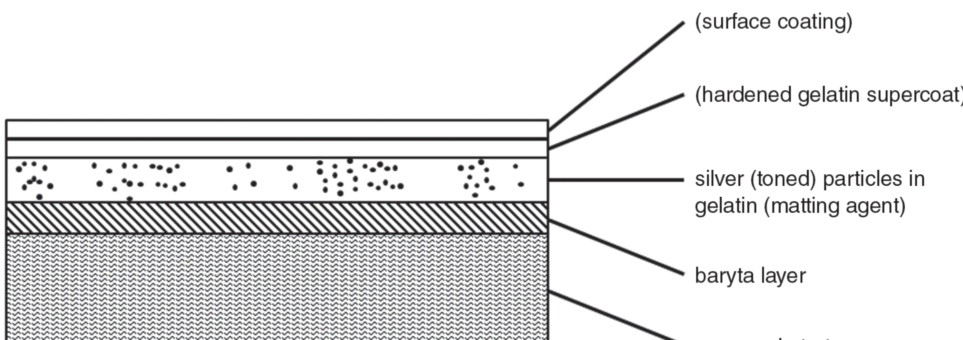


Figure 25 Schematic cross section of a typical baryta-coated, fiber-based, black-and-white DOP photograph.

Main Application of the DOP Silver Gelatin Process

The DOP silver gelatin photographic process was the most important photographic printing process of the twentieth century. Only in the late 1960s did the number of processed color photographs exceed the production and processing of silver gelatin DOP photographs.

DOP silver gelatin photographs, in all their variants, were used for all photographic and imaging applications, including art photography, commercial portraiture, and documentary photography, and in all specialized imaging tasks from criminology to scientific imaging, using all parts of the visible spectrum, infrared photography, and X-ray imaging.

Noted Photographers Using the DOP Silver Gelatin Process

Almost all iconic photographers of the twentieth century used DOP silver gelatin photographic material, exclusively or in combination with several other photographic processes.

Berenice Abbott
Ansel Adams
Richard Avedon
Henri Cartier-Bresson
Lewis Hine
Dorothea Lange
Man Ray
Edward Weston

IDENTIFICATION: DOP SILVER GELATIN PHOTOGRAPHS

Visual Signatures

Visual Characteristics

Chemically developed silver particles present in the image layer of silver gelatin DOP photographs are on average about two orders of magnitude larger than the silver particles found in POP photographs. As such, silver particles are able to absorb a larger portion of incoming light waves. This gives DOP photographs a typical image tonality that ranges from dark gray-black to blue-black (fig. 26).

Figure 26 Typical image tonality of a standard silver gelatin DOP photograph.

Figure 27 Typical image tonality of a warm-tone silver gelatin DOP photograph.

The technology of manufacturing of some black-and-white photographic papers was slightly modified to restrict the growth of silver particles during development. These so-called warm-tone photographic papers produced slightly browner and visually warmer photographic prints even during standard chemical development (fig. 27). The same visual effects can also be achieved using specially formulated developing solutions.

Silver gelatin DOP photographic papers were produced in several different "weights." Visual observation and tactile quality of unmounted photographic papers allow at least some assessment as to which weight category the inspected paper belongs. The most common were "single weight" (SW) and "double weight" (DW) papers, but some "extra thin," "light weight," "extra," or "premium weight" photographic papers were also available.

Different manufacturers used different nomenclature for photographic papers of different weights. In many cases, "double weight" did not mean two times the weight but only a 25%–50% increase over the actual weight of "single weight" papers. The weight of photographic papers was described in different ways in Europe, where manufacturers used the metric system (g/m^2), and in the United States, where the weight was described as the weight of 1000 square feet of paper ($lb/1000\ ft^2$). This was not entirely followed because some US manufacturers, in anticipation of the adoption of the metric system, started but later abandoned describing the photographic paper weight in g/m^2 (fig. 28).

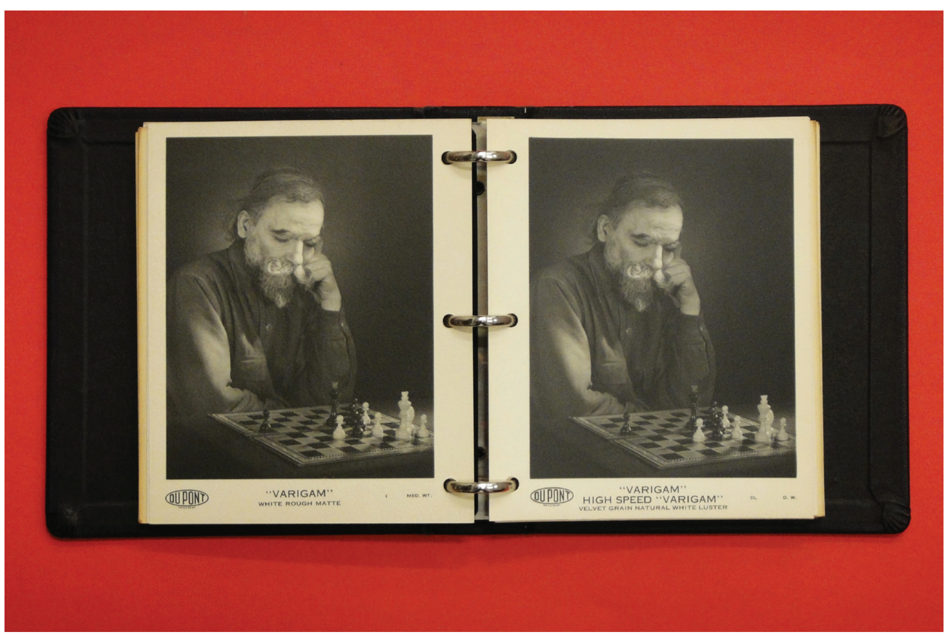
When commercial production of DOP photographic papers began, only glossy and matte versions were available. Once fully adopted by both professional and amateur photographers, these papers became available in many different texture variants to fulfill the varying needs of photographers and to comply with current fashion trends or fads.

Figure 28 Examples of the description of the weight of photographic papers on packaging labels.

The surface finish and texture of photographic papers were produced by combining the photographic emulsion with different matting agents (starches, barium sulfate, glass particles, etc.) and working with heavily calendered papers or rough baryta layers. Heavily textured photographic papers were produced by texturing the paper substrate or baryta layer. During the golden era of silver gelatin DOP photographic paper production, between about 1930 and 1970, almost all manufacturers included in their catalogs a number of different textured photographic papers (fig. 29).

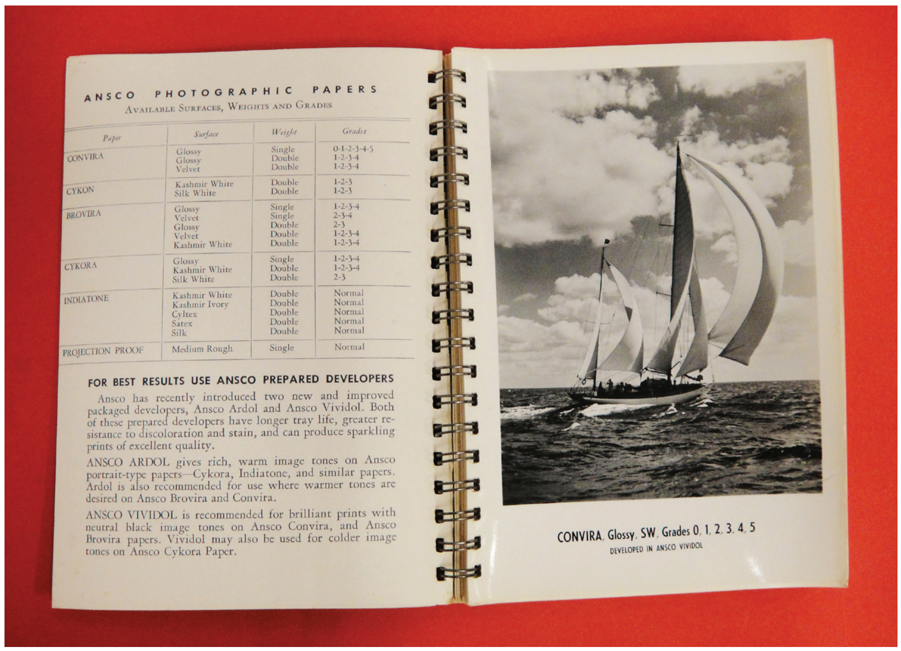
Silver gelatin DOP photographic papers were also manufactured using color paper stock or by adding inorganic or organic colorants to the baryta layer. Kodak manufactured photographic papers of different tints, ranging from pure white to light beige, were available under descriptive

Figure 29 Examples of a photograph printed on two types of textured photographic paper.



names such as snow white, pearl white, natural white, Kashmir white, Kashmir ivory, warm white, cream white, old ivory, or buff. Similar photographic papers were available from different manufacturers under identical, similar, or quite different names (fig. 30).

Sample books or displays of variants of photographic papers were on display at supply houses of photographic material and camera stores, where photographers could see, touch, and select the material. These books represent valuable experimental material for research in photographs today (fig. 31).



ANSCO PHOTOGRAPHIC PAPERS

Available Surfaces, Weights and Grades

Paper	Surface	Weight	Grades
CONVIRA	Glossy	Single	0-1-2-3-4-5
	Glossy	Double	1-2-3-4
	Velvet	Double	1-2-3-4
CYKON	Kashmir White	Double	1-2-3
	Silk White	Double	1-2-3
BROVIRA	Glossy	Single	1-2-3-4
	Velvet	Single	2-3-4
	Glossy	Double	2-3
	Velvet	Double	1-2-3-4
	Kashmir White	Double	1-2-3-4
CYKORA	Glossy	Single	1-2-3-4
	Kashmir White	Double	1-2-3-4
	Silk White	Double	2-3
INDIATONE	Kashmir White	Double	Normal
	Kashmir Ivory	Double	Normal
	Cyltex	Double	Normal
	Satex	Double	Normal
	Silk	Double	Normal
PROJECTION PROOF	Medium Rough	Single	Normal

FOR BEST RESULTS USE ANSCO PREPARED DEVELOPERS

Ansco has recently introduced two new and improved packaged developers, Ansco Ardol and Ansco Vividol. Both of these prepared developers have longer tray life, greater resistance to discoloration and stain, and can produce sparkling prints of excellent quality.

ANSCO ARDOL gives rich, warm image tones on Ansco portrait-type papers—Cykora, Indiatone, and similar papers. Ardol is also recommended for use where warmer tones are desired on Ansco Brovira and Convira.

ANSCO VIVIDOL is recommended for brilliant prints with neutral black image tones on Ansco Convira, and Ansco Brovira papers. Vividol may also be used for colder image tones on Ansco Cykora Paper.

CONVIRA, Glossy, SW, Grades 0, 1, 2, 3, 4, 5

DEVELOPED IN ANSCO VIVIDOL

Figure 30 Page from an Ansco catalog (1950), indicating the commercial availability of various tinted photographic papers.

Figure 31 Silver gelatin DOP sample books, produced and distributed by various manufacturers of photographic material.

During the first half of the twentieth century, several manufacturers of photographic paper printed a company logo or the name of a photographic product on the back of photographic papers. Company logos or product names, sometimes even the logo printing process, were often modified. Printing had to be done in light colors so that the logos or names would not be visible through the paper. Printing inks were required that would not dissolve or bleed during wet chemical processing. Surveys of printed logos and product descriptions, and their changes over time, are valuable visual clues when provenancing or authenticating photographs.

Microscopic Characteristics

Most microscopic signatures of DOP silver gelatin photographs are similar to those described for POP silver gelatin photographs. Even though the silver particles of DOP photographs are about ten times larger than the silver particles of POP photographs, observation of individual particles is well beyond the capabilities of standard laboratory stereomicroscopes (5×–100× magnification). Observation of the silver particles usually requires microsampling, preparation of a very thin cross section, and the use of a transmission electron microscope (TEM).

Analytical Signatures

In general, the analytical signature of baryta-coated, fiber-based, silver gelatin DOP photographs is similar to that of POP photographs. The more complicated internal structure and chemical composition of DOP photographs is based on the fact that these materials were made industrially since the last decades of the nineteenth century and are still produced by several surviving factories of silver halide photographic material today. Many more variants (thickness, texture, color, sheen, tonality, etc.) were introduced and used by photographers during the more than one hundred years of history of silver gelatin photographic papers.

Major changes and developments took place in the production of the paper stock that was used as the substrate of DOP photographic paper. The original "rag"-based paper was slowly modified by the introduction of different types of cellulosic fiber materials. After the 1920s, processed wood cellulosic material was introduced. The internal chemistry of the paper substrate was also modified by the addition of new synthetic resins that were tested and introduced as internal binders and sizes to increase the wet strength and hot process stability of photographic papers. The identification of all of these chemical changes is important for provenance and authentication studies of DOP silver gelatin photographs, but this type of analysis so far requires physical sampling of paper material and is beyond the capabilities of nondestructive analytical techniques, which are the main focus of this publication.

Many more chemical procedures were developed for the modification of the appearance of DOP photographs based on chemical toning and surface varnishing and coating of DOP photographs. Surface varnishing also progressed from the early use of natural resin varnishes to the later application of specialized varnishes and coatings containing synthetic resins and polymer materials.

XRF

Figure 32a shows a 1990s untoned silver gelatin photograph printed using Ilford Multigrade IV, baryta-coated, fiber-based photographic paper. Its XRF spectrum appears in figure 32b.

Figure 32a Silver gelatin untoned DOP photograph from the 1990s.

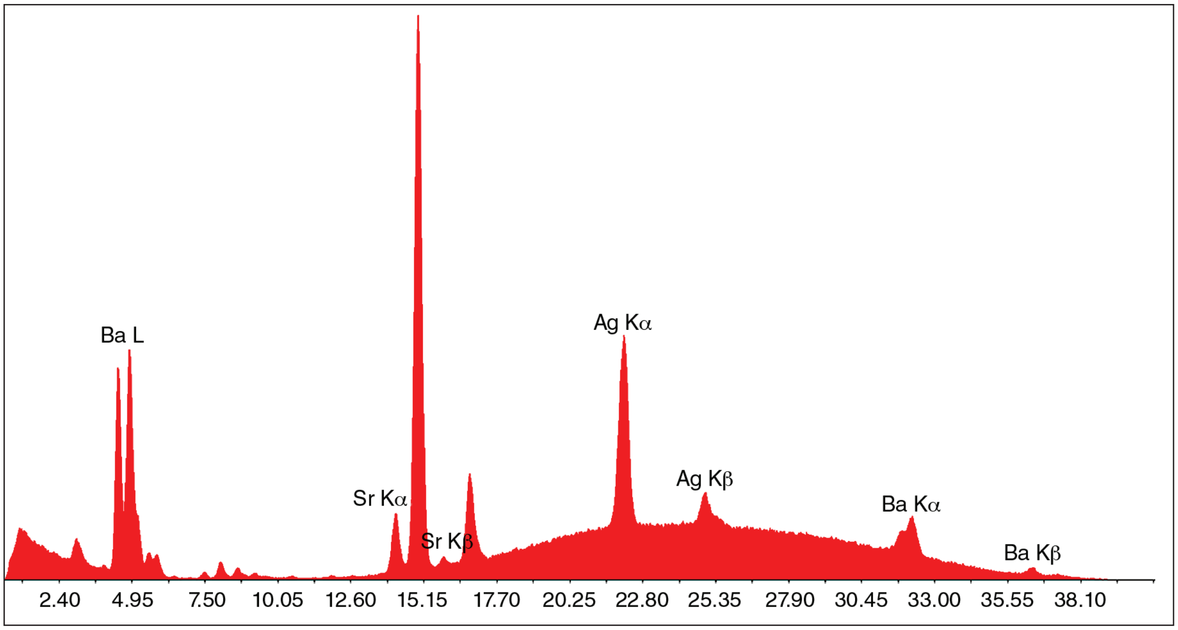


Figure 32b XRF spectrum recorded from the Dmax area of the photograph in fig. 32a.

The XRF spectrum shows the presence of silver (Ag) originating from the image layer of the photograph and the presence of barium (Ba) and strontium (Sr) from the baryta layer.

To produce photographs of different colors from the usual dark brown or black, photographers have several options:

- the use of photographic papers producing slightly different image colors;
- the use of special developer formulas that produce slightly different image colors; or
- the use of different types of chemical toning formulas and procedures.

The first two options do not bring about any pronounced chemical changes that can be detected analytically. We know that many professional portrait photographs exhibiting a greenish tonality (fig. 33) were printed using photographic paper containing a large concentration of silver iodide (AgI). There is no iodide left in the image after processing, so it is only the color of the image that may indicate the possibility of using these types of photographic papers (the same green tonality can also be achieved by vanadium toning).

A number of DOP photographic papers were also produced in two different variants, black and white and warm-tone black and white, including Ilford Multigrade IV (fig. 34). The emulsion chemistry of warm-tone photographic papers was slightly modified to restrict the growth of silver particles during development. The smaller size of the developed particles created the warmer tonality of the image. As in the case of AgI photographic papers, there is no clear chemical signature of warm-tone DOP prints (besides its visual appearance) that could be used to identify a warm-tonality photograph as being printed on the warm variant of the paper.

FTIR

The internal structure of DOP photographs is similar to the internal structure (layering) of POP silver gelatin photographs. In later years some manufacturers worked to protect the emulsion layer against mechanical damage by applying a thin "overcoat" or "topcoat" layer of hardened gelatin. This results in a thicker emulsion layer and very well developed spectral peaks of gelatin in the

Figure 33 DOP photograph printed on silver iodide (AgI)–based photographic paper, showing a greenish tonality.

Figure 34 Two types of Ilford Multigrade IV photographic paper.

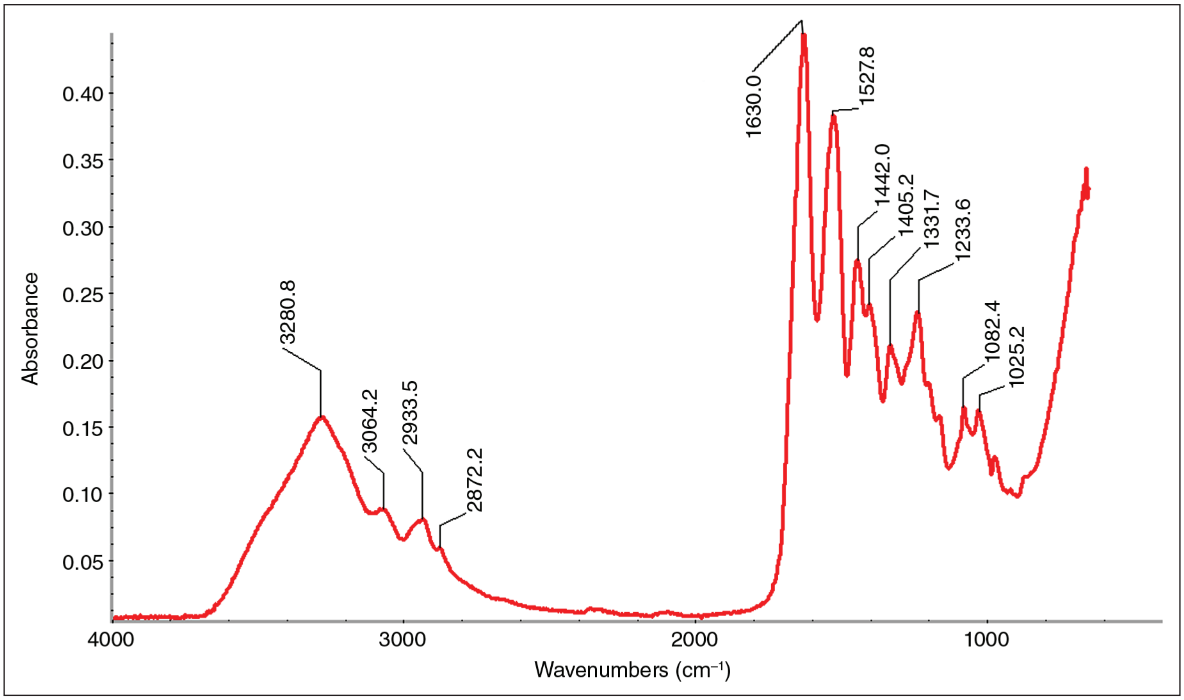


Figure 35 ATR-FTIR spectrum of an uncoated silver gelatin DOP photograph.

ATR-FTIR spectrum (fig. 35). The spectrum shows strong Amide I (at 1630 cm^{-1}) and Amide II (at 1527 cm^{-1}) peaks, together with the fine structure of additional Amide peaks (1442, 1405, and 1331 cm^{-1}), that usually allow for differentiation between albumen and gelatin photographs (figs. 36a, 36b).

Both the spectra positions and relative intensities of these peaks allow for the analytical differentiation of both types of photographs. ATR-FTIR spectrometry is very effective when detecting and identifying varnishes or coatings of DOP photographs. This type of analysis is covered in the post-processing part of this section.

Other Analytical Signatures

To increase the desired brilliance of silver gelatin photographs, several manufacturers started to experiment with the addition of optical brightening agents (OBAs) to the paper base, baryta layer, or photographic emulsion. Some OBAs were also added to the processing chemicals. OBAs are fluorescent dyes that absorb energy in the UV portion of the spectrum and re-emit it in the blue portion of the visible spectrum (fig. 37).

Images printed on photographic papers that contain optical brighteners appear richer and brighter. The idea of increasing the brightness of photographic papers by adding these agents was developed in the late 1940s and was tested after 1951. Systematic research of photographic papers performed by Paul Messier and colleagues showed that the industrial production of OBA-containing papers started by about 1953 and was used by many photographic paper manufacturers after 1955. Not all photographic papers after 1955 contain OBAs, but their presence in pre-1953 photographs raises suspicion of incorrect dating or possible forgery of photographic images.

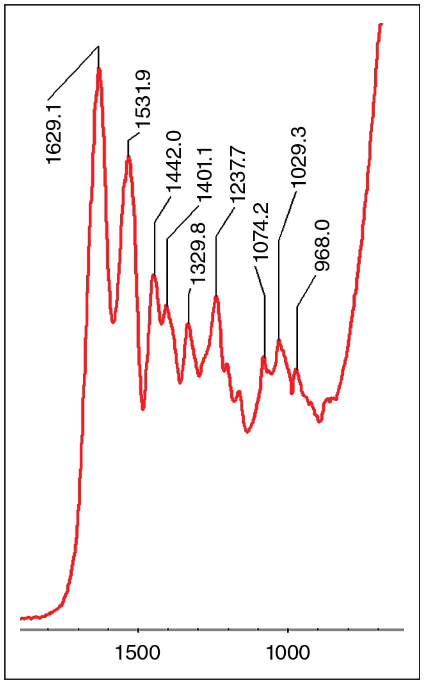


Figure 36a Detail of the ATR-FTIR analysis showing spectral peaks typical for gelatin-based photographs.

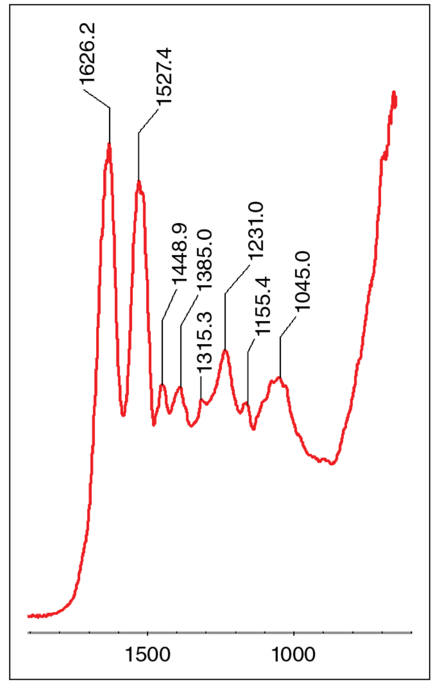


Figure 36b Detail of the ATR-FTIR analysis showing spectral peaks typical for albumen-based photographs.

Figure 37 The pre-1953 photograph (left) does not contain OBAs and has a dull appearance. Compare its fluorescence with the post-1953 photograph (right), which contains OBAs.

It is important to understand that the concentration of OBAs can be affected by extensive washing of photographs and that some accidental or deliberate treatment with chemicals (certain organic compounds, heavy metals, or oxygen-containing material) can quench the fluorescence or remove the brightness of OBA-containing photographs under UV inspection. The concentration of the brightening agents in photographic papers is too low for their detection using methods of infrared spectrometry.

Post-Process-Treated DOP Silver Gelatin Photographs

Several toning procedures were developed during the twentieth century to produce monochrome images of different colors.

Sulfur Toning

The most common toning used during the early twentieth century was brown sulfur toning. A number of direct or indirect toning procedures were developed and used to impart brown tonality primarily to matte surface photographs, which were in vogue at the time among portrait photographers between World War I and World War II (fig. 38).

The XRF spectra of the photograph in figure 38 show the presence of all chemical elements typical in DOP silver gelatin photographs, including sulfur (figs. 39a, 39b). In interpreting the XRF spectra of sulfur-toned photographs, it is important to understand that even when clearly visible in the XRF spectrum, the main source of the spectral signal of sulfur is not from the Ag_2S toned silver image. Rather, it is from the sulfur of the $BaSO_4$ composing the baryta layer, which is almost always present in these types of photographs and makes differentiating the source of the sulfur signal extremely difficult.

Figure 38 Typical sulfur-toned, brown, matte silver gelatin photograph from the 1920s.

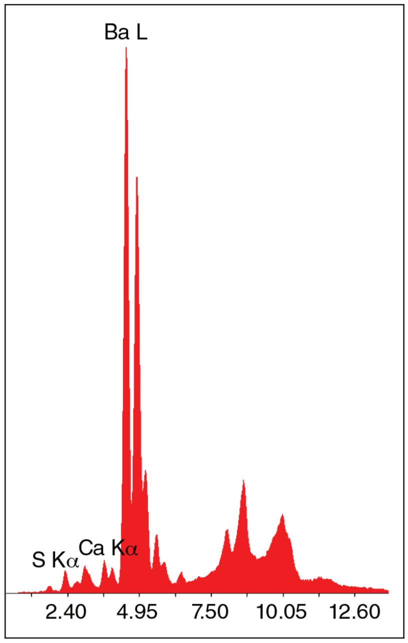


Figure 39a XRF spectrum of the Dmax area of the sulfur-toned, silver gelatin photograph in fig. 38, recorded under vacuum.

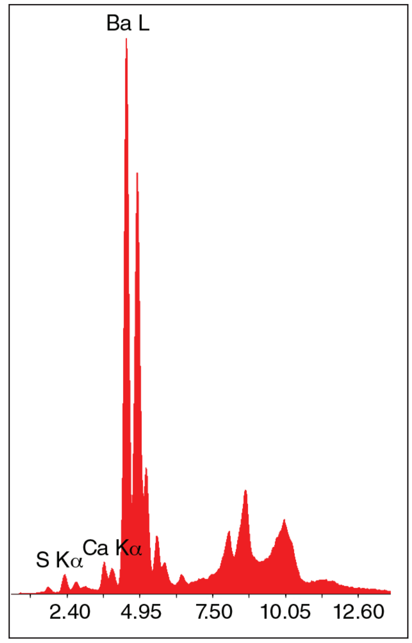


Figure 39b XRF spectrum of the Dmin area of a sulfur-toned, silver gelatin photograph in fig. 38, recorded under vacuum.

Several toning procedures used several different heavy metal elements to change the color of black-and-white photographs. These elements usually remain in the toned photograph and can be easily detected using XRF instrumentation.

Gold Toning

In addition to producing black-brown-violet DOP images similar to gold-toned POP photographs, toning with special gold-toning formulas produced very pleasing bright-red DOP photographs (fig. 40). The XRF spectrum of the photograph clearly shows the presence of gold (fig. 41).

Many researchers who work with photographs find it surprising that gold toning can produce beautiful bright-blue tonality in a DOP photograph. Figure 42 shows a pre–World War II wedding photograph toned blue using a gold toner. The XRF spectrum of the photograph also shows the presence of gold (fig. 43).

Uranium Toning

Treatment of a silver image with a mixture of a soluble uranium salt and ferricyanide of potassium yields brown to dark orange-red images, the color being dependent on the ratio of the two salts and the duration of toning. Figure 44 shows a 1960s uranium-toned silver gelatin DOP photograph. The XRF spectrum of the photograph (fig. 45) shows the presence of uranium based on the two major uranium peaks at 13.64 keV and 17.22 keV, respectively.

The presence of uranium, slightly radioactive, can be confirmed quickly using a very sensitive radiation meter. Figure 46 shows the noncontact radioactivity measurement of a uranium-toned photograph using a Victoreen Advanced Survey Meter. The radioactivity level produced by

Figure 40 Red-tone silver gelatin DOP photograph produced using a gold toner.

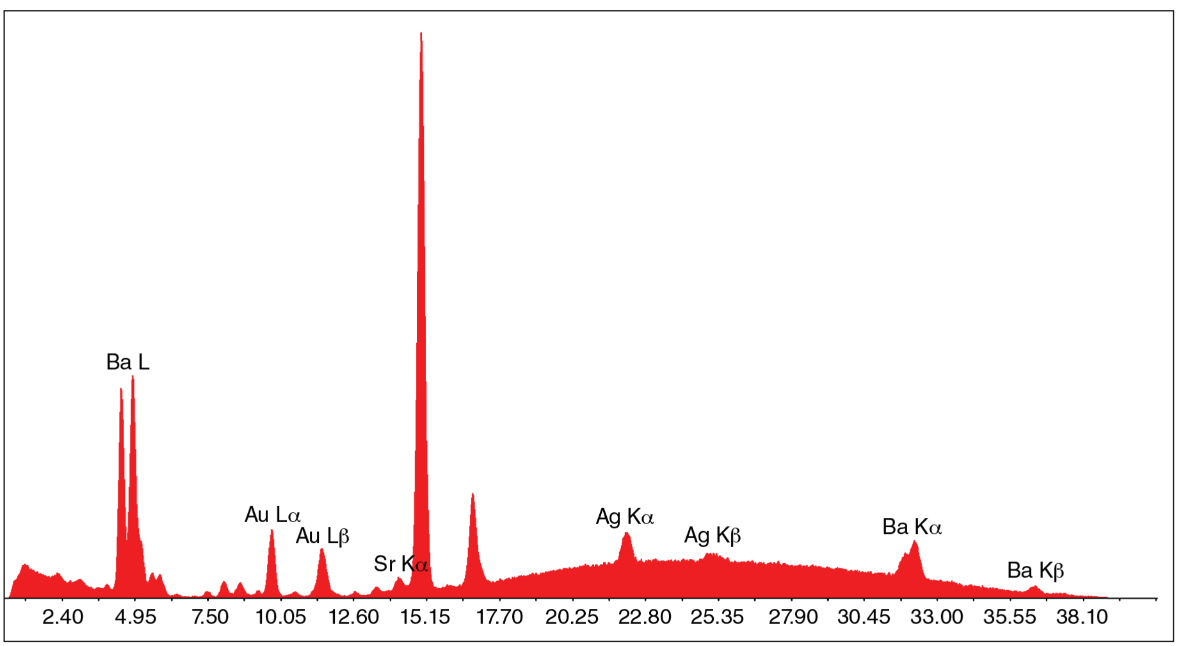


Figure 41 XRF spectrum of the DOP photograph in fig. 40, showing the presence of gold.

Figure 42 Blue-tone silver gelatin DOP photograph produced using a gold toner.

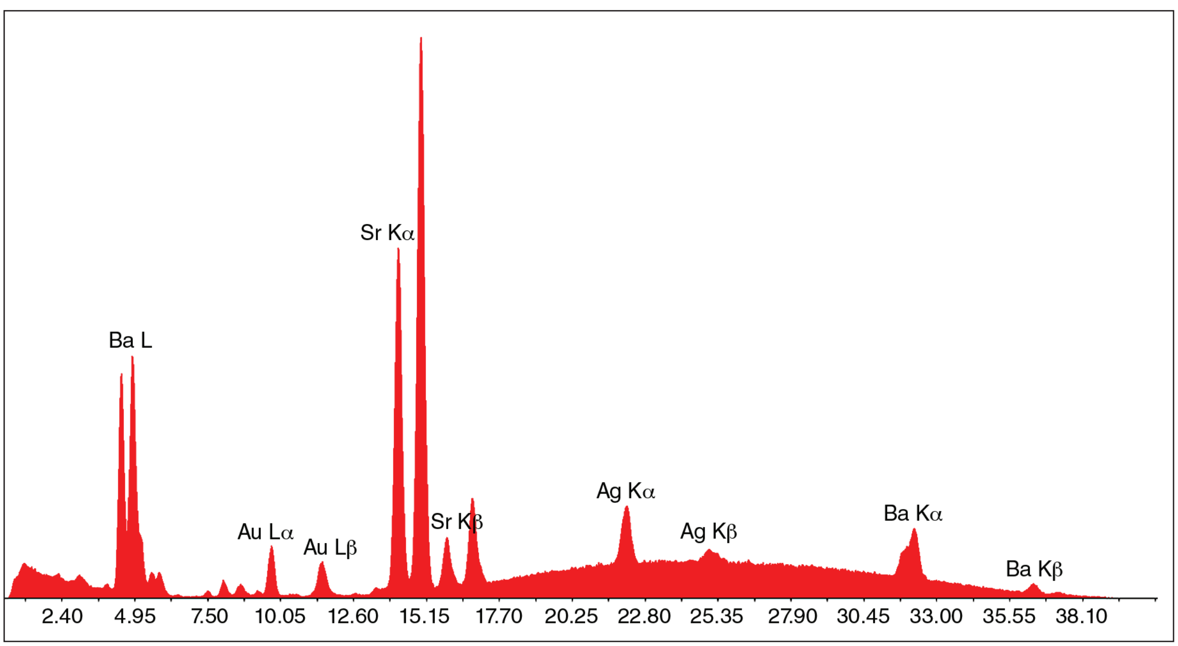


Figure 43 XRF spectrum of the DOP photograph in fig. 42, showing the presence of gold.

Figure 44 Uranium-toned DOP silver gelatin photograph from the 1960s.

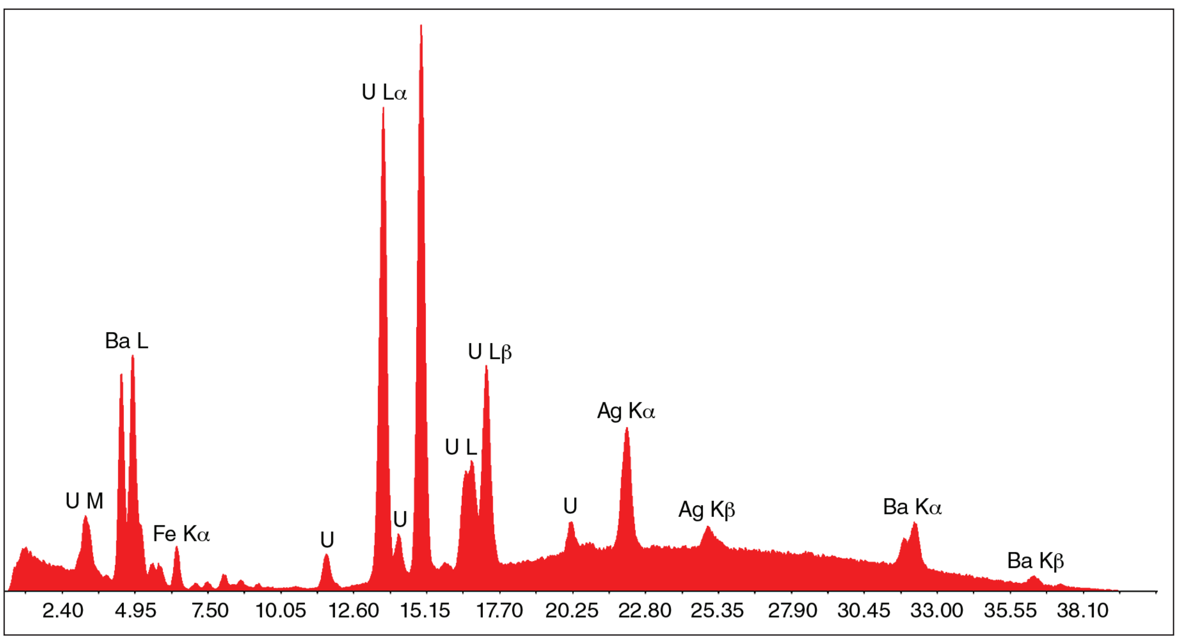


Figure 45 XRF spectrum of the DOP photograph in fig. 44, indicating the presence of uranium based on two major uranium peaks.

uranium-toned photographs is not harmful to collection staff or to photograph conservators. Because the uranium is well embedded in the gelatin layer of the photograph, handling can be carried out using standard conservation procedures. The measured radioactivity of the uranium-toned photograph in figure 44 was about 117 micro REM/hour (measured about 1 cm above the print). This level of radioactivity is well above the natural radiation background (about 10 micro REM/hour) but not high enough to cause any health issues in occasional handling.

Iron Toning

A number of toning formulas were published for blue toning of silver images based on converting silver particles to silver salts and then forming a blue image by reaction with a solution of iron salt. Different chemical mechanisms of these reactions often yield blue images composed of Prussian blue pigments (fig. 47).

Figure 46 Noncontact radioactivity of a uranium-toned photograph is measured using a highly sensitive Victoreen Advanced Survey Meter.

Figure 47 Blue-toned silver gelatin photograph.

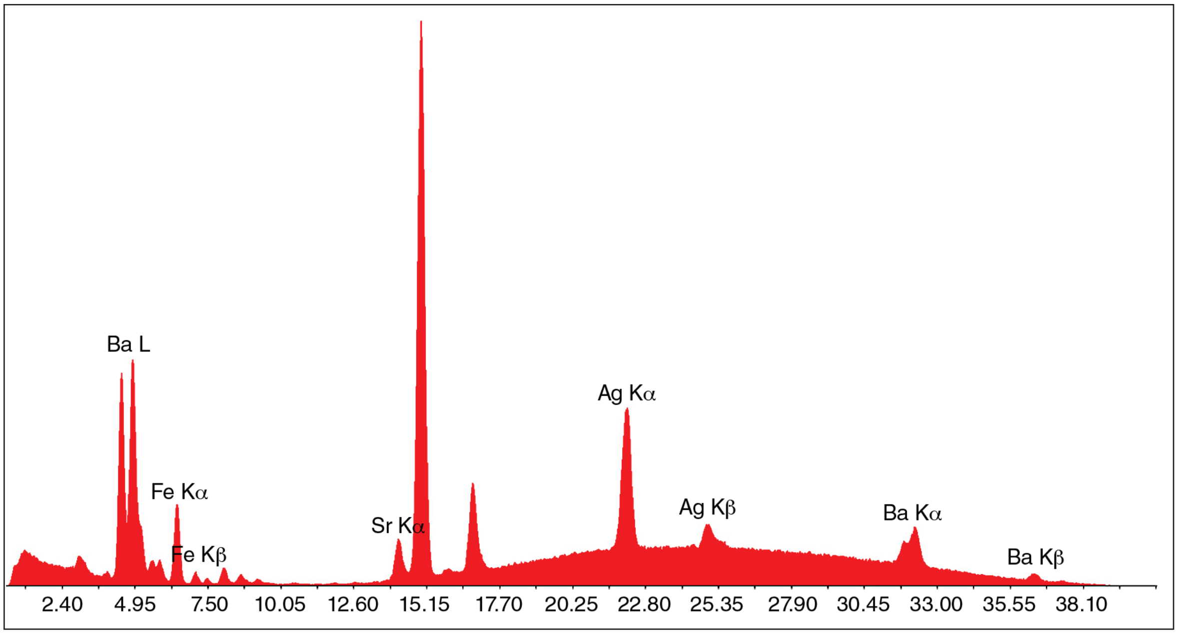


Figure 48 XRF spectrum of a blue-toned (Prussian blue) silver gelatin DOP photograph recorded from the Dmax area.

The presence of Prussian blue in the toned photograph in figure 47 can be determined based on XRF analysis, which shows a higher concentration of iron in the Dmax area in comparison with the Dmin area of the image (fig. 48). The concentration of iron in the Dmin area of the image represents the superposition of traces of Prussian blue in combination with iron (if any) in the paper base of the photograph.

Blue toning was also known as cobalt toning. This name indicated the color of the image (cobalt blue) rather than the presence of cobalt in the toning solution, which was absent of any traces of cobalt.

Copper Toning

Figure 49 shows a DOP photograph toned using a copper sulfate-potassium ferricyanide formula. The XRF spectrum of the copper-toned photograph (fig. 50) shows the presence of both copper and iron from the precipitate of copper ferricyanide complex, which is responsible for the red color of the image.

Selenium Toning

Selenium toning holds a special place among the different toning procedures. It was first used to give silver gelatin photographs a dark brown-orange tone (fig. 51). Later, selenium was recognized for its ability in increasing the chemical and environmental stability of silver particles. Photographers began to use selenium toning as an important step in the archival processing of photographs, which was designed and developed for reaching maximum long-term stability of printed black-and-white photographs. Archival processing of photographs became a standard treatment of black-and-white photographs for the art and museum market during the second half of the twentieth century.

Figure 49 DOP photograph toned using a copper sulfate-potassium ferricyanide formula.

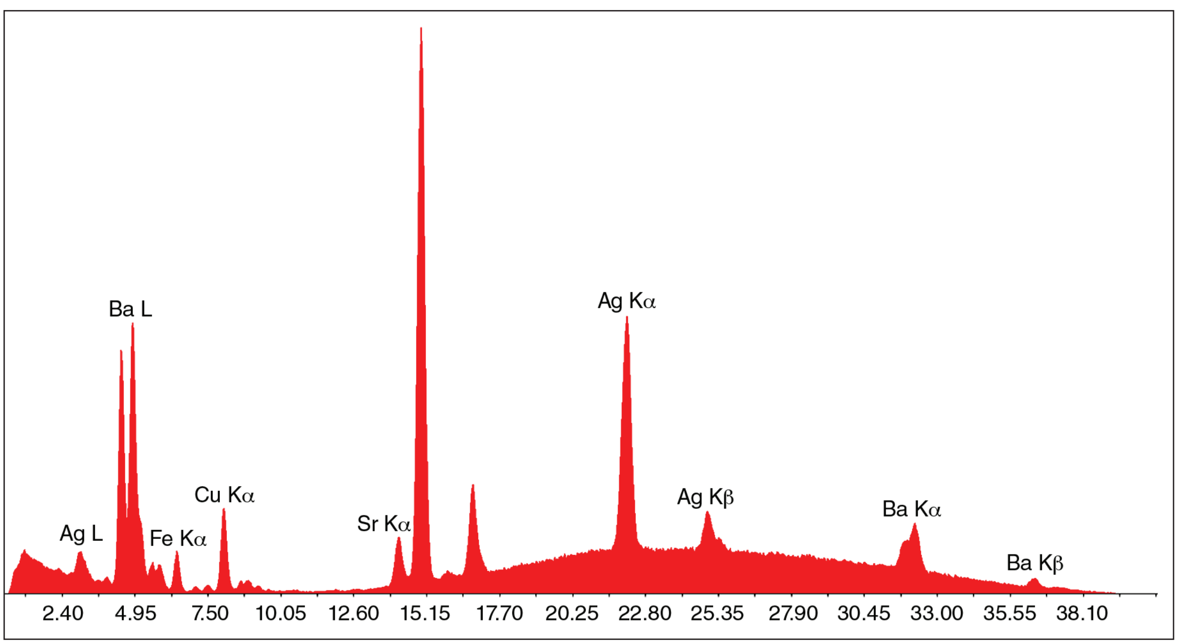
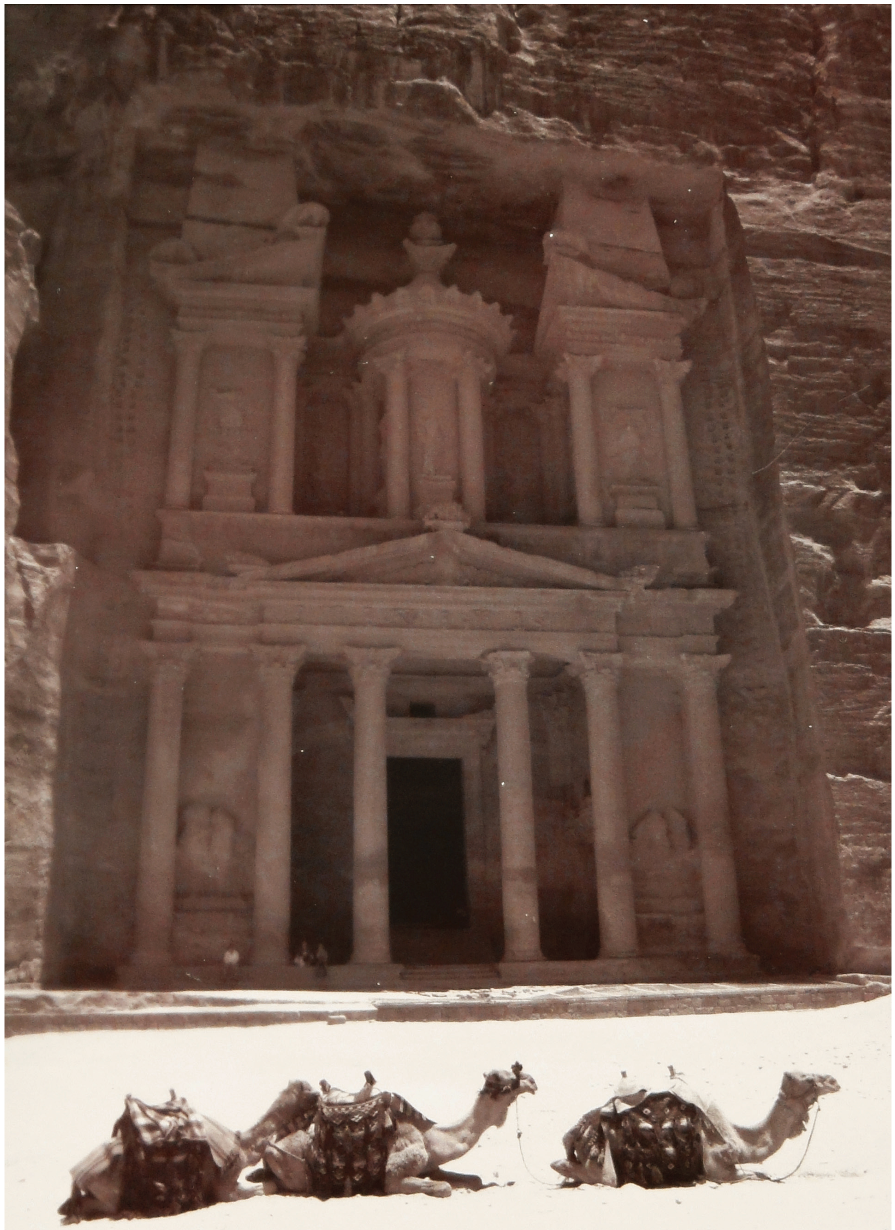


Figure 50 XRF spectrum of the copper-toned photograph in fig. 49.

Figure 51 Fully selenium-toned DOP silver gelatin photograph exhibiting a dark brown-orange color.



Properly done, archival selenium toning did not cause any major color changes or shifts in the toned photograph. The only perceivable visual effect was a slight increase in image contrast and brilliance, which was considered a side benefit of archival selenium toning.

Figure 52 shows a baryta-coated, fiber-based, silver gelatin DOP photograph selenium toned as part of archival processing. Even when the archival selenium toning cannot be recognized visually, the presence of selenium toning can be detected using XRF spectrometry (fig. 53). The high sensitivity of the XRF instrument allows the detection of selenium even in photographs toned for a very short period of time as part of archival processing.

Figure 52 Baryta-coated, fiber-based, silver gelatin DOP photograph toned with selenium for image stability.

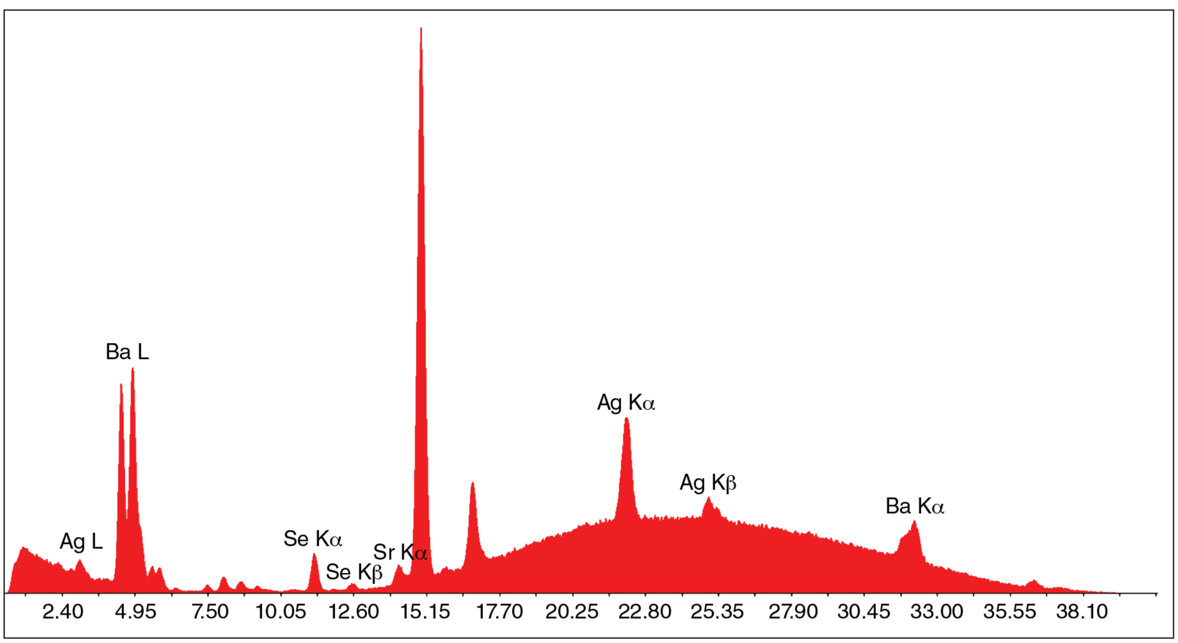


Figure 53 XRF spectrum of the selenium-toned photograph in fig. 52.

IMPORTANT VARIANTS OF THE DOP SILVER GELATIN PROCESS

RC ("resin-coated") photographs
Baryta-less silver gelatin DOP photographs
"Metallic" DOP photographs
Gevaluxe photographs
"Liquid emulsion" photographs

RC ("Resin Coated") Photographs

The development of resin-coated (RC)—known in Europe as polyethylene (PE) photographic papers—grew out of the military's need for material that would not absorb processing solutions, would require shorter washing and drying times, and would allow for much faster processing of exposed paper. Early test versions and specialized production versions of these materials were actually coated on both sides of the paper base by thermosetting resins. The name "resin coated" stuck, even after new commercial material was developed that used thin layers of polymer (polyethylene) attached to both sides of the paper. For this reason the European PE designation of such materials better reflects its material composition. Figure 54 is an example of an RC photographic print.

The first commercially available RC paper was introduced by Kodak in 1968. Most photographic paper manufacturers later introduced their own versions. RC variable contrast black-and-white photographic papers are the most common types still available on the market today.

Figure 55 shows a schematic cross section of a typical silver gelatin print on RC photographic paper.

The paper base is sealed on both sides by a thin layer of extruded PE. The PE film attached to the verso of the photographic paper is made of matte polyethylene to resemble ordinary paper that

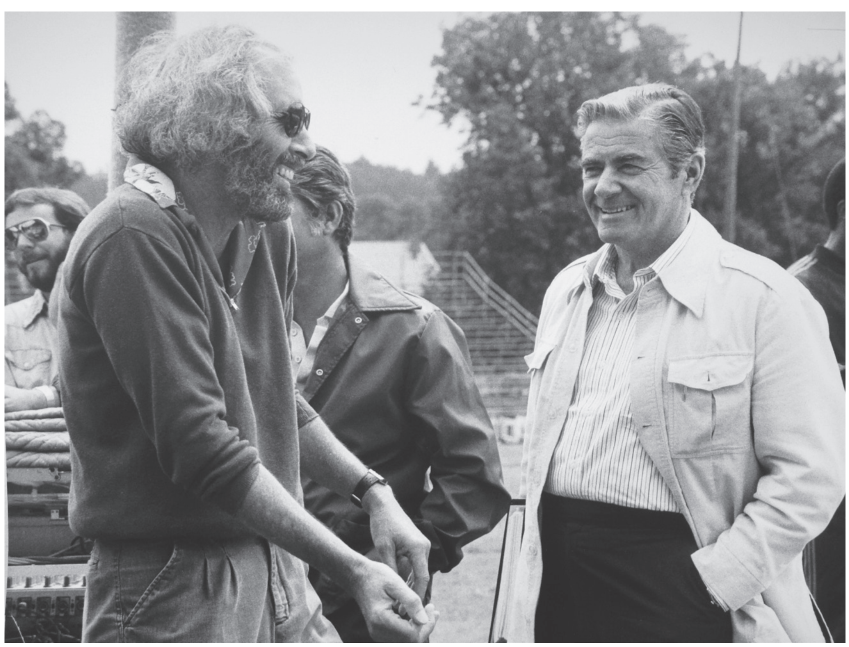
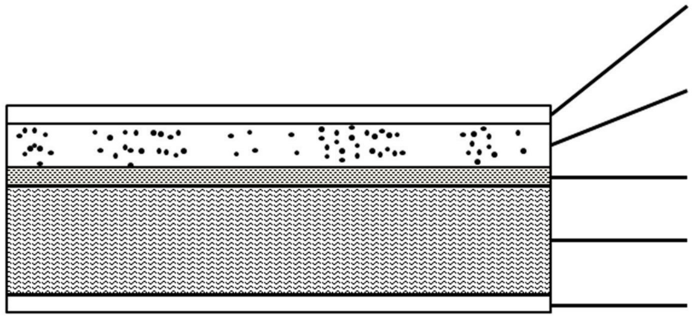


Figure 54 Black-and-white silver gelatin photograph printed on RC photographic paper.

Figure 55 Schematic cross section of a typical RC silver gelatin DOP photograph.



can be written on (this is not as easily done for RC papers produced by different manufacturers). The emulsion side of the paper is coated with PE filled with titanium dioxide (TiO_2). The bright-white pigmented layer simulates the visual effect of the baryta layer of fiber-based, baryta-coated photographic papers. The emulsion layer is coated onto the pigmented layer and overcoated by a topcoat or supercoat of hardened gelatin as protection against mechanical damage.

IDENTIFICATION: RC B&W DOP SILVER GELATIN PHOTOGRAPHS

Visual Signatures

Visual Characteristics

RC photographic papers can be recognized visually by looking for a characteristic sheen on the back of the paper. They can also be recognized by touch, brushing one's bare fingers lightly across the back side. The slippery feel of the paper can be detected more easily when doing a direct touch comparison with some fiber-based photographic papers.

RC photographic papers were and still are produced with glossy, matte, semi-matte, satin, or pearl surface finishes. A direct positive variant of the paper is also available commercially.

Analytical Signatures

XRF

Figure 56 shows a typical XRF spectrum of an untoned silver gelatin photograph printed on RC paper.

XRF analysis of untoned photographs printed on RC paper shows the presence of titanium (Ti) at 4.51 keV and 4.93 keV. The problem with interpretation of XRF spectra of RC paper is that the main spectral peaks of Ti and barium (Ba) almost overlap perfectly. Both elements can be differentiated when checking for the presence of the $K\alpha$ and $K\beta$ Ba peaks at 32.19 keV and 36.38 keV, respectively, observing the different intensity ratios of both major spectral peaks and by identifying other barium peaks to the left (lower energy) of the Ba L peaks, which are missing in XRF spectra of material containing only titanium.

FTIR

The ATR-FTIR spectrum of the recto side of the RC paper shows well-developed spectral peaks of gelatin (fig. 57). The verso side of the same image clearly shows the presence of the PE layer (fig. 58).

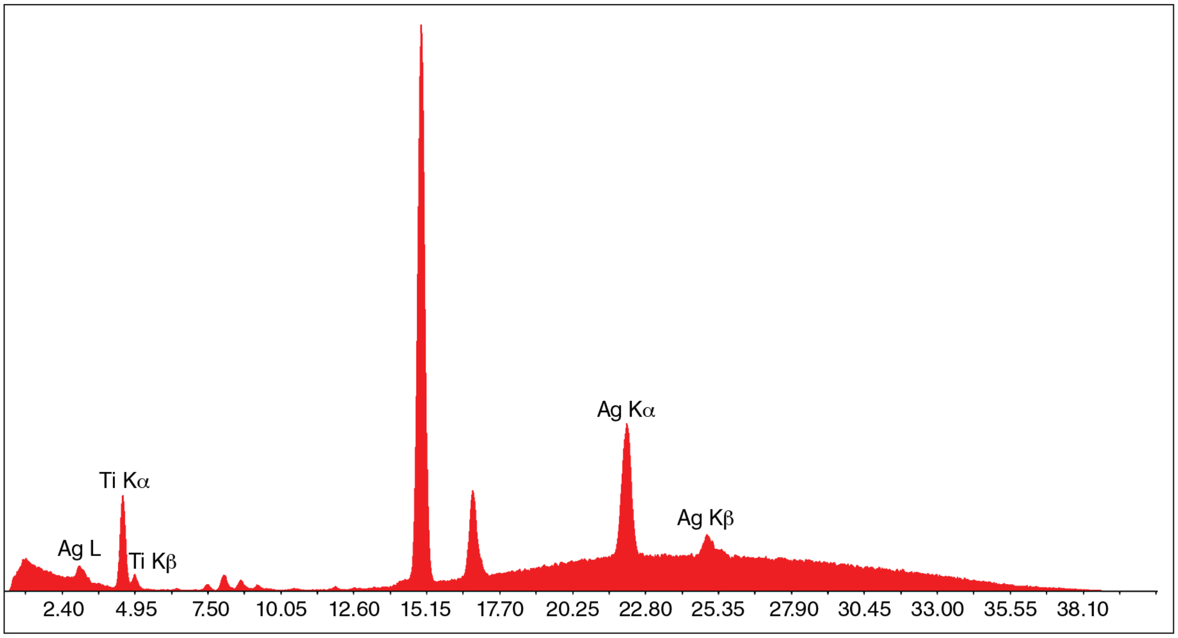


Figure 56 XRF spectrum of a photograph printed on RC paper.

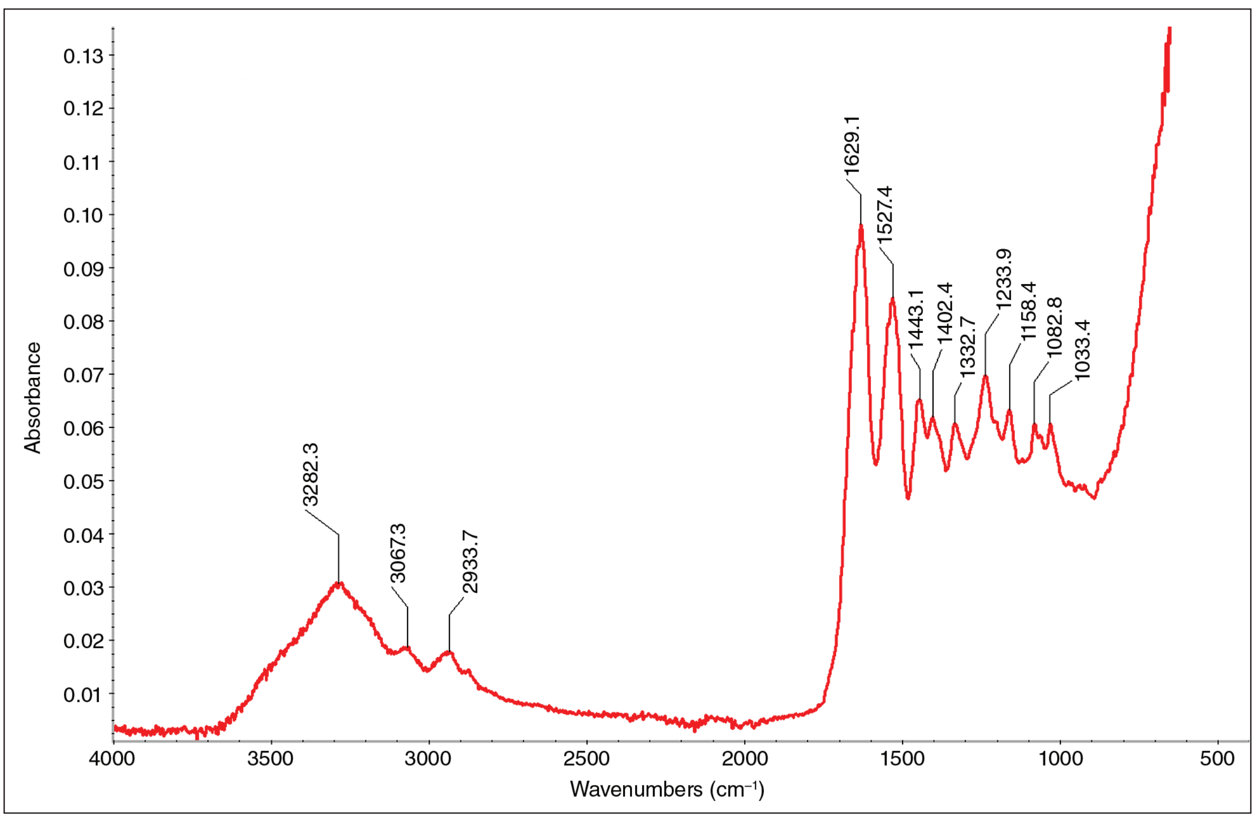


Figure 57 ATR-FTIR spectrum of the recto side of an RC photographic paper, showing the presence of gelatin.

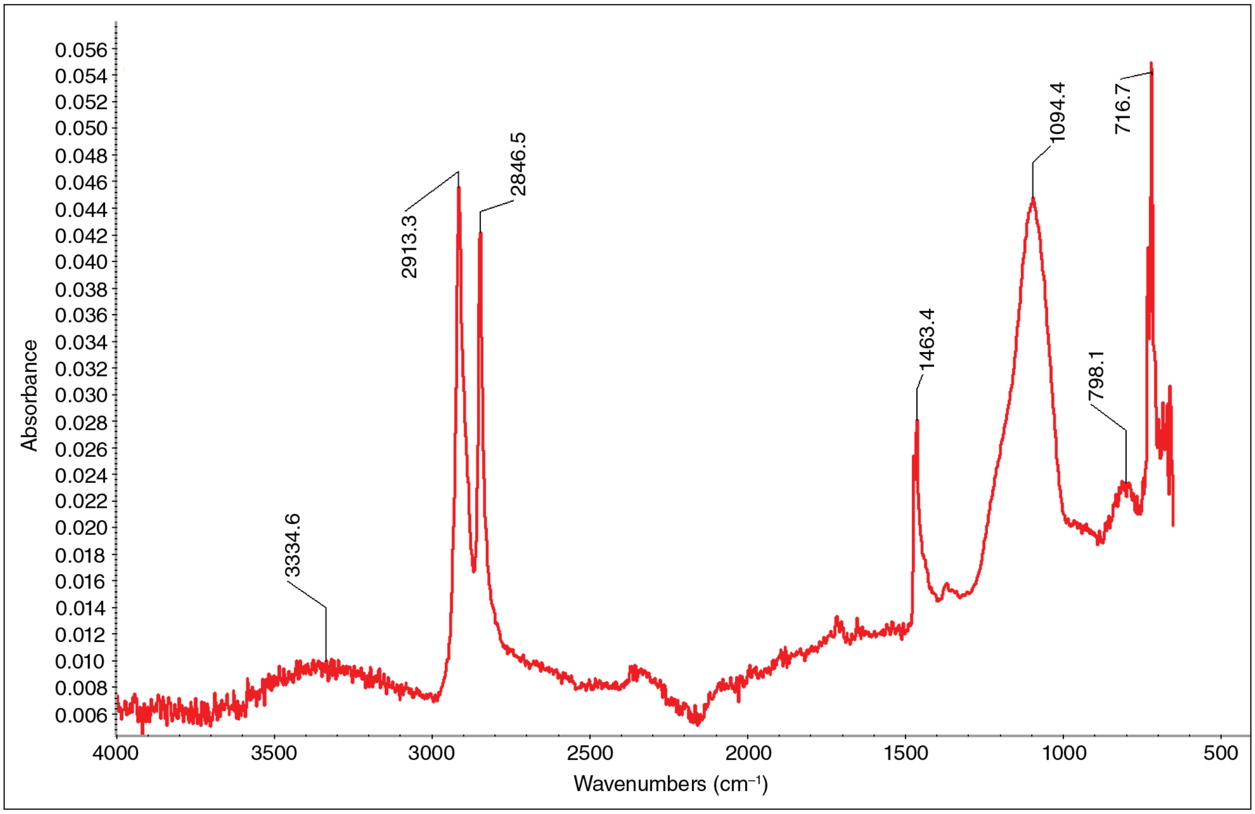


Figure 58 ATR-FTIR spectrum of the verso side of an RC photographic paper, showing the presence of polyethylene.

Post-Process-Treated RC Silver Gelatin Photographs

Arriving in the late 1960s, after the introduction of RC photographic papers, most of the RC photograph variants reflect the photographic style of the time period in which they were used. RC photographs were considered to be a more technical material used for proofing of images before printing and for creating photographs of limited service life. As such, not many of these photographs were toned or surface coated. When such a treatment could be found, it would reflect toning and coating practices used when working with fiber-based, silver gelatin DOP papers.

Variable Contrast Photographic Material

Until about 1940, the only option photographers had when dealing with different contrast photographic negatives was to print photographs on so-called graded papers. These papers were manufactured with silver halide particles of different sizes. In general, photographic emulsions containing silver halide particles of very uniform size yielded high-contrast photographic papers well suited for printing low-contrast negatives. Photographic emulsions containing silver halide particles of different sizes yielded photographic papers of lower contrast that were usually used to print high-contrast negatives. The usual designation of graded papers was usually from 0 or 1 (for photographic papers of lowest contrast), to 5, which designated high-contrast photographic papers. These number designations and contrast levels of photographic papers, produced by different manufacturers, differed slightly but that was the general trend. A great disadvantage was that a photographer or photographic laboratory had to keep a wider selection of different graded photographic papers for different photographic printing situations.

In 1911 the German scientist Rudolph Fisher obtained a patent for a black-and-white photographic paper with variable response to different colors of light and subsequent contrast control. This paper was never marketed, and it was only in 1940 that the US Defender Company (later acquired by the DuPont Co.) introduced the first variable contrast black-and-white photographic paper, called Varigram.

At about the same time, in England, Ilford Ltd. introduced the first Multigrade photographic paper. This paper was, because of World War II, commercially available only in 1950 and exported to the United States only beginning in 1956. Kodak introduced its Polycontrast papers in the spring of 1957. For a long period of time both graded and variable contrast photographic papers were available side by side. Not until the 1990s did variable contrast (VC) papers become the dominant black-and-white photographic papers on the market.

VC papers are coated with a mixture of two or three silver halide emulsions, all of equal contrast and of the same sensitivity to blue light but each sensitized in different proportions to green light. Upon exposure to blue light, all emulsions act in an additive manner to produce a high-contrast image. When exposed to green light alone, the emulsions yield a low-contrast image because each is differently sensitized to green. By varying the ratio of blue to green light, the contrast of the print can be continuously varied between these extremes, creating all contrast grades from 0 to 5. A specific color of light, needed for the exposure of photographic paper to yield desired contrast levels, is produced by using specialized filters made by the same company that manufactured the VC papers. As of 2013, some photographic enlargers are still available with so-called dichroic light sources that allow for direct dialing of light color for any desired final paper contrast. VC photographic papers later became available in both fiber-based and RC (PE) variants. Figure 59 shows several varieties of VC papers available to photographers in the 1900s. If no product name is printed on the back of the photographic paper, there is no simple way to determine if a given photograph was printed on a graded or VC paper.

Baryta-less DOP Silver Gelatin Photographs

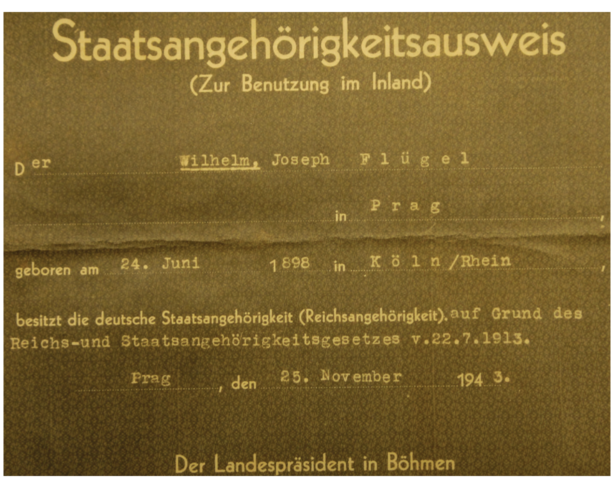
Several types of silver gelatin photographic papers used in the past were manufactured without the presence of a baryta layer. The most important category of these papers was "document papers" made without a baryta layer. The absence of a baryta layer gave the material a certain level of translucency. When, for example, a typed document on normal paper was copy printed on a baryta-less photographic paper, an image of white letters on a black opaque background was created. This document "negative," translucent to light in its white areas, could be multiplied many times by copying the document "negative" onto other photographic materials—which could but were not required to be of the baryta-less paper type—by direct contact and standard chemical processing of the resulting positive (figs. 60a, 60b). This completely eliminated the need for making large, more expensive photographic negatives on glass or plastic substrates.

The XRF spectrum of the document (fig. 61) shows the presence of the image-forming silver and the absence of baryta.

Figure 59 Several types of VC papers produced by various manufacturers.

Figure 62 shows the ATR-FTIR spectrum of the printed and processed document paper. A thin gelatin layer was coated directly onto the paper substrate, and the resulting ATR-FTIR spectrum shows both the gelatin (protein) peaks and the spectral envelope of cellulosic material. The FTIR signature of the silver gelatin document paper is closer to that of an albumen photograph than to standard gelatin photographs.

Some special silver gelatin photographic papers were printed on heavier paper stock without a baryta layer. These photographs do not have the brilliancy of baryta-coated photographs, and their use was intended for special decorative purposes rather than for high-quality photographs.

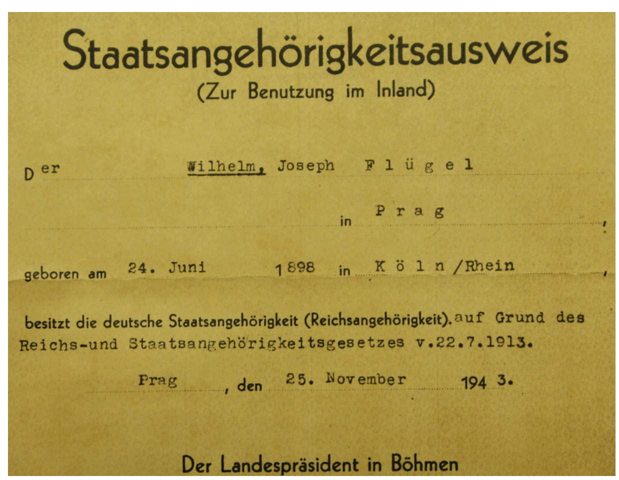


Staatsangehörigkeitsausweis
(Zur Benutzung im Inland)

Der Wilhelm, Joseph Flügel
in Prag,
geboren am 24. Juni 1898 in Köln/Rhein,
besitzt die deutsche Staatsangehörigkeit (Reichsangehörigkeit).auf Grund des Reichs-und Staatsangehörigkeitsgesetzes v.22.7.1913.
Prag, den 25. November 1943.

Der Landespräsident in Böhmen

Figure 60a Document "negative" printed by contact with the original typed document.



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Prag, den 25. November 1943.

Der Landespräsident in Böhmen

Figure 60b Document positive printed by contact with the document "negative."

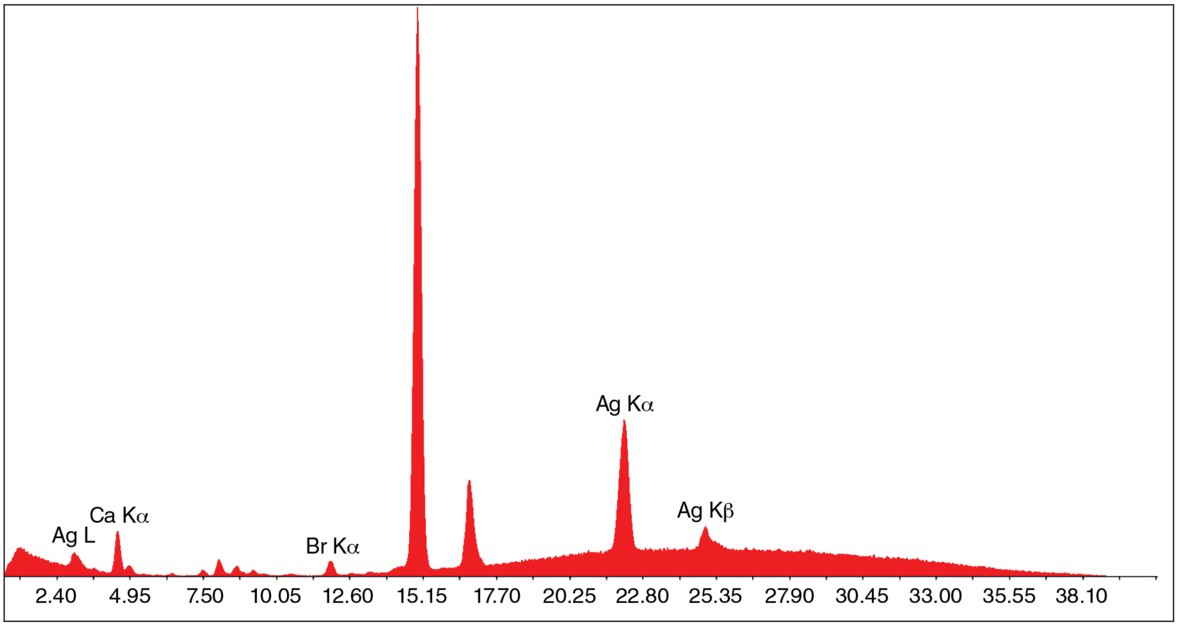


Figure 61 XRF spectrum of the document paper, showing the presence of image-forming silver and the absence of baryta.

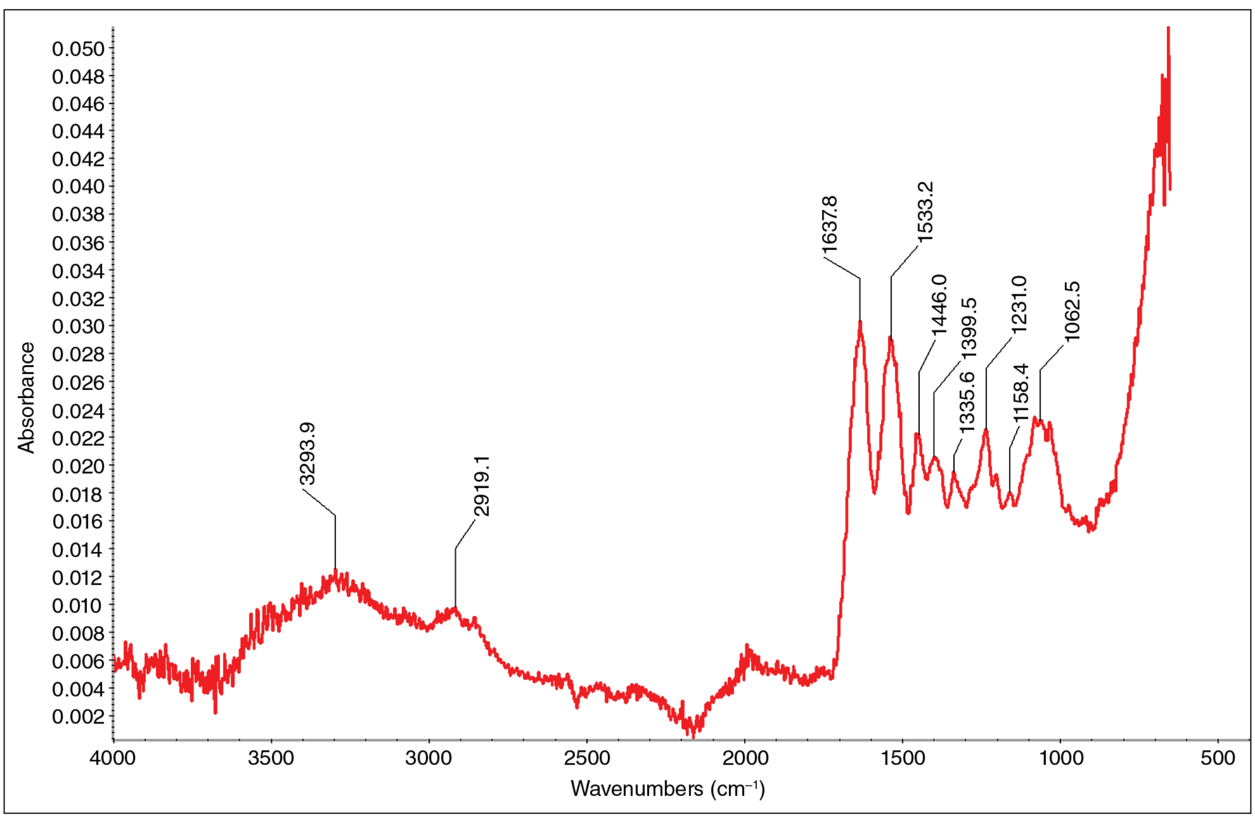


Figure 62 ATR-FTIR of the baryta-less printed and processed document paper, showing the gelatin peaks and cellulosic material.

“Metallic” (“Metotype”) DOP Photographs

Since the latter part of the nineteenth century, some photographers and later several photographic manufacturing companies introduced different types of photographic papers that allowed for the production of silver-, gold-, or copper-toned photographs (figs. 63a, 63b). Early versions of these “novelty” photographs were handmade using a paper substrate coated with “silver” (aluminum powder) or bronzing (brass powder) powder and sealing the metal-powder layer with an isolating varnish before applying the silver gelatin emulsion. Some photographers also started using industrially produced metallic decorative papers. Metallic, or “metotype,” silver gelatin photographic papers were available until the 1970s as special surface photographic papers with different types of surface coatings that often did not contain metals. Instead, they contained material that produced a metallic appearance for the photographic paper. Even today, some photographic papers (such as Endura) provide a metallic look for analog or digitally printed images.

Figure 63a Modern “metallic,” or “metotype,” silver-toned photograph.

Figure 63b Modern “metallic,” or “metotype,” gold-toned photograph.

XRF analyses were performed on two "metotype" photographs. The air and vacuum XRF spectra for figure 63a appear in figures 64a and 64b. The air and vacuum XRF spectra for figure 63b are shown in figures 65a and 65b.

The XRF analysis of both the silver and gold metotype photographs shows the presence of barium (Ba), strontium (Sr), and silver (Ag), which are typical components of DOP silver gelatin photographs. The XRF analysis under vacuum also identifies the presence of silicon (Si),

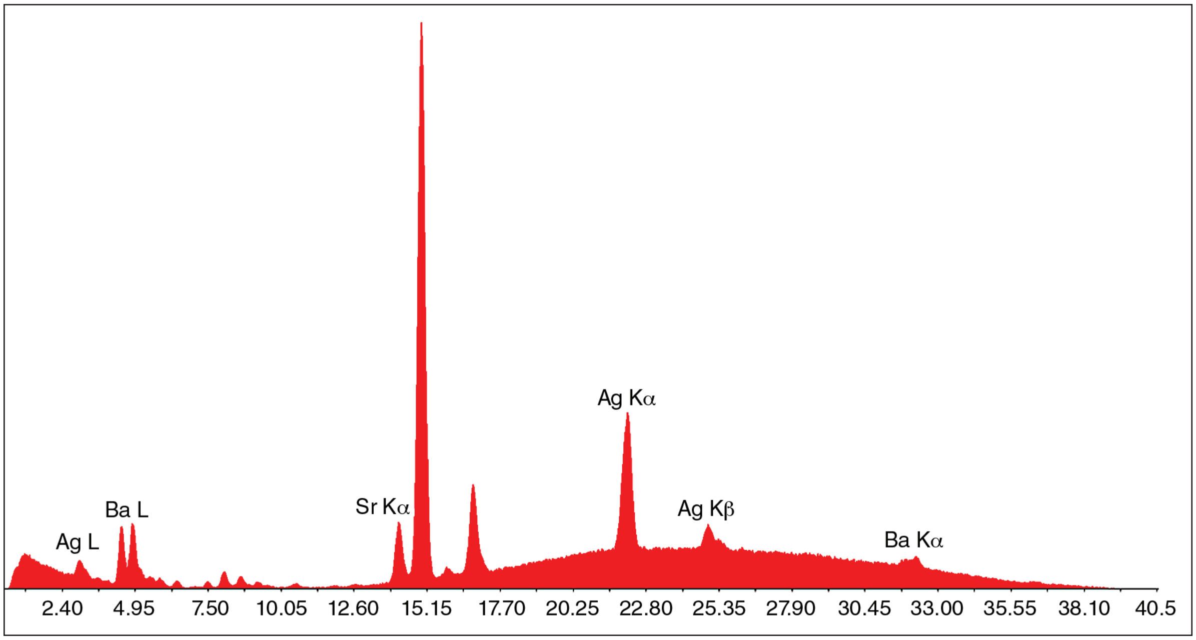


Figure 64a XRF spectrum of the silver-toned "metotype" photograph in fig. 63a, in air.

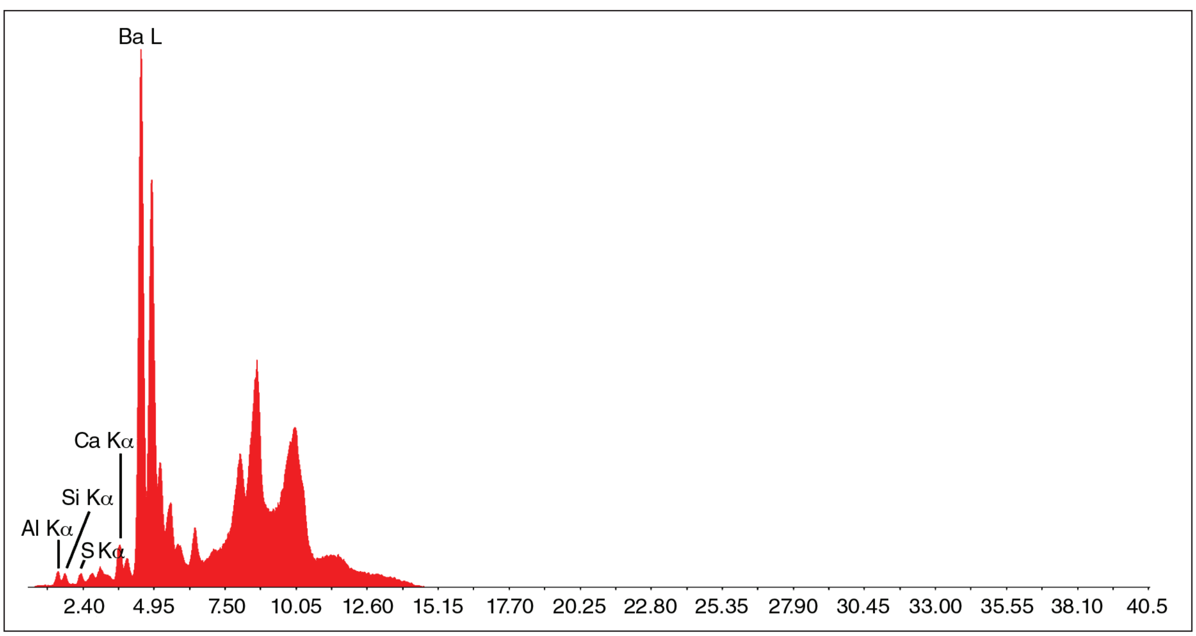


Figure 64b XRF spectrum of the silver-toned "metotype" photograph in fig. 63a, under vacuum.

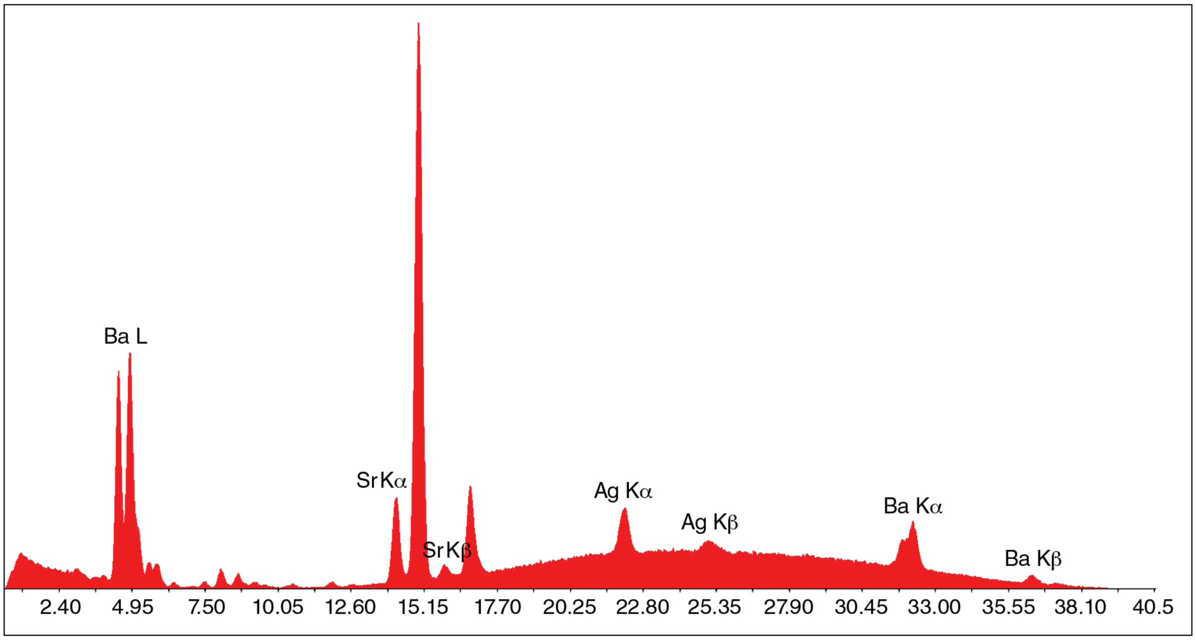


Figure 65a XRF spectrum of the gold-toned "metotype" photograph in fig. 63b, in air.

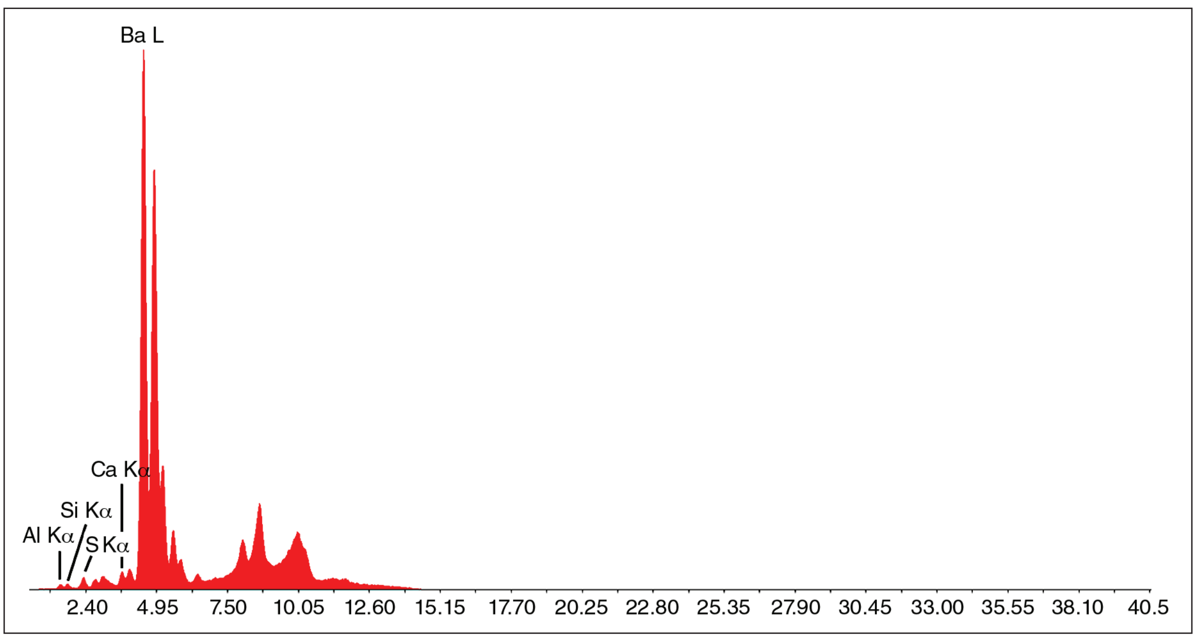


Figure 65b XRF spectrum of the gold-toned "metotype" photograph in fig. 63b, under vacuum.

aluminum (Al), and calcium (Ca), all of which are present in natural mica. Mica-based "pearlescent" pigments contain mica microparticles with a deposited layer of titanium dioxide (TiO_2) and iron oxides. Depending on the thickness of the TiO_2 layer, the resulting pigments can be silver, gold, or bronze in color. The XRF cannot confirm the presence of titanium due to the strong spectral overlap of barium with titanium.

Gevaluxe Photographs

In the 1930s the Belgian company Gevaert introduced to the photographic market one of the most interesting black-and-white photographic papers, the Gevaluxe (fig. 66). The most interesting and distinguishing feature of this silver bromide paper was its special surface. Using patented electrostatic coating technology, the Gevaert Company was able to densely coat the surface of the paper with a randomly oriented and overlapping net of cellulosic microfibers. When printed, fully developed, and processed using darkroom procedures similar to those for other silver bromide photographic papers, the visual appearance of the printed image was unusual, striking, and beautiful. The net of surface fibers coated with developed silver particles virtually eliminated any specular reflectance from the dark areas of the image, producing deep, velvety dark tones of the Dmax areas of an image.

Advertising material described Gevaluxe paper as the Stradivarius of photographic paper, one that imparted almost 3-D qualities to printed photographs. A number of known photographers, including Laura Gilpin and Frederic Evans, and a number of pictorial photographers used Gevaluxe to print some of their photographs from its introduction to the end of its production in the late 1950s. Even when very successful as a specialty photographic paper, the production of Gevaluxe was expensive and thus was not continued after the Gevaert Company merged with the German company Agfa in 1964. During production Gevaluxe paper was available only in a neutral-black tonality and was supplied only on a cream-colored, card-based substrate. The paper was very delicate when processed or handled. Any extensive mechanical pressure on its surface layer could irreversibly collapse the fine net of surface fibers.

Visual Characteristics

The most important visual characteristics of Gevaluxe-based photographs is its almost complete lack of any surface gloss and its velvety black appearance in the Dmax areas of the image.

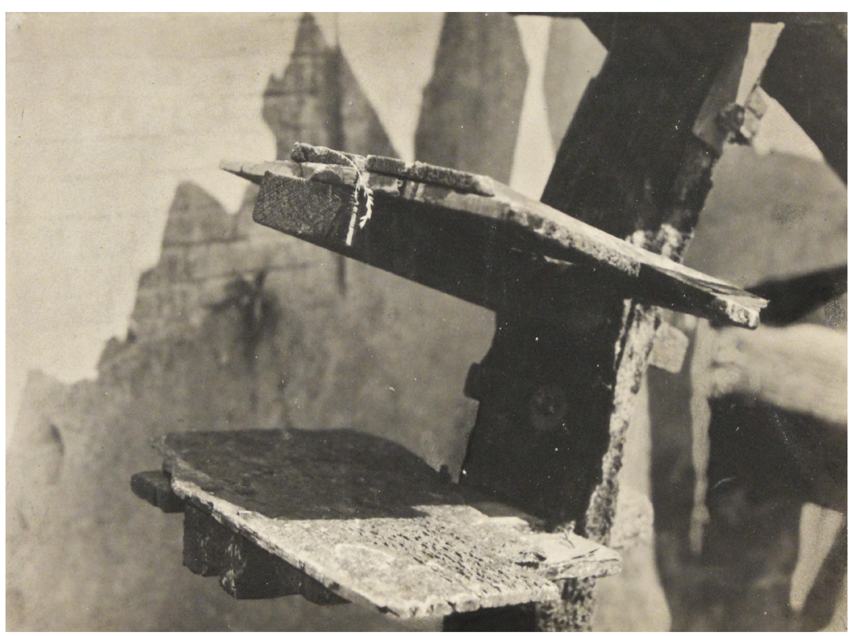


Figure 66 Black-and-white silver gelatin photograph printed on Gevaluxe photographic paper.

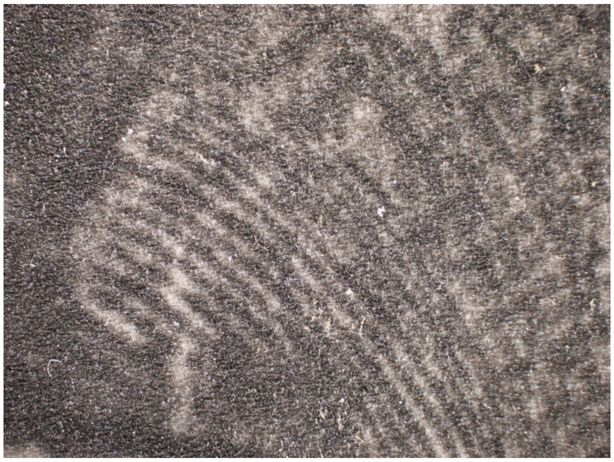


Figure 67a Detail of a Gevaluxe photograph (10× magnification).

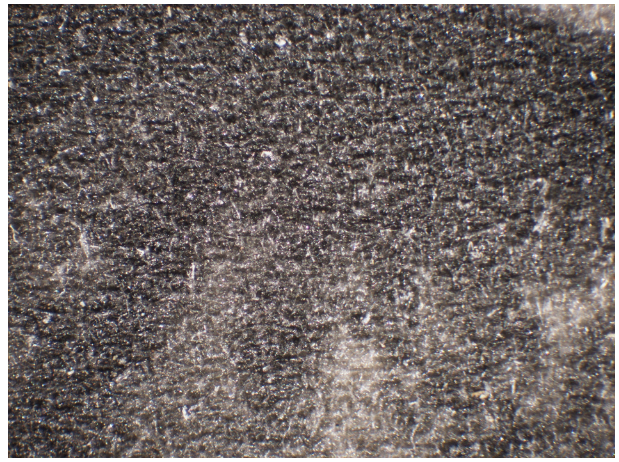
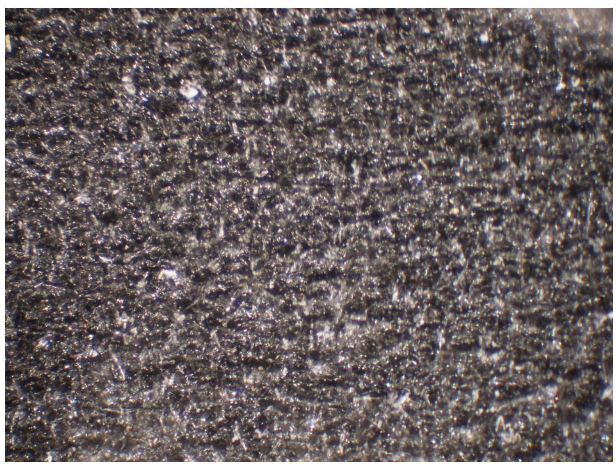


Figure 67b Detail of a Gevaluxe photograph (25× magnification).

Figure 67c Detail of a Gevaluxe photograph (40× magnification).



Microscopic Characteristics

The most important signature of Gevaluxe printed photographs is their very characteristic surface filamentary structure. This can be observed with a powerful loupe but shows up best under a high-power stereomicroscope. Observation under a stereomicroscope clearly shows the 3-D structure of the net of surface fibers (figs. 67a–67c).

The surface structure of the Gevaluxe paper is so characteristic that there is usually no need for any further analytical investigation. Our XRF analysis provides only some analytical insight into the internal chemical structure (fig. 68).

The XRF spectrum of the Gevaluxe paper shows a relatively high concentration of silver and very small concentrations of both barium and strontium. This indicates that the photographic paper does not contain a baryta layer and that the barium sulfate might be part of the paper substrate. The ATR-FTIR spectrum (fig. 69) shows the presence of protein (gelatin) and a very strong signal of cellulose. A dense deposit of microfibers may be attached to the paper substrate using a gelatin-based adhesive. Gelatin was also a carrier of light-sensitive silver halide compounds.

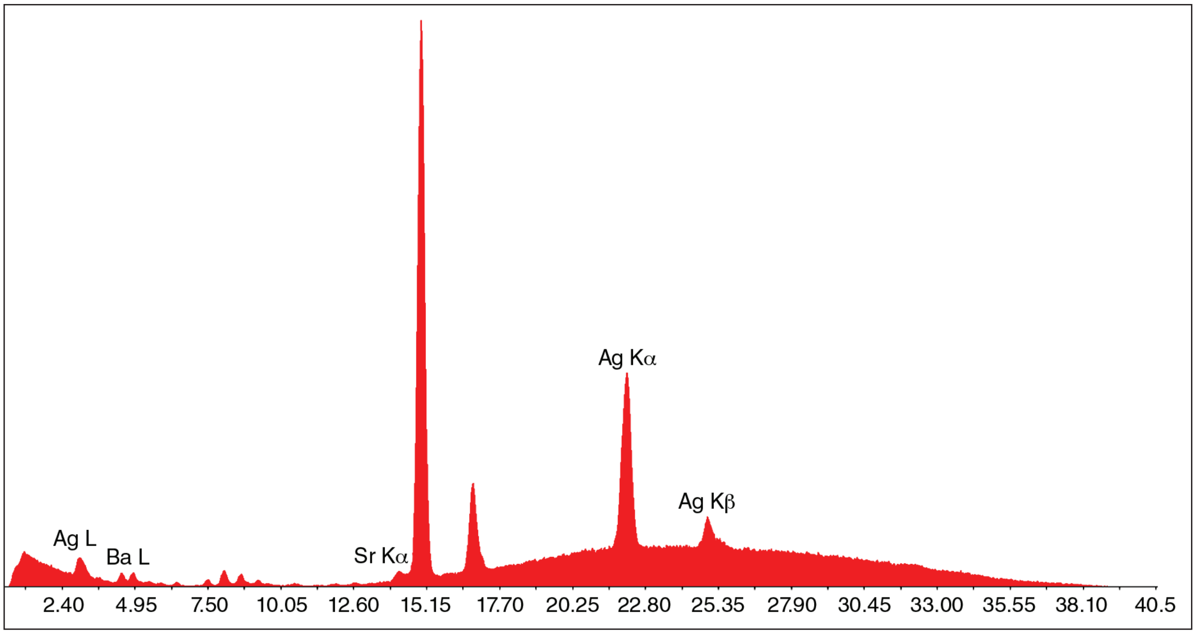


Figure 68 XRF spectrum of a Gevaluxe photograph.

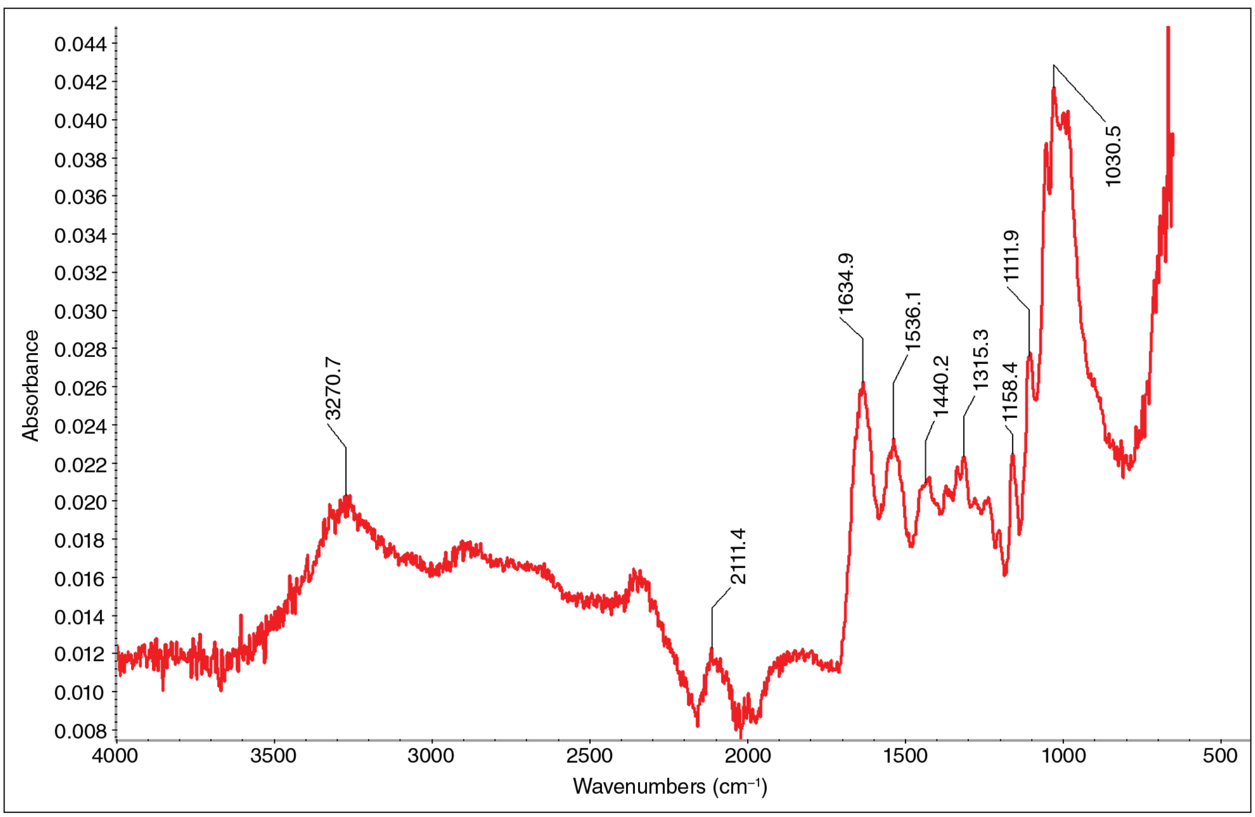


Figure 69 ATR-FTIR spectrum of a Gevaluxe photograph.

“Liquid Emulsion” Photographs

Commercially prepared silver halide POP and DOP photographic papers were by far the most common positive photographic printing material available to photographers. There usually was no good reason for self-made photographic papers even when some types of prepared silver halide photographic emulsions could be obtained from photographic supply houses. Photographers coated photographic emulsions only when they wanted to achieve special effects or when they needed to create photographic images on material substrates that were not available commercially (fig. 70). Later on, liquid emulsions (fig. 71) were developed and used by artists working under the umbrella of the so-called alternative process photography movement. When the remaining photographic paper producing companies in operation today abandon the already small photographic paper trade, it is possible that the images created using silver gelatin emulsions will be the only photographic images still utilizing more than a hundred years of silver gelatin technology.

The artist who made the print in figure 70 used a silver-based photographic process; this is confirmed by XRF analysis (fig. 72). ATR-FTIR analysis of the image side of the photograph determines that a gelatin-based photographic process was used (fig. 73).

Finding various concentrations of gelatin across the image leads to speculation that a hand-coated photographic emulsion was used. These hypothetical conclusions were later fully confirmed by the artist himself.

Figure 70 Untitled, produced in 2008 by Jean-Luc Debève. Silver gelatin photograph created using a liquid emulsion and printed on handmade Nepalese vegetable fiber paper.

Figure 71 Liquid Light photographic emulsion, used to create the image in fig. 70.

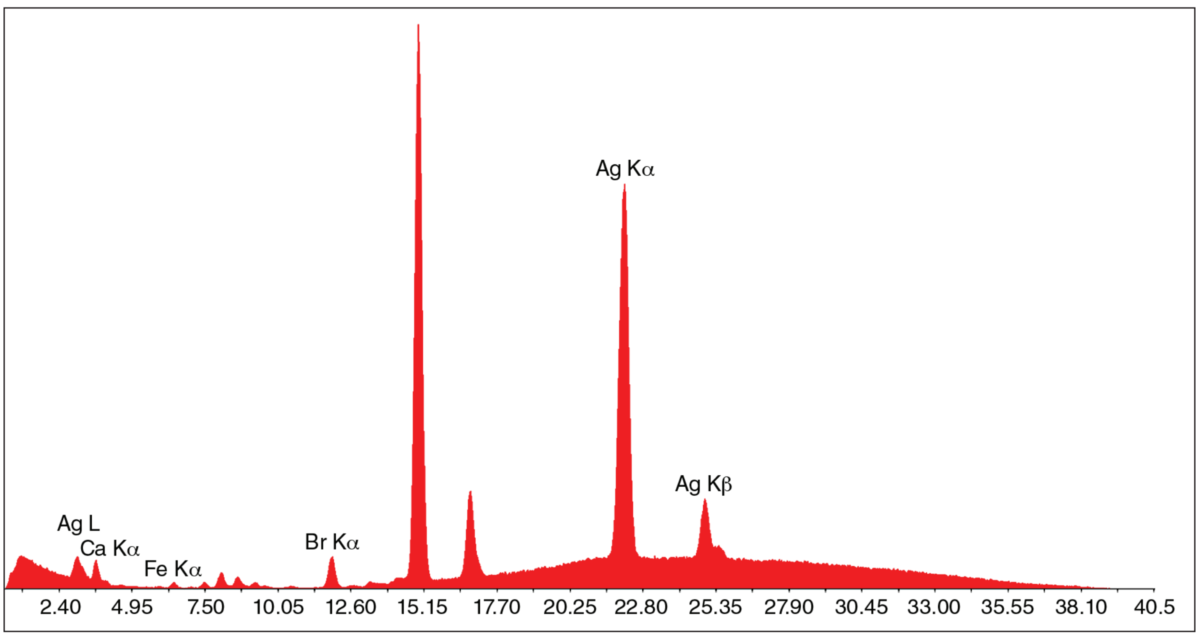


Figure 72 XRF analysis of the silver gelatin photograph on handmade Nepalese paper substrate in fig. 70.

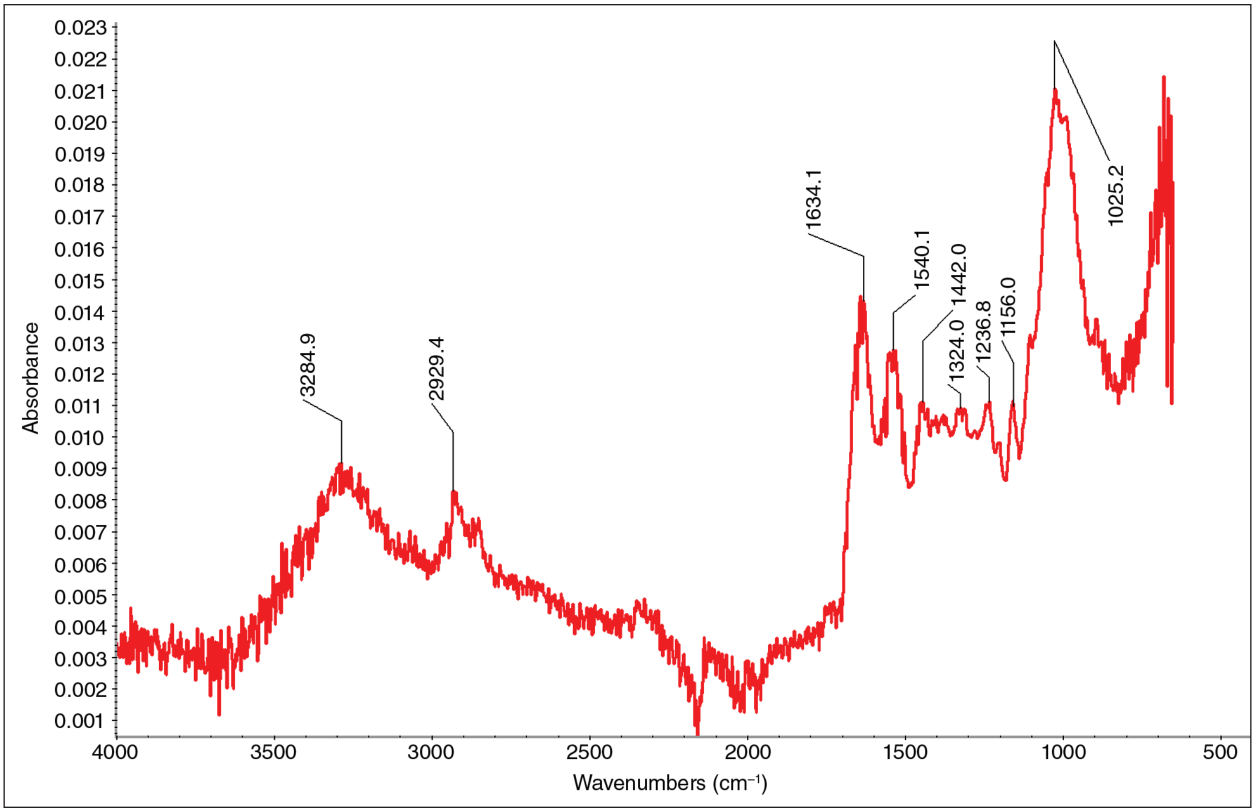


Figure 73 ATR-FTIR analysis of the image side of the photograph in fig. 70.

INTERPRETATION GUIDE

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

Silver Gelatin Prints

Process	Surface Coating	Paper Fibers	Ag	Au	Pt	Ba	Sr	Other Inorganics	Cellulose	Albumen	Collodion	Gelatin	Tonality
Gelatin POP	–	–	X !	(X)	–	(X)!**	(X)!**	(Ti)*	–	–	–	X !	Brown
Gelatin DOP	–	–	X !	(X)	–	(X)!**	(X)!**	(Cr), (Ti)*	–	–	–	X !	Brown-black
Albumen	(X)	X	X	(X)	(X)	–	–	–	X	X	–	–	Brown-purple
Collodion	–	–	X	(X)	(X)	X	X	–	–	–	X	–	Brown (matte black)
Carbon	(X)***	(X)	–	–	–	–	–	(Cr), (Fe), (Ti)*	–	–	(X)***	X	Brown-black
Woodburytype	(X)***	X	–	–	–	–	–	(Cr), (Fe)	–	–	(X)***	X	Brown-black

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

(X)!** Some gelatin POP and DOP papers have no baryta
(X)*** Carbon and Woodburytype prints were sometimes coated with collodion
(Ti)* Some modern prints on 20th- and 21st-century substrates containing TiO_2
(Fe) May be present if iron-based pigments were used

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