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Technical note

Understanding the gum dichromate process in pictorialist photographs: A literature review and technical study

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In the late 1800s, pictorialist photographers favored a diversity of photographic techniques, including the gum dichromate process. Sometimes superimposed over other photographic images such as platinum and silver prints, the gum dichromate process utilizes a light-sensitive mixture of gum arabic, pigment, and a potassium dichromate solution hand-applied onto a sheet of paper and exposed to light while in direct contact with a negative. The definitive identification of this process has proven to be a challenge due to many variations and intermingling of techniques used by photographers of this period. This research began with a search through the historic literature, followed by the creation of test samples based on historic recipes, and the X-ray fluorescence analysis of these tests. The identification of pigments and the presence of chromium have been associated with the gum dichromate or other dichromated colloid processes in the past. Research results reveal that the presence of chromium may have more complex sources, requiring a more discriminating approach and a modified protocol for the identification of gum dichromate photographs.

Keywords: Gum dichromate, Gum bichromate, XRF, Pictorialist, Photography, Chromium compounds

History of the process

In the late nineteenth century, pictorialist photographers such as Edward Steichen, Adolph de Meyer, Gertrude Käsebier, Henrich Kühn, Clarence White, Emile Constant Puyo, Robert Demachy, and other contemporaries employed the gum dichromate process among a variety of techniques. During this period, photography was becoming highly manufactured, standardized, and readily accessible to the public. The pictorialists countered this popularization of the medium by turning to meticulously handcrafted processes that allowed them full control and flexibility to fully express their creativity, thereby enhancing the medium's place within the sphere of fine art (Tulloch, 1898). Artists moved away from commercially produced photographic materials and created unique works carefully combining choice materials with specialized techniques. They handcoated papers, locally manipulated images during development, used multiple negatives, and often layered one process on top of the other.

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As early as 1839, the year the invention of photography was announced to the world, the Scotsman Mungo Ponton discovered and reported on the light sensitivity of potassium dichromate-coated papers (Hunt, 1853; Brown, 1890; *The British Journal of Photography*, 1897a, 1897b, 1898b, 1898c; Lewis, 1898). William Henry Fox Talbot of England and Alphonse Louis Poitevin of France experimented with the light sensitivity of dichromated colloids including gelatin. Poitevin went on to introduce photomechanical processes utilizing this principle (Fleury-Hermagis & Rossignol, 1898). The gum dichromate process, utilizing gum as the colloid and commonly known as gum bichromate or 'gum' by pictorialist artists, was officially announced by John Pouncy in 1858 (Wall *et al.*, 1924). Between the 1850s and the 1860s, the process was refined and improved by artists such as Alphonse Louis Poitevin, Thomas Sutton, and Charles John Burnett, although it became popular largely through the efforts of Robert Demachy, Alfred Maskell, A. Rouillé-Ladevèze, and others (Wall, 1902; Wall *et al.*, 1924). In 1894, Alfred Maskell and Robert Demachy published *The Photo-Aquatint*, a treatise providing instructions and

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waxing poetic on the great advantage and flexibility of this artistic medium (Maskell & Demachy, 1897).

Overview of the process

A gum dichromate print is made by brushing a mixture of gum arabic, pigment, and a potassium dichromate solution onto a sheet of paper and, after drying, exposing it to light through a negative placed in contact with the coated paper. The dichromate acts as the light-sensitive component causing, in the exposed areas, the hardening and insolubilization of the gum that consequently traps the pigment. The process by which organic colloids in the presence of dichromate harden upon exposure to light is initiated by the photoreduction of Cr(VI) ions to Cr(III). The questions as to whether the Cr(III) ions form a complex with the organic molecules in the colloid or what other relevant chemical reactions take place have not been satisfactorily answered (Kosar, 1965; Samoilovich *et al*., 1980; Sjolinder, 1981).

After exposure, the pigment-coated paper is placed in a water bath and the unexposed areas soften and dissolve, revealing the white paper substrate and forming the light tones of the image. The gum in the exposed areas has hardened and remains intact as a pigmented colloid layer, making up the darker tones in the image (Scopick, 1978; King, 2000) (Figs. 1 and 2). The resulting images tend to be high contrast and grainy, but are perfect for the soft, impressionistic aesthetic favored by the pictorialists. Mid-tones tend not to be well rendered unless a rough-surfaced paper is used, as the colloid layer hardens from the top down, leaving mid-tones unsupported when the water bath solubilizes the under-layer that would anchor the image to the paper during development. Artists sometimes chose to print platinum- or silver-based photographic images underneath or above a gum dichromate print to impart more delicate details and image subtleties. Pigment colors were sometimes chosen for their similarity to chalk or charcoal drawings.

Research objectives

The primary objective of this research was to characterize and re-create the different gum dichromate processes represented in the technical literature, and to develop suitable protocols to identify the technique through non-invasive methods, thus deepening our understanding of pictorialist artworks. The various pictorialist photographic processes are difficult to differentiate through visual examination alone due to the hand-made and unique nature of each image; to the diversity of materials used; and to the fact that many of the techniques could be layered in the same print. The project included thorough bibliographic research of manuals and artists' notes from the pictorialist period; re-creations of the variations in technique presented in the historic recipes; and the analysis of these historically accurate reconstructions by X-ray fluorescence (XRF) to formulate suitable methodologies for identifying artworks.

The gum dichromate process: a review of historic sources

Forty manuals and journals related to the gum dichromate process, together with historical artists' notes, all dating from the 1850s to the 1930s, were reviewed for the present study (Hunt, 1853; Baldwin, 1865; Brown, 1890; Ewing, 1897; Packham, 1897; Pretzl, 1897; *Wilson's Photographic Magazine*, 1897; Maskell & Demachy, 1897, 1898; *The British Journal of Photography*, 1897a, 1897b, 1898a, 1898b, 1898c, 1899; Bennett, 1898; C, 1898; Carlin, 1898, 1899; Gaedicke, 1898; Lewis, 1898; Pouncy, 1898; Tulloch, 1898; Wallon, 1899; Abbott, 1900; Stevens, 1900; Gennert, 1901; Tennant, 1901; Wenzel, 1901; Wall, 1902; Puyo, 1904; Levoy, 1907; Todd, 1907; Zimmerman, 1910; Demachy, 1915; Anderson, 1917, 1923, 1934, 1939; Wall *et al*., 1924; Jordan, 1937). Sources were chosen based on their importance during the period (Demachy (Demachy, 1915), Maskell (Maskell & Demachy, 1897, 1898), Puyo (Puyo, 1904)) or based on the publication dates. Some earlier sources were studied to understand the origins of the techniques and later sources were included to follow the development of the procedure over time. The information obtained from these sources allowed us to gain an in-depth understanding of the variations in materials and techniques as well as of the most popular combinations used by the pictorialists. Despite reports that artists, in general, experimented and did not rigorously follow prescribed recipes (*The British Journal of Photography*, 1898b), the most frequently described materials for this process, including the papers, sizing, pigments, colloids, and sensitizers, as well as the methods used, are compiled and discussed below.

Historic papers

The paper is the support onto which the light-sensitive chemicals are applied and on which the final image resides. Various types of suitable papers were discussed in the literature. The papers most frequently recommended from the end of the nineteenth to the beginning of twentieth century include 'fine linen', watercolor, or drawing papers, as well as ordinary writing paper. The surface quality of the paper, whether rough or smooth, will have a defining influence of the final appearance of the image. Robert Demachy and others (Carlin, 1898; Demachy, 1915) describe medium grain and smooth papers as good supports for gum dichromate printing, being easier to coat evenly, less susceptible to flaking during

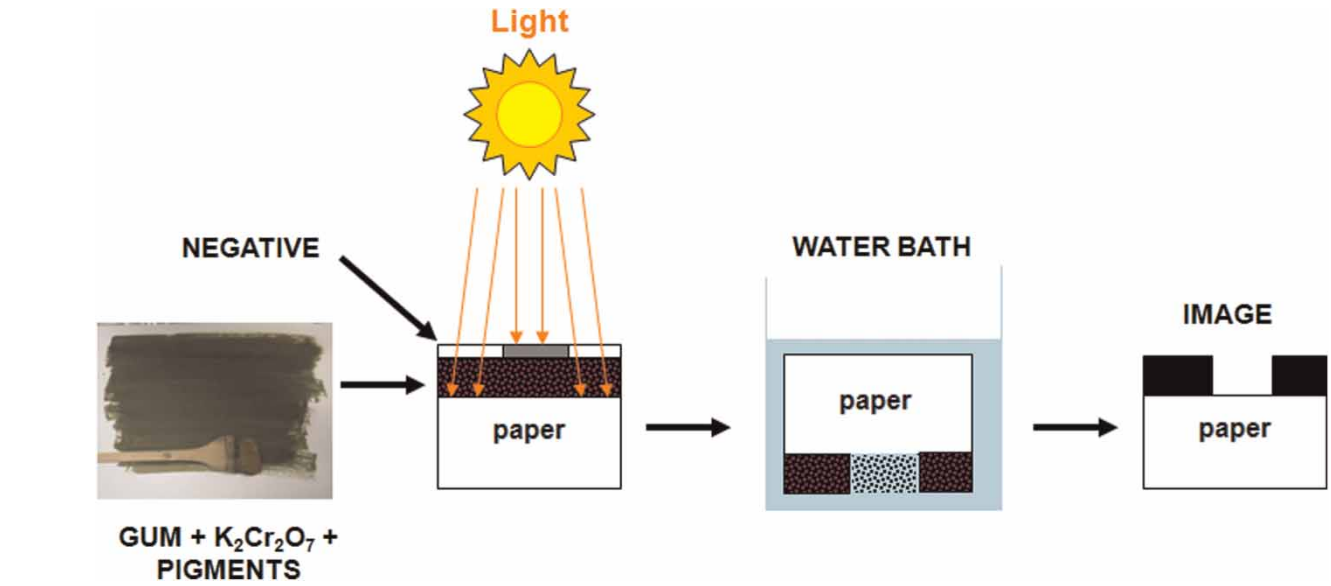

Figure 1 Sketch of different steps in a typical gum dichromate process.

water development, and producing good rendering of shadow detail. Authors such as Constant Puyo (1904) recommend fine grain papers for small format artworks and rough grain papers for landscapes and more expressive prints. Although recommendations vary somewhat, most authors agree that the choice will ultimately depend on the artist's personal taste.

The full list of paper brands in the sources studied includes Canson, Ingres, Michallet, Allonge, Lalanne, Julio, Montgolfier, Schleicher & Schull, Steinbach, Johannot, Whatman, Cartridge, Joynson, Helios, Van Gelder, Zander, Angora (Whiting Paper Co., Menasha, WI, USA), and Rives. The favorites appear to be Michallet, Whatman, and Lalanne. Some authors warn against using papers such as Whatman, Rives, and Steinbach because they have irregular sizing layers and, as a consequence, are difficult to coat successfully (Ewing, 1897; C, 1898; Maskell & Demachy, 1898).

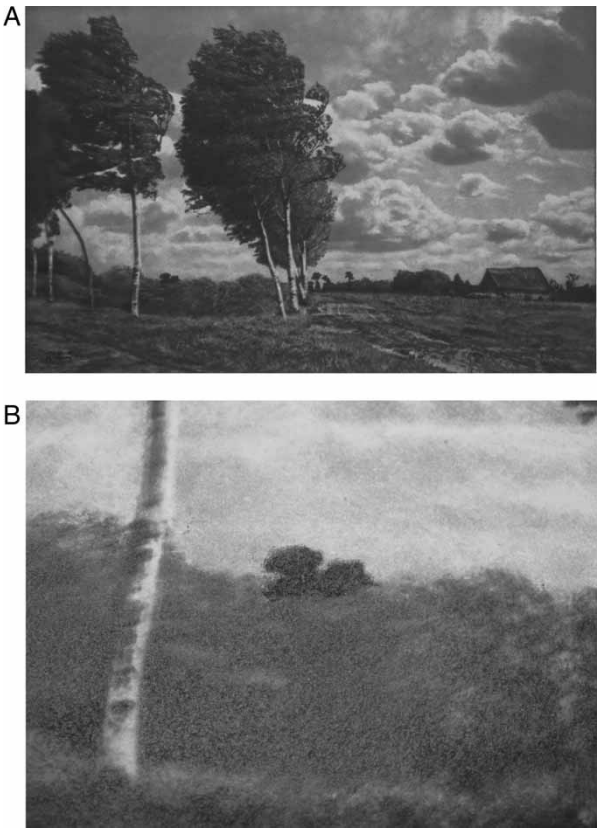

Figure 2 Heinrich Kühn (Austrian, born Germany, 1866–1944), *Lansdcape-Windy Weather, 1902*. The Metropolitan Museum of Art, Alfred Stieglitz Collection, 1933 (33.43.281). Image © The Metropolitan Museum of Art (A), and details taken in the same print (B), showing its contrast and grainy surface texture.

Historic sizing

Sizing such as gelatin or starch is added to the paper to limit its absorption and to prevent the pigment from sinking into the paper fiber interstices, thus improving image quality. Most papers are pre-sized and this may be internal or external. The more efficient the sizing, the less likely the pigment particles will be trapped in the light areas of an image, where pigment is not desired. In order to avoid the formation of indelible pigment 'stains' in the light areas, some manuals recommend applying additional sizing to any type of paper, especially when multiple impressions are to be printed on the same sheet. The additional sizing layer helps to keep the image on top of the paper fibers, preventing the 'muddying up' of the minimum densities. In general, there are no disadvantages to applying an additional sizing to the paper; however, not all authors mentioned its use and there are authors that state that with good quality papers, sizing is not necessary (Anderson, 1917).

The recipes most frequently repeated in the sources studied refer to gelatin or starch (chiefly arrowroot)

and chrome alum (potassium chromium sulfate, $KCr(SO_4)_2{\cdot}12H_2O$). Generally, between 2 and 5% (w/v) pure gelatin or arrowroot solutions in water are recommended, with a 3% concentration being the most favored while a 2% (w/v) solution of chrome alum in water is the most frequently recommended in the historic sources. Some authors cite other materials that can be added to the gelatin or starch solutions such as chrome alum to harden the gelatin; formaldehyde as a preservative; or alcohol. The arrowroot solution must be brought near its boiling point to have the appropriate working properties (King, 2000), whereas the gelatin has to be fully dissolved, then used slightly warm. When the gelatin solution is mixed with the chrome alum solution prior to the application of the mixture on the paper, the volume proportion typically recommended is 1:1 (Wall *et al.*, 1924).

When papers were sized, two different procedures were generally followed (Abbott, 1900). In both cases, before applying the sizing, the first step is to soak the paper in hot water for 15 minutes to one hour, the same time the paper will be in the developing bath, followed by hang drying. This step insures that any shrinkage of the paper will take place prior to printing upon it. One method of applying the sizing consists of brushing it out on one side, first in one direction and then in the other, and subsequently drying the sheet flat. Several layers of sizing can be applied after the previous application has dried depending on how porous the paper is and on the desired results. In a second approach, the previously dampened sheet is immersed for one minute in the sizing solution. In both cases, horizontal drying of the sheet is recommended.

Historic pigments

Finely ground dry pigments or watercolor paints in tubes, cakes, or pans 'from a good maker' are recommended. The color most frequently used by the pictorialists is black, especially rich, dark lampblack. Other pigments cited in the sources include animal black (an impure black prepared by burning animal bones), ivory black, Indian red, Prussian blue, indigo, ultramarine blue, cobalt blue, burnt Sienna, burnt umber, Venetian red, English red, carmine, ochres, Vandyke brown, chrome yellow, cadmium yellow, gamboge, barium white, chalk, sepia, bistre, and caput mortuum. Lampblack together with the Prussian blue, iron oxides, and iron ochres, such as burnt Sienna, burnt umber and Venetian red, and Vandyke brown, are the most frequently cited by the manuals and artists' notes. Some blues and ochres do not work well by themselves in the gum dichromate technique, but are useful to modify black tonalities to obtain warmer or colder hues. The quantities to be used for each color are not indicated. Authors recommend experimenting with different amounts of pigment and colloids to arrive at the most successful proportions.

Historic colloids

A variety of colloids are used as binders for the pigments. Sources mention egg white, gelatin, glues, albumen, or mixtures (Maskell & Demachy, 1897; Wall *et al.*, 1924); however, gum arabic is the favorite because of its softness and good solubility (Maskell & Demachy, 1897). Gum arabic, also called gum acacia, is derived from the resin exuded from certain trees and shrubs that are grown in Asia, Africa, and Australia (Mills & White, 1994). It is recommended that lumps of gum be used instead of powdered gum, as the latter may contain impurities. The recommended concentrations of gum arabic in water range from 10 to 70% (w/v) with 40% mentioned the most frequently. Other additives like sugar, carbolic acid (phenol), formaldehyde, ammonia, chloroform, or dichloride of mercury could be added as preservatives in the colloids if these were to be kept for some time, although many artists prefer to prepare and use them fresh, without any additives. The percentage of gum to water and the viscosity of the solution are very important in obtaining an even coating with an appropriate thickness that does not have brush marks or encourages delamination and flaking during the water development step.

Historic sensitizers

The sensitizer is applied to the paper or added to the colloid before coating in order to render it sensitive to light. A 10–20% (w/v) solution of potassium, ammonium, or sodium dichromate, or a mixture of potassium and ammonium dichromate may be used for this purpose. Gennert (1901), Tennant (1901), and Todd (1907) prefer ammonium or sodium dichromate because they work slightly more rapidly, and they are softer and smoother than potassium dichromate. A 10% (w/v) potassium dichromate solution in warm water appears to be the sensitizer composition most frequently cited.

Three different methods to sensitize the paper have been repeatedly found in the manuals. In the first method the sheet of paper is immersed in the dichromate solution for one to four minutes, then the paper is hung and dried in the dark. After this step, the sensitized paper is coated with the gum and pigment mixture (Wall *et al.*, 1924). The second method consists of coating the paper first with the mixture of gum and pigment, letting it dry and then soaking it in the sensitizing dichromate solution. The last procedure is based on coating the paper with a mixture of gum, pigment, and dichromate. Maskell

and Demachy describe the first method as the one that renders the paper the most sensitive (Maskell & Demachy, 1897). The dichromate to pigment–gum solution volume ratios mentioned in the manuals researched vary between 1:1 and 1:6. In fact, the authors suggest that each artist should choose the proportions based on personal interests and experience. Moreover, these proportions may vary depending on the pigments used. For example, small amounts of lampblack are needed to obtain a rich dark black with the right working properties, whereas sepia, bistre, and umber need larger proportions of pigment to dichromate to have a good consistency (Maskell & Demachy, 1897). Zimmerman states that proportions do not have to be established by measuring, but by appearance during preparation (Gaedicke, 1898; Zimmerman, 1910).

To obtain 'perfect results', some authors recommend performing a coating test before preparing the printing paper in which the consistency of the brushstrokes with different pigment–gum–dichromate proportions is judged (Maskell & Demachy, 1897; Carlin, 1898; Abbott, 1900; Todd, 1907). A preliminary test to determine the right proportions to obtain a 'good white' in the minimum density areas can also be done by brushing different ratios of gum to pigment on a sheet of paper and, after drying, by placing the paper in cold water with the coating side down. If the gum–pigment is released from the substrate in this test, a good white paper results, indicating success (Ewing, 1897; Abbott, 1900).

Historic exposure, development, clearing, and coating

Gum dichromate prints are exposed to sunlight or a 'strong' light source while in contact with a negative (Ewing, 1897; Wall, 1902). Exposure times vary greatly depending on the artist's experience and taste, keeping in mind several parameters such as the quality of the negative, the intensity of the light, the paper, the pigment(s), and the thickness of the coating. Lampblack and burnt umber require exposures twice as long as an ordinary light brown or sepia, and thicker coatings demand longer exposures than thinner coatings.

After exposure, the print is immediately washed with water to prevent further hardening of the gum layer. Gum dichromate prints are developed with water for a variable amount of time ranging from 15 minutes to hours depending on the exposure time, quality of the negative, and the artist's preference (Gaedicke, 1898; Abbott, 1900). Although the water bath is referred to as a 'developing process,' the water actually solubilizes the gum from the unexposed areas of the print, washing away the pigment with it rather than chemically reducing the light-sensitive salts – as with traditional developers in silver-based photography. According to the manuals researched, automatic development – soaking the entire print in a water bath without manipulation – was the favored process during the pictorialist period. In this method, the print is immersed face up in a tray of water for a couple of minutes, and then placed face down to allow the coating from the unexposed areas to dissolve and sink to the bottom of the tray. Changing the water frequently is recommended to avoid stains in the paper. Hand-controlled development through brushing or running water directly over specific areas was also mentioned. By locally manipulating the gum, the artist has greater control of the densities throughout the print. Cold water development (15–21°C) slows the process and allows for better control. Conversely, warm water (38–52°C) speeds up the process, especially in overexposed prints. Historically, some artists also added a soap or sawdust to the water bath to bring out the details faster.

A final clearing bath was suggested by several authors to remove the yellowish 'staining' of the residual dichromate (Todd, 1907; Wall *et al.*, 1924). The recommended baths typically were a 1–5% (w/v) solution of alum (potassium aluminum sulfate, $KAl(SO_4)_2{\cdot}12H_2O$) or sodium bisulfite ($NaHSO_3$). The clearing bath was followed by a final water wash and by air drying. Some authors do not agree upon the advantages of using alum in the clearing bath. For example, Carlin and Wenzel prefer sodium bisulfite (Carlin, 1898; Wenzel, 1901). Kühn was opposed to using a clearing bath because he felt that it diminished the intensity of the shadows (Ewing, 1897).

Analytical challenges posed by gum dichromate prints

Non-destructive elemental analysis by XRF is frequently conducted to identify elements associated with image densities, ground layers, and paper and plastic supports in photographs (McCabe & Glinsman, 1995; Mantler & Schreiner, 2000). Evidence indicates that, in addition to the visual observation of pigments, chromium, and elements associated with pigments typically confirm dichromated colloids such as gum dichromate, direct carbon or carbon transfer processes. Questions arose when a group of pictorialist photographs by Edward Steichen and other artists in the Metropolitan Museum's collection were analyzed by XRF and chromium was found to be either absent or present in different amounts where pigments had been identified by Raman spectroscopy. Visually the prints appeared to have a non-continuous pigmented layer over or under a continuous-tone image – often either

platinum- or silver-based photographic image. In other prints, when chromium was found to be present, sometimes the amounts detected correlated with the image density and sometimes they were constant throughout. It is known that chrome alum was recommended for sizing papers for different photographic processes during the nineteenth century. Dichromate salts were also used in photographic processes such as bromoil, ozotype, and carbon transfer, among others (Cembrano, 1888; Manly, 1901). These facts prompted an investigation into whether the presence of chromium, along with pigments, could be used as an indicator of a dichromated colloid photographic process. The present study focused on the gum dichromate process. In order to systematically evaluate the presence of chromium in gum dichromate prints, test samples were prepared following some of the most popular recipes found in the historic sources and using similar materials, and XRF elemental analysis was conducted.

Table 1 Summary of the results obtained by XRF in two different paper supports, sized with different mixtures applied either by brushing or by immersion. H indicates a relatively high amount, M a medium amount, L a low amount, and VL a very low amount of the elements, as determined by XRF. Square brackets denote that the compounds were applied as a mixture

Paper/sizing	Method of application of the sizing	Ca	Si	S	K	Cr
Arches 88/raw	No sizing	H	VL	–	–	–
Arches 88/starch	Brushed	H	VL	–	–	–
Arches 88/starch	Immersed	H	VL	–	–	–
Arches 88/gelatin	Brushed	H	VL	VL	–	–
Arches 88/gelatin	Immersed	H	VL	VL	–	–
Arches 88/gelatin + $KCr(SO_4)_2{\cdot}12H_2O$	Brushed + brushed	H	VL	VL	VL	M
Arches 88/[gelatin + $KCr(SO_4)_2{\cdot}12H_2O$]	Brushed	H	VL	VL	VL	M
Arches MBM/raw	No sizing	H	–	VL	–	–
Arches MBM/starch	Brushed	H	–	VL	–	–
Arches MBM/starch	Immersed	H	–	VL	–	–
Arches MBM/gelatin	Brushed	H	–	VL	–	–
Arches MBM/gelatin	Immersed	H	–	VL	–	–
Arches MBM/gelatin + $KCr(SO_4)_2{\cdot}12H_2O$	Brushed + brushed	H	–	VL	VL	M
Arches MBM/[gelatin + $KCr(SO_4)_2{\cdot}12H_2O$]	brushed	H	–	VL	VL	M

Table 2 Summary of the results obtained by XRF on samples prepared using the Arches MBM paper, both raw and sized with gelatin and chrome alum, $KCr(SO_4)_2{\cdot}12H_2O$, sensitized with different mixtures and methods, and immersed in different baths. VH (very high) and H (high) indicates a relatively large amount, M indicates a medium amount, L a low amount, and VL a very low amount of the elements as determined by XRF. Square brackets indicate that the compounds were applied as a mixture

Paper/sizing	Sensitizer		Ca	Cr	S	K
Arches MBM/raw	$K_2Cr_2O_7$	Dmax	H	M	VL	VL
		Dmin	H	L	VL	VL
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	M	VL	VL
		Dmin	H	L	VL	VL
	[Gum–pigment] + $K_2Cr_2O_7$	Dmax	H	M	VL	VL
		Dmin	H	L	VL	VL
	$K_2Cr_2O_7$ + [Gum–pigment]	Dmax	H	M	VL	VL
		Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	M	L	–
	+ $NaHSO_3$ bath	Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	M	VL	–
	+ $KAl(SO_4)_2{\cdot}12H_2O$ bath	Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$] (2 layers)	Dmax	H	VH	VL	–
		Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	VH	VL	–
	(2 layers) + $NaHSO_3$ bath	Dmin	H	L	VL	–
	$K_2Cr_2O_7$	Dmax	H	H	VL	–
Arches MBM/		Dmin	H	M	VL	–
[gelatin + $KCr(SO_4)_2.12H_2O$]	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	H	VL	–
		Dmin	H	M	VL	–
	[Gum–pigment] + $K_2Cr_2O_7$	Dmax	H	M	VL	–
		Dmin	H	L	VL	–
	$K_2Cr_2O_7$ + [gum–pigment]	Dmax	H	H	VL	–
		Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	VH	L	–
	+ $NaHSO_3$ bath	Dmin	H	L	VL	–
	[Gum–pigment–$K_2Cr_2O_7$]	Dmax	H	VH	VL	–
	+ $KAl(SO_4)_2{\cdot}12H_2O$ bath	Dmin	H	L	VL	–

Preparation of gum dichromate samples as described in historic sources

A group of approximately 60 samples was prepared and analyzed in the laboratory.

The first set consisted of 14 samples – two different papers, raw and sized with different materials and methods – and was prepared to study the influence of the paper surface on the resulting gum dichromate prints. A second set of samples – prints prepared with three different sizings, and four different sensitizing processes – was tested. Based on the results obtained from the preparation and analysis of these first two sets, a group of 30 samples was prepared printing one layer and two layers, washing out the prints during one, two, five, and 45 hours, at room temperature and in hot water, and with acid, neutral, and basic pH; finally a group of these prints was washed out in two different clearing baths (Tables 1 and 2 list all samples along with XRF analysis results).

Papers

Two papers with different textures and weights were selected based on their similarities to the papers used during the pictorialist period (see the paragraph above about historic papers): Arches 88 and Arches MBM, both from the French company Arjo Wiggins, Boulogne Billancourt Cedex, France one of the biggest producers of fine-quality papers. The 300-g Arches 88 paper, called Arches silkscreen in the United States, is described by Turner (1998) as an unsized waterleaf 100% cotton paper, which freely absorbs ink. It is described as acid-free with a neutral pH and it has only one hot pressed finished, smooth surface achieved by passing the paper sheets between heavy metal rollers. According to Turner (1998), the 150 g Arches MBM paper contains a mixture of 75% cotton fibers and 25% sulfate pulp, it has a laid surface and is acid-free with a neutral pH. Under UV light neither of these papers show

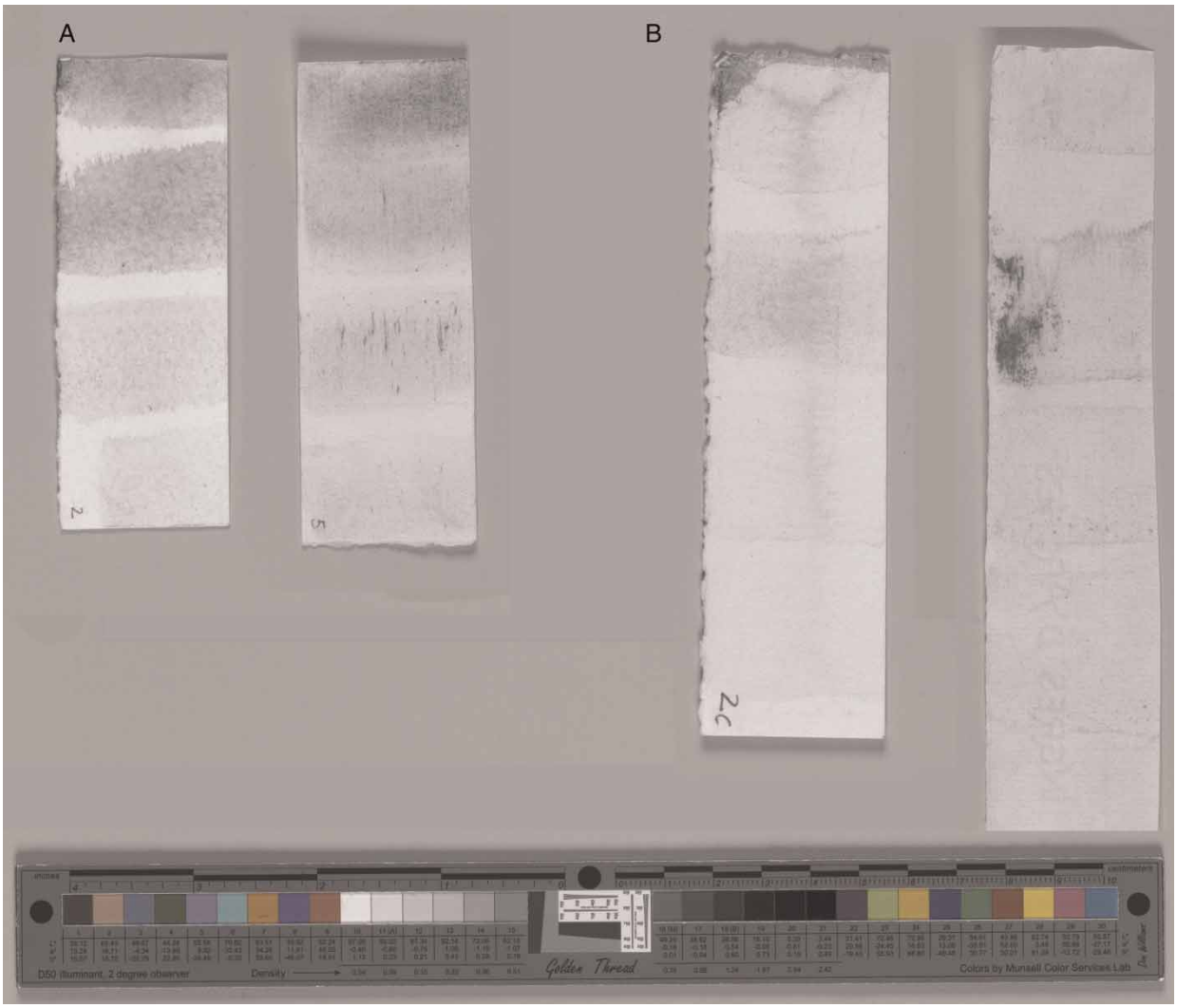

Figure 3 Samples obtained in a test of whites performed using a mixture of a lampblack and gum arabic, shown before exposure to light and after soaking in a water bath. The proportions of pigment–gum arabic in each strip are, from the top to bottom: 0.5 g of lampblack in 10, 20, 30, and 40 ml of gum arabic solution, respectively. Samples in (A) were prepared on two raw papers (Arches 88 and Arches MBM from left to right); samples in (B) correspond to the same papers shown in A, sized with a mixture of gelatin and chrome alum.

the typical fluorescent behavior indicative of optical brighteners (Messier *et al.*, 2005).

Sizings

Three different sizing materials were used based on the most frequently recommended in the historic sources reviewed: gelatin, a gelatin and chrome alum mixture, and arrowroot starch. For the gelatin and arrowroot, 3% (w/v) solutions in deionized water were used; a 2% (w/v) solution was used for the chrome alum. The mixture of gelatin and chrome alum was prepared by two different methods: first by applying the 3% gelatin solution to the paper, letting it dry, and then applying the 2% chrome alum solution on top. The second method consisted of mixing equal parts of the gelatin and the chrome alum solutions and applying the mixture to the paper. The gelatin and starch sizing were applied by brush and by immersion. Starch was dissolved in water, the solution was brought close to its boiling point, and when it achieved a sticky consistency it was ready to be used.

Binder and pigment

A test of whites was done as described above. Based on the results, the best gum arabic to pigment ratio was determined for the two papers chosen with three different sizings. A 0.5 g of lampblack pigment was determined to be the best amount for 40 ml of the 40% (w/v) gum arabic solution for all papers and all sizings used (Fig. 3). Using dry pigment permitted more control of the proportions and composition than would have been the case with tube watercolors.

Sensitizer

A 10% (w/v) solution of potassium dichromate in deionized water was the sensitizer selected. The three coating techniques described in the historic manuals were tested on the two papers chosen, with and without the three different sizings. For the first set, the sensitizer alone was also applied to the paper and then exposed to light. In the second set, the gum, pigment, and sensitizer were mixed and applied to the paper. The proportions were one part of the gum–pigment mixture to one part of the sensitizer solution. In the third set, the paper was first sensitized, allowed to dry, and then coated with the gum–pigment mixture. For the last set, the gum–pigment coating was applied first, dried, and then the sensitizer solution was applied over the gum–pigment layer. A polyester film 21 step sensitivity tablet from Stouffer Graphic Arts Equipment Co., Mishawaka, IN, USA was used as the negative. Each sample was exposed in contact with the negative to UV light for one to two minutes depending on the sizing and the sensitizing procedure used.

Water development

The exposed paper was developed in a pH 6 tap water bath at room temperature for one hour. Separate groups were washed for one, two, five, and 45 hours, either at room temperature (20°C) or in water at 60°C. The pH of water baths were adjusted to basic, neutral, or acidic pH ranges.

Clearing bath

Two sets of samples were immersed in a 4% (w/v) sodium bisulfite and in a 4% (w/v) alum clearing bath, respectively. The dried prints were immersed face

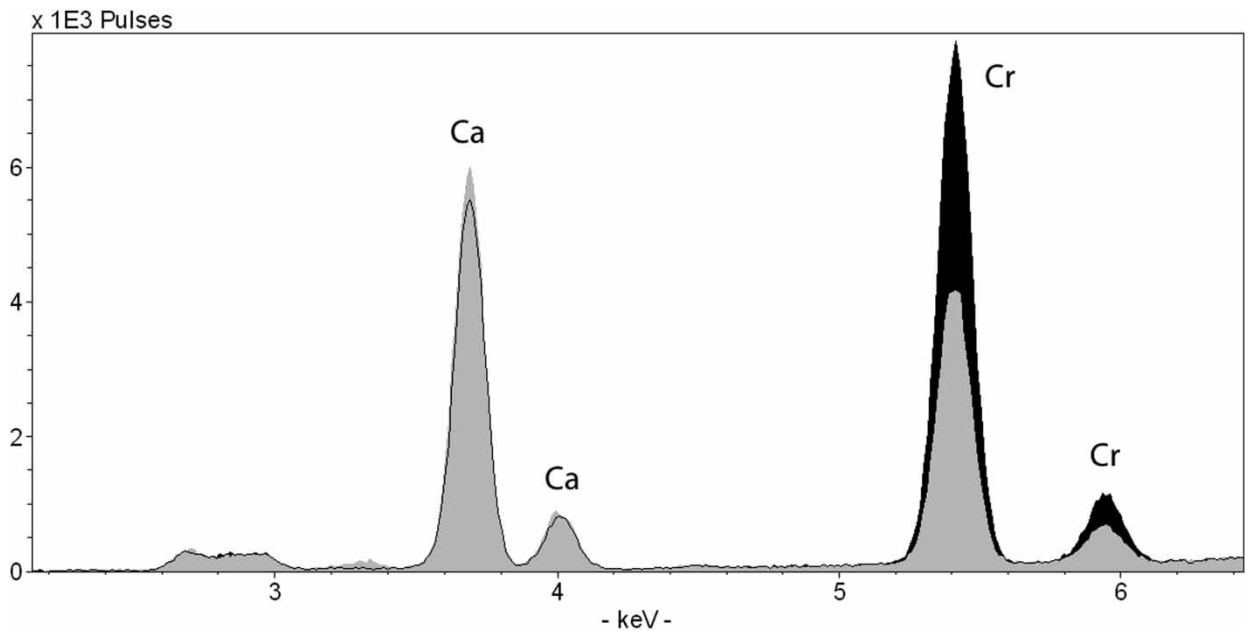

Figure 4 XRF spectra recorded on two Arches MBM paper samples: the gray spectrum corresponds to the raw paper, and the black spectrum to the same paper sized with chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$. These spectra have not been normalized.

down in these baths and left to soak for five minutes. After soaking, the samples were rinsed in a pH 6 tap water bath at room temperature for five minutes.

Analysis of gum dichromate samples

Non-invasive XRF elemental analyses were conducted on the experimental prints with a Bruker Artax 400 unit. Measurements were performed in air atmosphere on different areas of the samples for equal live-times of 200 seconds, using a Rh-target without filtration at 50 kV and 700 μA, an X-Flash detector that allows for a 165 eV resolution, and a 1.5 mm collimator. Spectra were not normalized. Five different areas were analyzed on the raw and on the sized papers. In each print, three maximum density areas and three minimum density areas were analyzed. Results are summarized in Tables 1 and 2.

Results and discussion

One key finding is that chromium was detected by XRF in all the chrome alum-sized paper support samples, regardless of the type of sizing (premixed with gelatin or individually applied over the gelatin sizing layer). The XRF results obtained for the papers, before and after sizing, are summarized in Table 1. A comparison of the spectra recorded in a sample of raw Arches MBM paper and on the same paper sized with chrome alum is presented in Fig. 4,

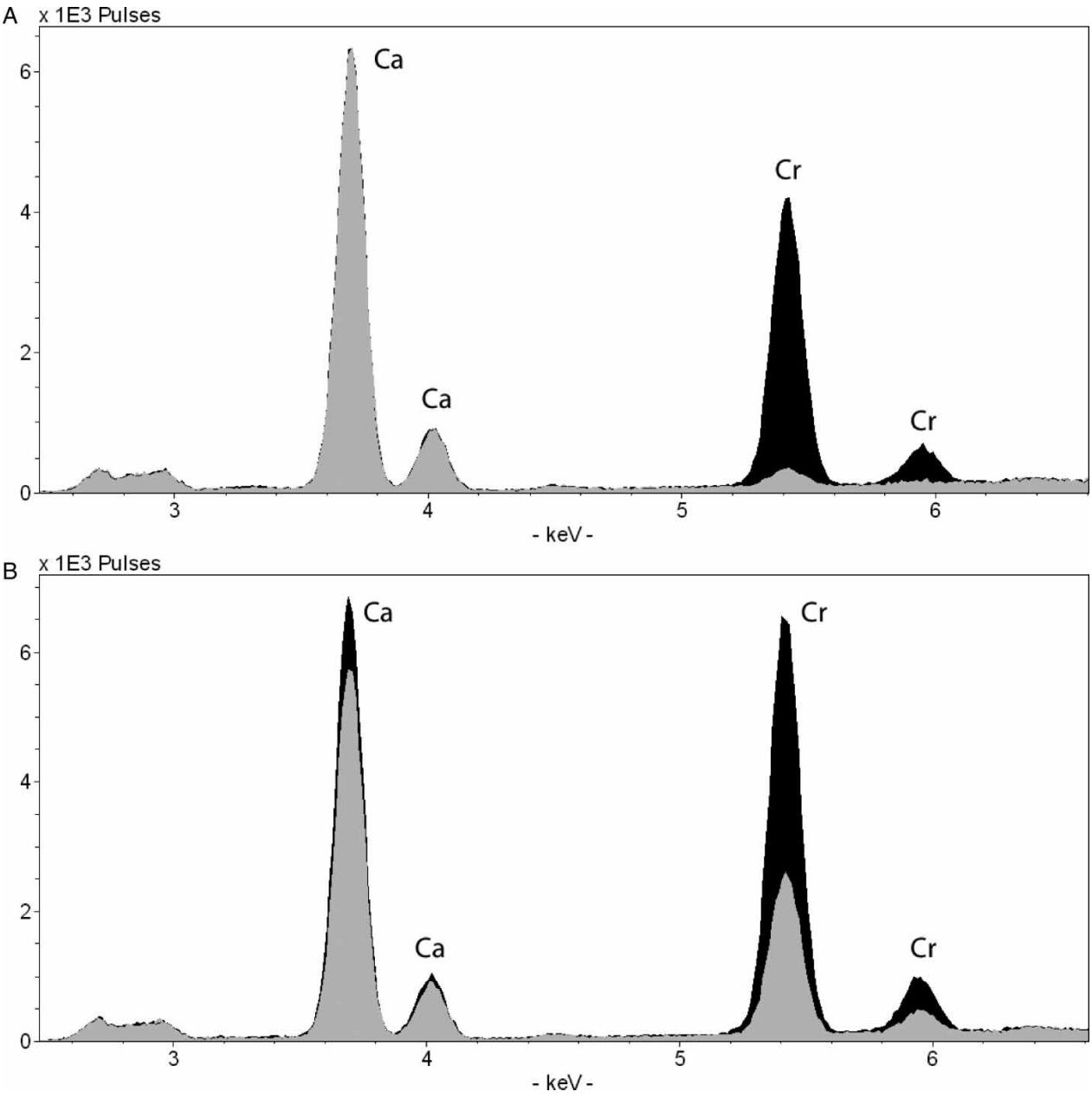

Figure 5 XRF spectra recorded on samples prepared with one layer of gum dichromate (gum–pigment–$K_2Cr_2O_7$) applied on an Arches MBM paper support, not sized (A), and sized with a mixture of gelatin and chrome alum, $KCr(SO_4)_2{\cdot}12H_2O$ (B), respectively. The gray and black spectra correspond, respectively, to areas of minimum and maximum image density. These spectra have not been normalized.

where relatively larger amounts of chromium, sulfur, and potassium can be clearly observed in the latter sample.

Table 2 summarizes the XRF results obtained in gum dichromate print samples prepared using the Arches MBM paper, both raw, and sized with gelatin and chrome alum, sensitized with different mixtures and methods, and immersed in different baths. Analysis of all these images showed relatively larger amounts of chromium in the areas of maximum image density when compared with the minimum density areas. Spectra representative of those acquired are shown in Figs. 5A and 5B; it should be stressed that these spectra have not been normalized. Moreover, and since the presence of calcium is due to the paper only and can be assumed to be approximately constant for all the samples, the chromium to calcium peak intensity ratios were calculated for all the samples and were found to be larger in the areas of maximum image density, supporting the statement made above.

A set of samples prepared using the raw Arches MBM paper and a set using the same paper sized with chrome alum and gelatin, and sensitized with the a gum, pigment, and dichromate mixture, were soaked in two different clearing baths, containing, respectively, sodium bisulfite and alum, in both cases followed by a final immersion in a water bath. XRF analysis carried out on these samples gave similar results as those obtained in the samples for which clearing baths were not used. Only in the case of the samples cleared in a sodium bisulfite bath, a relatively small characteristic peak for sulfur, most likely due to a residue from the sodium bisulfite, was detected by XRF (Table 2).

Another group of samples prepared on the Arches MBM paper, both raw and sized with chrome alum and gelatin, and sensitized with gum, pigment and potassium dichromate, was developed in a water bath for one, two, five, and 45 hours, at room temperature (20°C) and at 60°C, and with neutral, basic, and acidic pH. For the samples immersed in a water bath at 60°C during five or even 45 hours, XRF analysis showed that the chromium is by no means completely washed away by the bath (Fig. 6) and that the chromium to calcium peaks intensity ratios are still higher in the high image density areas. It should be emphasized that 60°C and five hours are rather extreme conditions for a water bath, and that these are rarely mentioned in the historic sources researched for this study; however, they were used to verify the results. Therefore, it is possible to state that if chromium is absent in the maximum image density areas of a print a process other than gum dichromate has been used.

Double-layer gum dichromate prints were prepared on the raw Arches MBM paper. For these samples, a mixture of gum, pigment, and potassium dichromate was applied, exposed to light, and subsequently developed. After drying, a second layer of the same mixture was brushed on. The dried samples were exposed to light and then developed. In Fig. 7, a comparison of XRF spectra acquired in a two-layer and in a one-layer sample are presented, where it can be clearly observed that the intensity of the chromium peaks for the two-layer sample are approximately double of

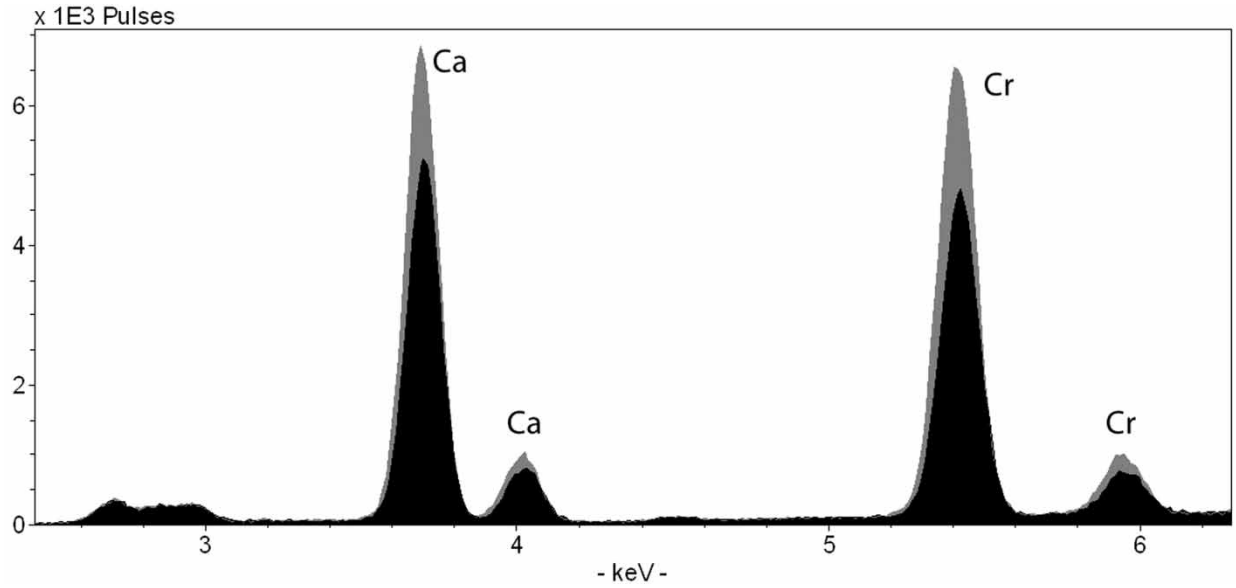

Figure 6 XRF spectra recorded in spots of maximum image density on a gum dichromate print sample (gum–pigment–$K_2Cr_2O_7$) prepared on a raw Arches MBM paper support. The gray spectrum corresponds to a print developed in a pH 6 water bath at room temperature (20°C) for 1 hour, while the black one was acquired in a print developed in a pH 6 water bath at 60°C for 5 hours. These spectra have not been normalized.

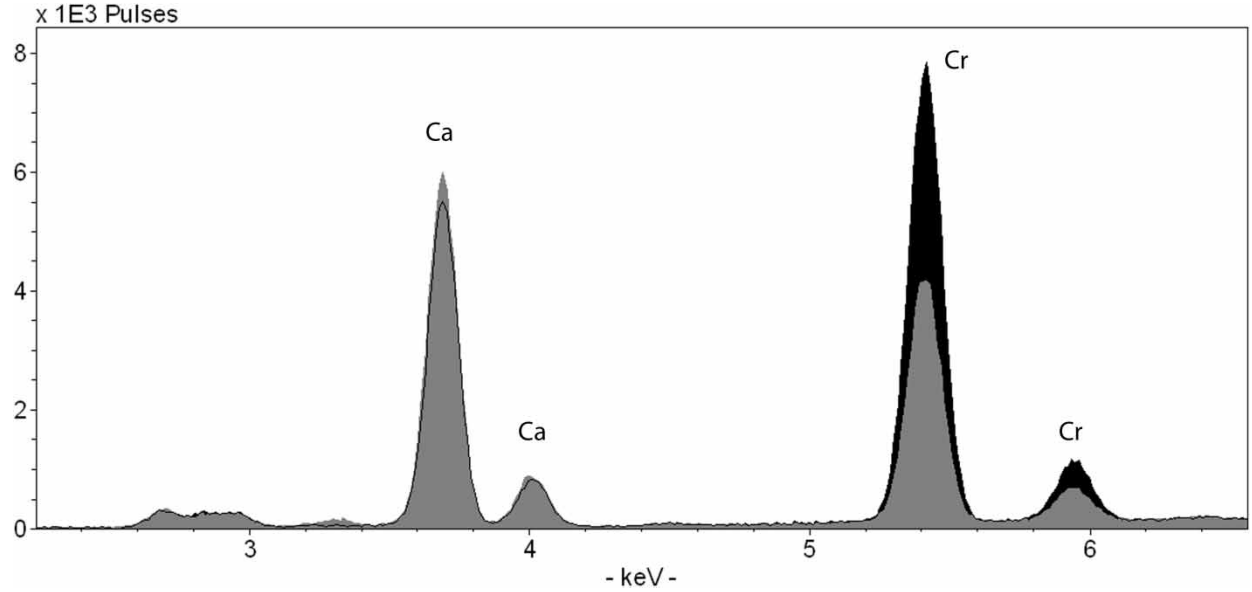

Figure 7 XRF spectra recorded in spots of maximum image density in a gum dichromate sample (gum–pigment–$K_2Cr_2O_7$) prepared on a raw Arches MBM paper support. The gray spectrum corresponds to a print sample with one layer of the sensitizing mixture, while the black corresponds to a print prepared by applying two layers of this mixture. These spectra have not been normalized.

those observed in the one-layer sample. Potassium was not detected in any of the gum dichromate print samples sized with a mixture gelatin and chrome alum, and sensitized by different methods (Table 2). However, a potassium peak was observed in the papers sized with gelatin and chrome alum before printing (Table 1), therefore the absence of this element in the prints is most likely due to its removal during the development in the water bath.

In summary, chromium from the photographic process is detected in all the gum dichromate print samples, with variations in the relative amounts observed due to the number of sensitizing layers, the development conditions, and differences in the image densities achieved. These results have facilitated the accurate identification of photographic processes used in pictorialist works in The Metropolitan Museum of Art's collection. A detailed discussion of case studies as well as the use of spectroscopic techniques to identify the pigments and colloids in gum dichromate prints are beyond the scope of this article and will be published in due course (Vila *et al.*, 2011, 2012).

Conclusions

Approximately 40 manuals and artists' notes from the pictorialist period were reviewed for this study, in which a variety of paper supports, sizing, pigments, colloids, sensitizers, developers, and clearing baths, along with the methods used to apply them, are recommended for making gum dichromate prints. Experimental gum dichromate print samples were created based on the recipes most frequently mentioned in these sources in order to develop a methodology for the identification of gum dichromate processes in artworks. These samples were analyzed with XRF using consistent experimental parameters to determine whether the presence of chromium can be used in an artwork as an indicator of a dichromated colloid process such as gum dichromate. The results indicate that if chromium is absent in the maximum image density areas, a process other than gum dichromate has been used. In a photographic image, when the quantities of chromium are relatively higher in the high image density areas, it is possible to state that a dichromated colloid photographic process was most likely used. On the other hand, because of the limitations of XRF to determine whether the chromium observed in the prints is due to the sensitizer or to the paper sizing, when the quantities of chromium are similar throughout the print, i.e. in different image densities, it is not possible to establish with certainty using this technique that a dichromated colloid process was involved due to the fact that chrome alum could have been used to size the paper substrate.

Reagents

Starch arrowroot powder $(C_6H_{10}O_5)_n$ was purchased from Spectrum Chemical (CAS# 9005-25-8) and a 3% (w/v) solution in deionized water was prepared. The solution was brought up to 60°C to have the appropriate working properties of a sizing for paper substrates.

Gelatin type A was purchased from Acros Organics, NJ, USA (CAS# 9000-70-8). A slightly warm 3% (w/v) solution in deionized water was used to size paper substrates.

Chrome alum, potassium chromium sulfate, $KCr(SO_4)_2{\cdot}12H_2O$, from Bostick & Sullivan, Santa Fe, NM, USA, was prepared as a 2% (w/v) solution in deionized water and used either alone, directly over a paper previously sized with gelatin, or premixed with a 3% (w/v) solution of gelatin in deionized water in proportions 1:1.

Potassium dichromate, $K_2Cr_2O_7$, from Fisher Scientific, Pittsburgh PA, USA; (CAS# 7778-50-9) was used as a 10% solution.

0.5 g of lampblack from Kremer Pigments Inc., NYC, NY, USA (Furnace Black, 47250) were grinded in a mortar to the smallest particle size possible and used mixed with gum arabic and potassium dichromate solution.

Gum arabic was purchased from Sigma-Aldrich (CAS# 9000-01-5) and a 40% (w/v) solution of the powder was prepared in deionized water.

A 4% (w/v) solution of sodium bisulfite, $NaHSO_3$, from Acros Organics (CAS#7631-90-5), and a 4% (w/v) solution of alum, potassium aluminum sulfate, $KAl(SO_4)_2{\cdot}12H_2O$, from Fisher Chemicals (CAS# 7784-24-9), were used in the baths.

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