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Characterization of Platinum Prints: Comparative Study of Platinum Prints in The Museum of Fine Arts, Houston Collection And The Early 20th Century Kodak Platinum Print Samples

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ABSTRACT – Nine historic platinum print paper samples produced by Kodak are studied via photographic documentation with UV-A and raking light, micro-raking texture characterization, X-ray fluorescence spectroscopy (XRF), and spectrophotometry. The subjects are commercial samples of platinum print papers Eastman Kodak Company marketed between ca.1902 and ca.1910, and they are identified by their product names printed within the image or stamped on verso. Ten platinum prints from the Museum of Fine Arts, Houston are selected for comparative study. Also, a group of platinum prints with varied toning and processing techniques are fabricated as known standards. XRF analysis of known standards suggests that mercury to platinum ration of 0.2-0.3 in image material points to the use of mercury additive in sensitizer, as opposed to 0.8-1.1 indicates addition of mercury in developer. Based on comparisons of the three groups of platinum prints, two sets of matches are proposed: Gertrude Käsebier, *Lucille Tomajon* and Kodak sample *Etching Sepia, Smooth*, and Karl Struss, *Nova Scotia* and Kodak sample *Kodak Platinum 1, Medium, Cream Base*.

1. INTRODUCTION

1.1. OBJECTIVE

The Museum of Fine Arts, Houston houses a collection of platinum prints by important photographers from the pictorial era. Pictorial photographers from the turn of the 20th century are known for their craftsmanship and their sensibility to painterly image quality. As these are integral aspects of pictorial photography, the ability to record subtle physical characters of their prints is essential to conservators and art historians. It is, however, difficult to quantify characteristics and record the features of platinum prints in an effective manner, because there are few historic examples of identified platinum papers available to serve as reference standards.

A group of nine historic commercial platinum paper samples by Kodak was identified in private collections, and they were generously loaned to MFAH for characterization study. Using these prints as reference standards, the aim of the project is to collect data that characterizes each sample and to find examples of these papers among MFAH collection photographs. Further, as an attempt to attribute observed characteristics to darkroom technique, a set of platinum print samples are prepared as another set of reference. It is hoped that the outcome of this investigation will be a contribution to connoisseurship of MFAH photographs as well as our knowledge of their makers. Even if no match is found, characterization information in relation to Kodak samples will provide us with a way to describe papers in a quantifiable manner.

1.2. PROJECT OVERVIEW

The project entails (1) preparation of platinum print samples representing various application methods of toning agents and clearing processes, (2) survey and analyses of nine historic Kodak platinum print samples and the prepared known samples, (3) characterization of platinum prints in the MFAH collection.

Total of twenty-four platinum print samples are fabricated following a guideline established by Dr. Mike Ware (Independent Chemist and Printmaker, UK) and the National Gallery of Art photograph conservators and scientists. This guideline describes recipes with chemicals that would have been used in the early 20th century. For the substrate, Cranes 100% cotton unbuffered paper is used. Each print is different in three aspects: addition of toning agent (mercury and/or lead), method of their application (via sensitizer and/or developer) and the lengths of clearing and washing.

Once the known standard prints are fabricated, the known samples, Kodak samples, and MFAH platinum prints are subjected to a series of analysis.

Characterization of platinum prints is an ongoing collaborative project, which is an exhaustive study of this photographic process from historic, chemical, and preservation points of view. The research presented here is a component of this platinum print study. Since it is a collaborative effort, it is critical that the parameter for data collection is standardized among all parties. In order to maintain consistency, detailed protocols for sample preparation and analyses has been established by NGA, and they are closely followed.

1.3. HISTORIC KODAK PLATINUM PRINT SAMPLES

Eastman Kodak Company started commercially producing platinotype paper by 1901 (Barro 2003). Photographic paper suppliers generated prints using the line of photographic papers they were marketing, and mailed them to customers upon request. These sample prints were identified by their product names printed within the image (0).

Vintage photographic paper samples are invaluable resource when characterizing a photograph. By identifying the paper of a given print, one may be able to estimate the print date, artist's aesthetic intent, and the paper's structural and chemical characters that inform storage and treatment options. While samples of popularly used silver gelatin paper are relatively easily found, platinum paper samples are extremely rare. This is probably due to both its earlier and shorter history, as well as the fact that the variety of paper was much more limited compared to silver gelatin papers. The key features of the variety were image tonality and surface texture.

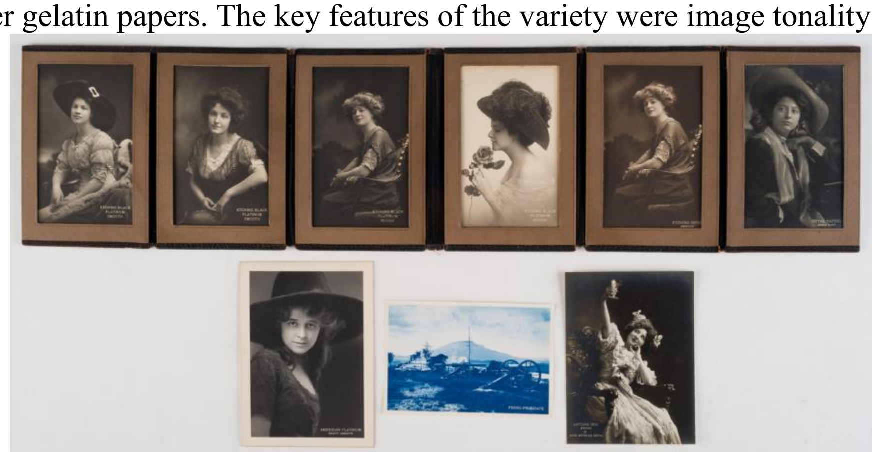


Fig. 1. Kodak Sample Set, ca.1909 (© 2011 Rob McElroy, Buffalo, NY): Sample number 1-9 from top left to bottom right

1.4. SELECTION OF MFAH PLATINUM PRINTS

In order to increase the chance of finding matches with historic samples, the photographs that were created in or around the year of the Kodak papers' manufacture are selected for comparative study. The earliest paper, *Water Development (W. D.) Platinum*, is dated 1902 (Andrew J. Lloyd & Company), and the latest example, *Etching Black Platinum Paper*, is dated ca. 1910 (Hafey, Shillea 1979). The second criterion is paper thickness, which is easy to measure using a micrometer during preliminary review. Since most of the photographs are mounted on a secondary support, paper thickness is estimated by subtracting the thickness of the mount from the combined thickness of the print and the mount. Based on the print date and paper thickness, ten photographs are selected for the study (0).

Table 1. Kodak Platinum Print Sample Set

Sample number	Paper name	Date	Paper thickness
1	Etching Black, Platinum, Smooth	ca. 1909	0.28 mm
2	Etching Black, Platinum, Smooth	ca.1909	0.28 mm
3	Etching Black, Platinum, Rough	ca. 1909	0.31 mm
4	Etching Black, Platinum, Rough	ca. 1909	0.31 mm
5	Etching Sepia, Smooth	ca. 1910	0.26 mm
6	American Platinum, Heavy Smooth	ca. 1902	0.23 mm
7	Kodak Platinum 1, Medium, Cream base	ca.1910	0.22 mm
8	Kodak Platinum 2, Medium, Cream base	ca.1910	0.20 mm
9	Eastman W. D. Platinum	ca.1902	0.17 mm

Table 2. MFAH Platinum Prints Selected for Study

Object number	Artist	Title	Date	Paper thickness
79.19	Adam Clark Vroman	Snake Priest Entering the Kiva	ca. 1902	0.24 mm
81.124	Farraud	Forked Tree	ca. 1903	≈ 0.23 mm
2004.437	Frederick H. Evans	Bourges Cathedral: South Nave Aisle	ca. 1903	≈ 0.325 mm
2004.440	Frederick H. Evans	Steps into Chapter House, Wells Cathedral	1903	not accessible
2004.669	Edward Steichen	John Woodruff Simpson	1903	0.48 mm
2004.794	Clarence Hudson White	Nude in Forest (Mabel Cramer)	1909	≈ 0.22 mm
85.82	Gertrude Käsebier	Lucille Thomajon	ca. 1910	≈ 0.23 mm
2004.678	Karl Fischer Struss	The Porch, Barnard College	1910	≈ 0.23 mm
91.1142	Karl Fischer Struss	Nova Scotia	1911	0.23 mm
2004.681	Karl Fischer Struss	Chester, Nova Scotia	1911	0.26 mm

2. FABRICATION OF PLATINUM PRINT SAMPLES

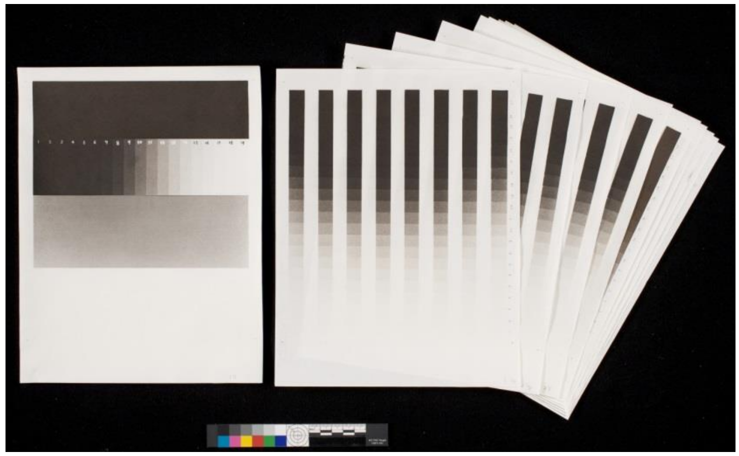


Fig. 2. Fabricated Platinum Print Samples

Based on historic literature and published sources, it is understood that mercury and lead were two of the most commonly used toning agents for platinum prints (Abney and Clark 1895, Anderson 1917, Crawford 1979, Willis 1887). The photographers in the late 19th to early 20th century noted that the use of mercury or lead in sensitizer and developer achieved sepia tones and finer image grains (Chapman 1904). In order to characterize effects of toning agents in a quantifiable manner, platinum print samples are prepared using traditional method and material as outlined in *Simulation of 'Traditional' Platinotype and Palladiotype*, by Dr. Ware and the NGA Photo Team (11/17/2011 first draft). Total of twenty-four platinum print samples represent various combinations of application methods of mercury and lead (via sensitizer and/or developer), as well as different lengths of clearing and washing.

3. SURVEY

Basic information of the study subject is collected through a survey prior to technical analysis. The criteria of the survey are; sheet dimension, thickness, texture (smooth/medium/rough), sheen (1 to 5, matte to glossy), discoloration (1 to 5, none to severe), and presence of image burn through to verso. With exception of dimension and thickness, observations are made visually without the aid of analytical instrument. Therefore, the collected information is not quantifiable, but useful for making comparisons among the group and discovering points of interest that may be pursued through further analysis.

3.1. RESULT AND OBSERVATION

On the basis of surface sheen, on the scale of 1 (matte) to 5 (glossy), all Kodak samples are 1, while MFAH photographs vary from 1 to 3. To provide a point of reference, 1 is dead matte and 5 is similar to the gloss of an albumen print. One print by Frederick Evans (2004.437) is categorized as 2 and four prints including Gertrude Käsebier (85.82), Edward Steichen (2004.669), Clarence White (2004.794), and Karl Struss (2004.678) are given a 3. These prints have a dull, yet noticeable specular reflection when using a flashlight to inspect the surface. All of these glossier prints have later dates among the group, 1909 or 1910, with an exception of Steichen, which is dated 1903.

All prints show moderate discoloration of the paper support and given the discoloration category of 2 or 3 on the scale of 1 to 5, 1 being no discoloration and 5 being severely darkened.

The only print that falls out of the norm is Steichen's *John Woodruff Simpson* (2004.669), which has dark reddish brown color in mid-tone and highlight areas.

Kodak sample 5, *Etching Sepia, Smooth* stands out on account of image burn, showing severe penetration of the image in high density area (fig. 3). Nine out of ten MFAH prints are adhered to a mount, and the verso is not accessible for observation. Since the Kodak sample 5 is the only sample that presents the image penetration, it may not be used as a parameter for finding a match between the two sets of samples. However, it is a unique character, and it may be useful information for future research.

Fig. 3. Kodak sample 5, *Etching Sepia, Smooth*, recto (left) and verso (right). High-density area of the image has penetrated through the paper and is visible on verso. Contrast of verso image is digitally enhanced for publication.

4. ANALYTICAL

A series of analytical methods are selected to understand optical property, physical structure, and elemental composition of platinum prints. Only non-contact and non-destructive analysis techniques are used (0).

Table 3. Analytical Techniques Employed

Type of analyses	Subject of interest	Instrument
UV-A induced visible fluorescence imaging	Sizing, coating, metallic deposit	Canon EOS-1Ds Mark II
Spectrophotometry	Color make up of D-max, D-min	Zeiss Discovery V12 outfitted with PlanApo S 0.63x FWD 81mm lens
Photomacrography (I):	Surface texture	Zeiss Axiocam imager, fiber optic lamp
Photomacrography (II): Texturescope	Surface texture	Luminera Infinity 2-3 Imager, microscope, LED line lamp ("Texturescope")
X-ray fluorescence spectroscopy	Elemental composition	Bruker Artax and Tracer X-ray spectrometer

4.1. UV-A VISIBLE FLUORESCENCE IMAGING

4.1.1. Method

The platinum prints are documented with a Canon digital SLR camera while they are exposed to UV-A radiation with a handheld UV lamp. The lamp emits 365 nm ultraviolet ray. The camera is outfitted with a UV filter, and aperture priority mode (at f8) is used. Exposures are made while the UV lamp is moved around the photograph continuously at a two to three feet distance. As a result, the shutter speed of all images comes out to thirty seconds.

UV-Vis documentation is useful for identifying sizing in the paper substrate and presence of coatings. Also, it is useful in observing metallic deposits in paper support.

4.1.2. Result

No fluorescence with UV-Vis is noted that may be attributed to sizing or superficial coating. Almost all samples have similar response to UV-A radiation, producing vague faint white color in highlight area that is intrinsic to paper (Tragni 2003), but no distinct fluorescence. There are some variations among the colors; however, they are most likely due to difference in the way the UV lamp is moved during exposure and artifact of digital image processing.

One print by Steichen, *John Woodruff Simpson* (2004.669), appears somewhat greener than other prints. This photograph is significantly darkened when viewed with normal lighting, and it is difficult to determine whether this difference is caused by deterioration of the print or by a factor that characterizes the paper in its original condition.

4.2. PHOTOMACROGRAPHY WITH RAKING ILLUMINATION

4.2.1. Method

Photomacrographs of MFAH and the Kodak platinum print samples are generated using Axiocam imager with a fiber optic line lamp at approximately 45 degree raking angle. This method of imaging enhances surface texture, which is an important aspect in detecting similarities and differences between the two sets of samples. At high magnification, morphology and distribution of paper fiber can also be observed. Photomacrographs are generated at three magnifications, 15x, 30x, and 63x, of an area containing wide density range such as an eye of the sitter, and at two magnifications, 15x and 30x, of a corner of each print. For the latter, areas with cracking or abrasion are selected whenever possible, as these areas of damage often reveal layer structure of the sheet.

4.2.2. Result

Similar fiber morphology and distribution are observed among all Kodak samples and MFAH prints. When comparing the smoothness/roughness of the surfaces, two prints by Frederick H. Evans (2004.437 and 2004.440) appear rougher than the others in MFAH group. Among the Kodak sample set, the samples 3 and 4 show rougher texture true to their shared name, *Etching Black, Platinum, Rough*. When comparing the two Evans prints and these Kodak

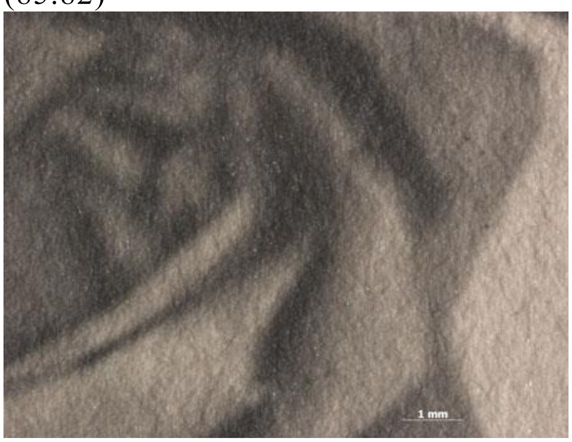
Platinum Rough prints, the surface of the Evan's prints are noticeably rougher, making them the most textured surfaces. The rest of the prints appear very similar with little variations (0).

Table 4. Examples of Surface Texture Comparison

Smooth

G. Käsebier, *Lucille Thomajon*, ca.1910 (85.82)

Kodak Sample 2, *Etching Black, Platinum, Smooth*



Kodak Sample 3, *Etching Black, Platinum, Rough*

Kodak Sample 4, *Etching Black, Platinum, Rough*

Rough

F. Evans, *Bourges Cathedral: South Nave Aisle*, ca. 1903 (2004.437)

F. Evans, *Steps into Chapter House, Wells Cathedral*, 1903

4.3. MICRO-RAKING IMAGING WITH TEXTURESCOPE

4.3.1. Method

A "texturescope" is a documentation device developed by Paul Messier (Paul Messier LLC., Boston, MA) that generates images of paper surface with enhanced topography information. The images are essentially photomacrographs with raking light, or micro-raking images. Texturescope is composed of a microscope, an image-capturing device, and an LED line lamp that is attached to the microscope mount at a fixed angle. The imager is tethered to a computer, and the captured image is processed via algorithm that removes color information and increases contrast to enhance the peak and valley information of the captured surface. The image file after processing is in TIFF format and approximately 2.0 MB in file size (1024 x 1024 pixels). The field of image capture is finely calibrated to 1.0 cm x 1.0 cm and the angle of light at 25 degree coming from the top of the image field. By maintaining the consistent dimension and angle of light, this technique allows compilation of images that are useful for identifying matching or un-matching paper surfaces.

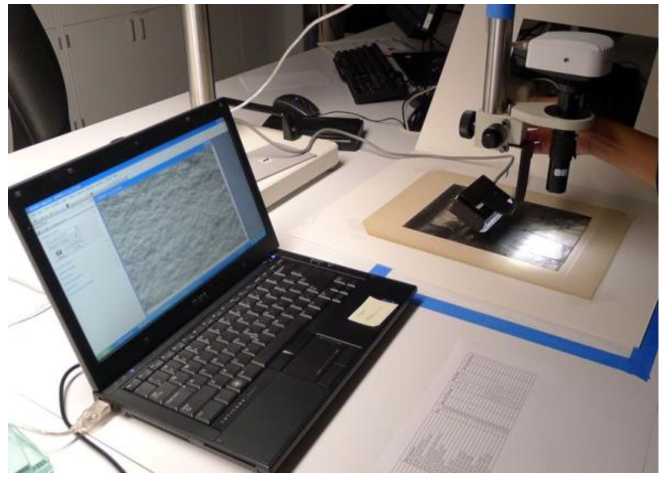


Fig. 4. Micro-Raking Documentation with Texturescope

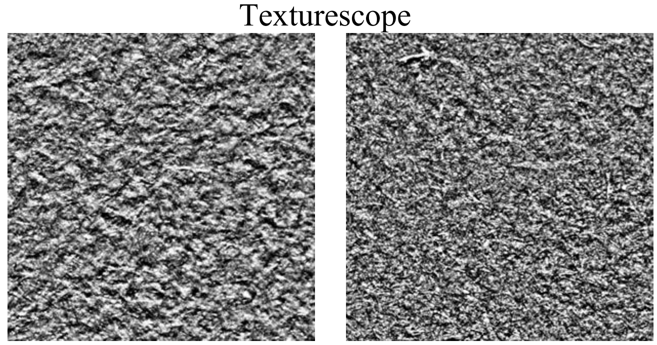


Fig. 5. Micro-Raking Images of *Kodak Etching Black, Smooth* (Kodak sample 2) Genearted from A Highlight Area (left) And Dark Area (left)

Micro-raking images of MFAH collection prints and Kodak sample set are generated. For Kodak samples, imaging of verso surfaces is performed as well. The samples are placed under microscope in proper viewing orientation. Photomacrographs were captured with Infinity Analyze software. After imaging of all samples is complete, all files are batch processed using Image J application.

Due to limitations with the image-processing algorithm, image density of the area of capture impacts the resulting texture image. In other words, two drastically different micro-raking images can be generated from a single photograph by capturing one area in shadow and another in highlight of a single print (0). Micro-raking images based on highlights appear much rougher than the images from the shadow areas. Between the two, the image derived from a highlight is believed to be more representative of actual surface. This is probably because shadows from paper topography blend into dark color of the image when the micro-raking capture is from high-density area, and they are processed as a continuous surface.

Many of the photographs studied in this research do not have large enough highlight area for micro-raking imaging. Highlight area is selected whenever possible, and lightest possible area is selected otherwise. In order not to confuse varied results, the micro-raking images are labeled by D-min, D-mid, and D-max based on the image density of the initial capture, and they are compared within the group.

The surfaces of MFAH prints are compared against Kodak samples by eye. In order to reduce subjectivity as much as possible, five staff members in the photography and paper conservation laboratories are asked to take a surface matching test individually. The participants are shown two sets of 5” x 5” printout of micro-raking images of Kodak samples generated from D-min and D-mid areas. They are, then, given two sets of MFAH print surface images separated by the source density area and asked to find matching surfaces with the Kodak samples within respective group.

4.3.2. Result

All Kodak samples in each density category appear to have different texture. The surface-matching test suggests that six MFAH prints are comparable with Kodak sample prints (0). It should be noted, however, that it is difficult to make fare comparisons between printout of surfaces, and even the matches designated by the test takers based on rough/smooth scale do not necessarily have an identical fiber morphology and distribution pattern. Although definitive identification of paper is not possible using this method, it allows one to characterize textures in relation to known samples as well as determine un-matching papers.

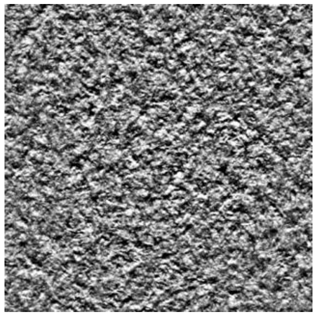
Table 5. Designation of Similar Surfaces Based on Visual Assessment

Image density	Kodak samples		MFAH prints	
D-min	Sample 7 base	Kodak Platinum 1, Medium, Cream	91.1142	K. Struss
	Sample 9	Eastman W. D. Platinum	No equivalent	
	Sample 3	Etching Black, Platinum, Rough	79.19	A. Vroman
	No equivalent		81.124	Farraud
D-mid	Sample 8 base	Kodak Platinum 2, Medium, Cream	2004.669	E. Steichen
	Sample 6	American Platinum, Heavy Smooth	2004.681	K. Struss
	Sample 2	Etching Black, Platinum, Smooth	2004.440 2004.437	F. Evans F. Evans
	No equivalent		85.82 2004.794 2004.678	G. Käsebier C. White K. Struss
D-max	Sample 1 Sample 4 Sample 5	Etching Black, Platinum, Smooth Etching Black, Platinum, Rough Etching Sepia, Smooth	No equivalent	

Table 6. Micro-Raking Images of Kodak Platinum Print Samples

Kodak sample set (D-min)

Sample 3, *Etching Black, Platinum, Rough*

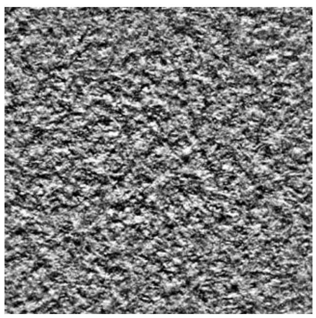


Sample 7, *Kodak Platinum 1, Medium, Cream base*

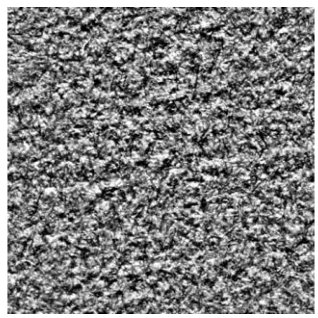
Sample 9, *Eastman W. D. Platinum*

Kodak sample set (D-mid)

Sample 2, *Etching Black, Platinum, Smooth*

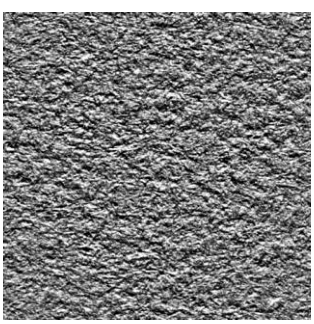


Sample 6, *American Platinum, Heavy Smooth*

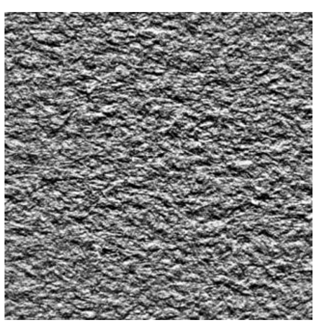


Sample 8, *Kodak Platinum 2, Medium, Cream base*

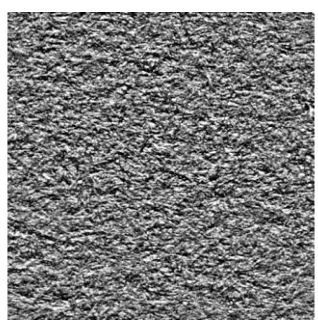
Kodak sample set (D-max)



Sample 1, *Etching Black, Platinum, Smooth*



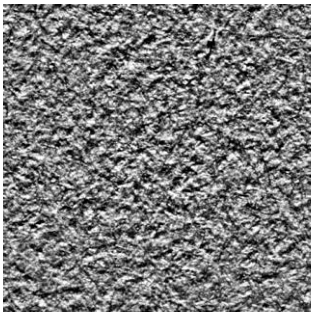
Sample 4, *Etching Black, Platinum, Rough*



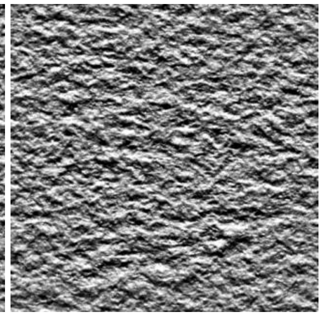
Sample 5, *Etching Sepia, Smooth*

Table 7. Micro-Raking Images of MFAH Platinum Prints

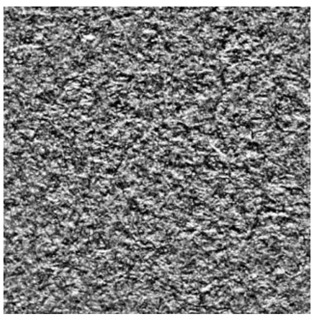
MFAH prints (D-min)

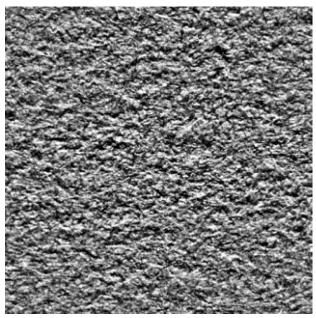

Struss (91.1142)

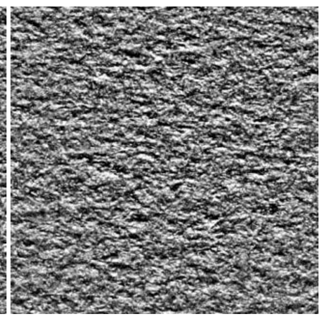

Vroman (79.19)

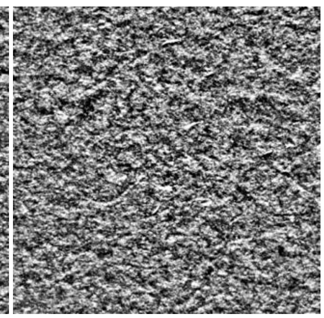

Farraud (81.124)

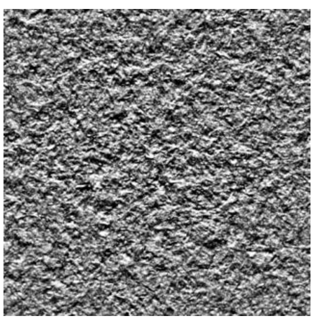
MFAH prints (D-mid)


Käsebier (85.82)

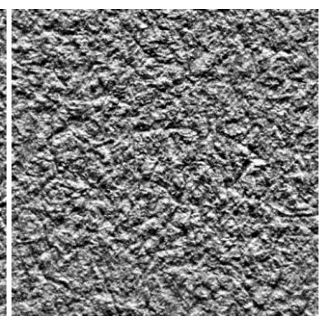

White (2004.794)


Struss (2004.678)


Steichen (2004.669)


Struss (2004.681)


Evans (2004.440)


Evans (2004.437)

4.4. SPECTROPHOTOMETRY

4.4.1. Method

Spectrophotometric analysis is conducted using X-Rite SP64 Portable Sphere Spectrodensitometer. CIE Lab color space D65/10° values are used. Two areas of maximum-density and one area of minimum-density are selected for measurements on each print whenever possible. Some of the study subjects do not have desirable area, in which case, closest-to-ideal density area is selected and the record is labeled as such to distinguish the difference between true D-max or D-min areas.

4.4.2. Result

All prints have similar L* values, representing similar level of darkness in their highest density area. Vroman (79.19) is the only drastically irregular image that has a lighter tone overall. On the other hand, a* and b* values present a broad distribution among the studied prints.

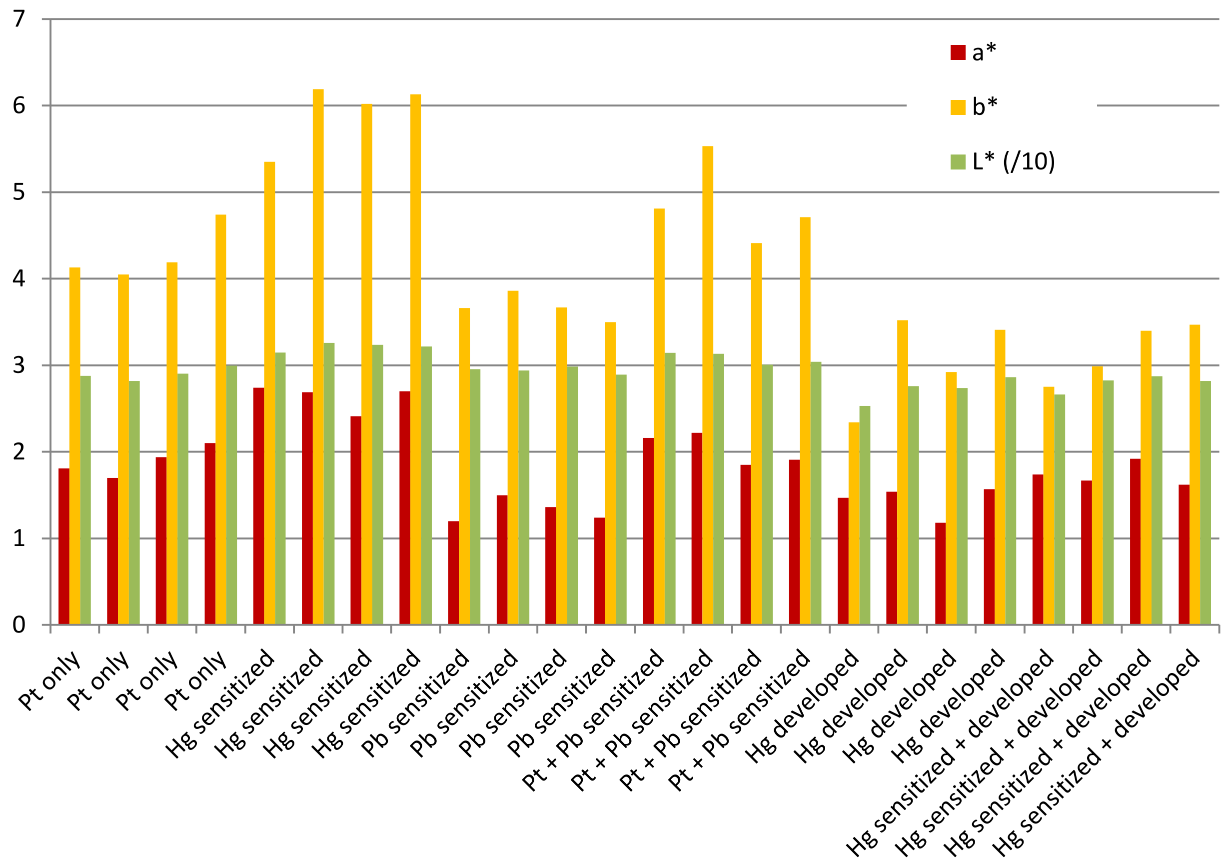


Fig. 6. L*a*b* Values of Handmade Samples: Measurements were taken in the darkest patch of central gray scale of standard step tablet. From color measurement of several darkest patches, it was confirmed that the D-max had reached its darkest possible density.

Handmade samples present loosely unique color characters to each chemical combination. Lead-sensitized samples have closest to neutral tone, followed by straight platinum, then mercury-and-lead-sensitized samples. Mercury-sensitized samples have the warmest tones. The samples with toning agents in the developer show less consistent results, but fall in close to neutral range similar to lead-sensitized prints. It is interesting to note that the mercury toned samples produced various colors ranging from close to neutral to warm depending on the application method of the toning agents. Mercury-sensitized samples have the warmest colors among all handmade samples, whereas mercury-sensitized-and-developed samples have much cooler tones, and mercury-developed samples are even cooler, even though the toning agent used is the same among these three variations.

Kodak samples 1 through 3, which bear the same name *Etching Black*, fall in close ranges of L*a*b* values with one another, while Kodak sample 4, which is also called *Etching Black*, shows lower L* and b* values, indicating darker and cooler tone. Kodak sample 5, *Etching Sepia* has the highest a* and b* values, warmest tone among the Kodak samples, true to its name *Etching Sepia*. The Kodak sample 8, *Kodak Platinum 2, Medium, Cream base* has uniquely neutral and darkest tone among the Kodak samples.

The variety of a* and b* values among the MFAH prints is even greater than that of Kodak samples. Vroman (79.19) has exceptionally high L*a*b* values. Käsabier (85.82) and one of Struss prints (2004.681) have distinctly warm tones similar to Kodak sample 5, *Etching Sepia*. None of the MFAH prints has true neutral tonality.

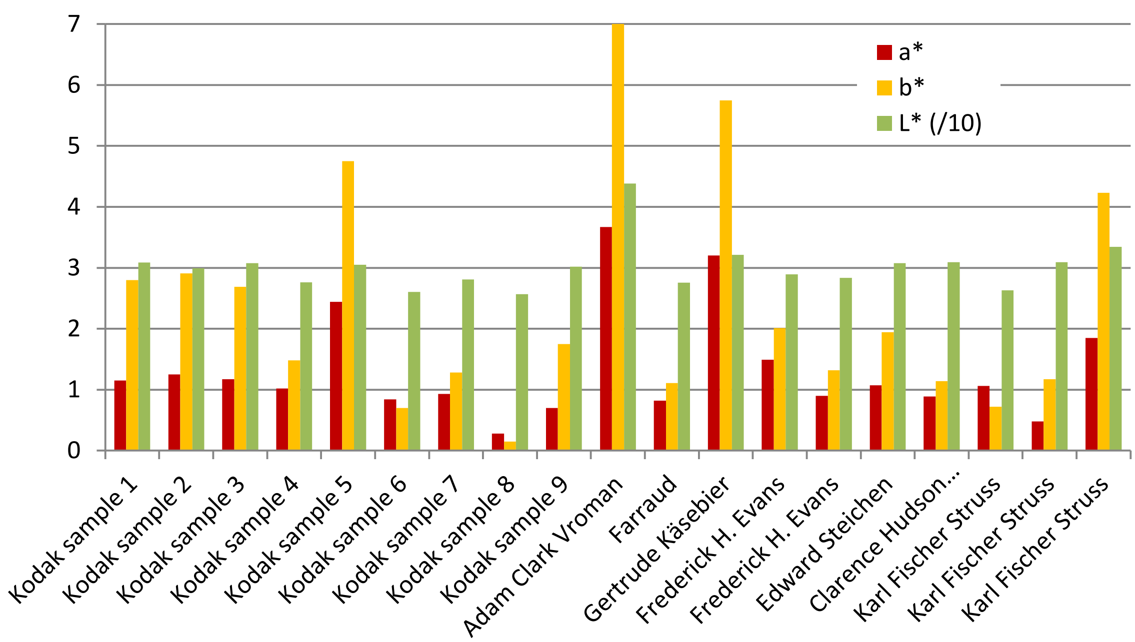


Fig. 7. L*a*b* Values of Kodak Samples And MFAH Prints: Measurements were taken in the darkest area that could be found on each photograph. Vroman (79.19) and Struss (91.1142, second from last on the graph) did not have continuous D-max area.

4.5. XRF

4.5.1. Method

XRF analysis is conducted using Bruker Artax Pro and Tracer III-V+. Artax Pro is capable of analyzing small areas with finely controlled settings; however many institutions do not have access to this instrument due to its cost. On the other hand, a handheld Tracer is relatively commonly seen in institutions with conservation laboratories. In order to maximize the compatibility of information, two sets of data are generated using both instruments.

Spectra are collected from two areas of maximum-density, two areas of highlight, one area in the margin if present. For the prints that are not mounted, one area on verso that corresponds to highlight of the image and one area of the mount, if mounted, are also analyzed. Whatman filter paper and Cranes paper used for handmade samples are also analyzed to establish a standard between MFAH and NGA analysis.

Table 8. XRF Analysis Settings

	Artax Pro	**Tracer III-V+**
Target	Rh	Rh
Voltage	40 kV	40kV
Current	200 µa	25 µa
Collimator	NA (capillary optics, 0.060 mm)	NA
Filter	None	Al (12 mm), Ti (1 mm)
Live time	300 seconds	300 seconds
Atmosphere	He flush	Air

In order to increase the ease of comparison between numerous spectra, mathematical method based on net signal counts is employed. Using the Bruker Artax Spectra v.7.2.0.0 software, the net pulse counts of selected elements are exported to Microsoft Excel. The elements of interest are: silicon, sulfur, chlorine, argon, potassium, calcium, titanium, chromium, manganese, iron, nickel, copper, zinc, rhodium, barium, platinum, mercury, and lead. In Microsoft Excel, all values are normalized by the rhodium count of Cranes paper. Sets of two D-max and D-min spectra are averaged, and subtraction value of D-max minus D-min is calculated to represent the elemental composition of image material. For further investigation, relative abundance of mercury to platinum, lead to platinum, and palladium to platinum are calculated using the subtraction values.

The calculations described above are repeated for the data generated from Artax Pro and Tracer. Both data sets resulted in the same trends. For the sake of simplicity, the data generated from Artax Pro is used for further discussion.

4.5.2. Result

Comparison of mercury containing handmade samples by their mercury-to-platinum ratio presents a distinct trend that is unique to each application method of mercury (0). Mercury-sensitized prints consistently have the Hg:Pt ratio of 0.2 to 0.3, while mercury-developed samples fall in the range of 0.8 to 1.1. The samples that do not contain mercury have the Hg:Pt ratio of below 0.1. The ratio values for these straight platinum prints are not zero because the numbers from which the ratio is calculated are normalized values. Positive count number does not necessarily indicate the presence of given element. Rather, the ratio of below 0.1 should be understood as its absence.

While presence of mercury is evident, lead is not discernible in the samples that are sensitized with lead-containing solution. The count of lead is so low that its subtraction values are more often negative than positive. The difference in Pb:Pt values between samples rely mostly on the difference in platinum counts instead of lead, resulting in seemingly random distribution of the ratio values.

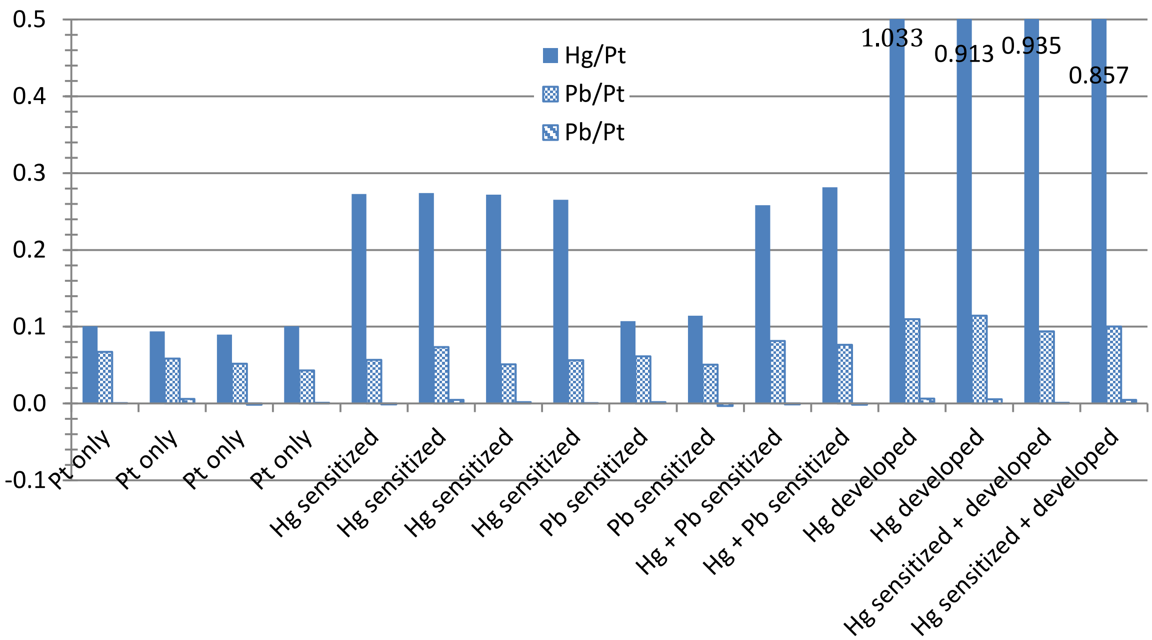


Fig. 8. Mercury-to-Platinum and Lead-to-Platinum Ratios of Handmade Samples: The ratio calculations are based on subtraction of D-max minus D-min of M-α line net counts.

The majority of the Kodak samples and five of ten MFAH prints have Hg:Pt ratio close to 0.1, suggesting they are not mercury-toned. Two of Kodak samples, sample 4, *Kodak Etching Black, Platinum, Rough* (Hg:Pt = 0.215) and sample 5, *Kodak Etching Sepia, Smooth* (Hg:Pt = 0.273), and three MFAH prints by Adam Vroman (79.19) (Hg:Pt = 0.241), Clarence White (2004.794) (Hg:Pt = 0.278), and Gertrude Käsebier (85.82) (Hg:Pt = 0.228) have Hg:Pt ratio similar to that of mercury-sensitized samples. A print by Edward Steichen (2004.669) has a markedly high relative mercury abundance of 0.846, which is similar to the mercury-developed samples. One print by Frederick Evans (2004.440) has intermediate ratio of 0.383, leaving it as an outlier.

The ratio comparison of palladium and platinum clearly divides the studied prints into two categories; palladium containing and palladium free prints. Four of the *Kodak Etching Black* samples, Kodak samples 1-4, have Pd:Pt ratio ranging between 0.113 and 0.139, and one print by Karl Struss (2004.681) has the highest value of 0.196. Although these values are very low, they are ten to twenty times higher than the Pd:Pt values of the other prints. Due to the marked distinction, relative abundance of palladium above 0.1 is considered as one of unique characteristics of the five prints.

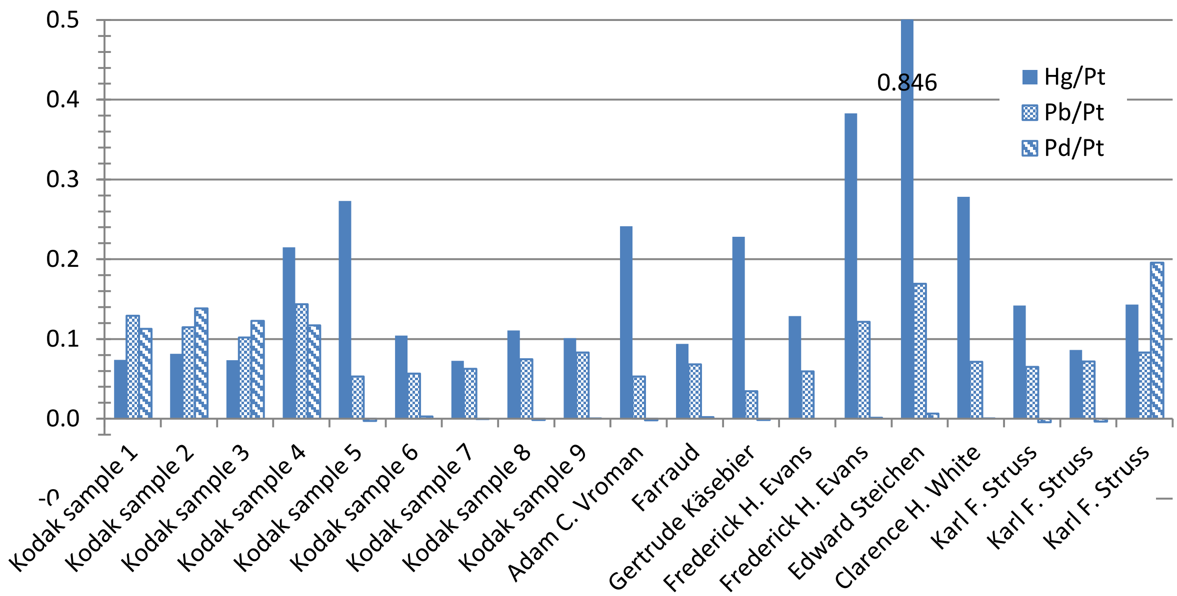


Fig. 9. Mercury-to-Platinum and Lead-to-Platinum Ratios of Kodak Samples and MFAH Platinum Prints: The ratio calculations are based on subtraction of D-max minus D-min of M-α line net counts.

5. DISCUSSION

5.1. POTENTIAL MATCHES

Based on the comparison of elemental composition of image forming material, a few sets of potential matches between MFAH prints and Kodak samples are identified. This comparison is made primarily on the basis of two types of calculations – the relative abundance of mercury to platinum and that of palladium to platinum. XRF is the least subjective analytical technique employed in this research, thus the findings based on XRF is used as the initial parameter to narrow down the search for matching papers. The results of spectrophotometric analysis and surface texture analysis, as well as the information collected during basic survey, such as the date, paper thickness, surface sheen, presence of image burn, and discoloration characteristics are, then compared.

5.1.1. Gertrude Käsebier, *Lucille Thomajon*, ca.1910 (85.82) and Kodak Sample 5, *Etching Sepia, Smooth*, ca.1909

The Hg:Pt value of *Lucille Thomajon* (ca. 1910) by Käsebier is 0.228, which is within the range unique to mercury-sensitized handmade samples. The Kodak samples that share this character are sample 4, *Etching Black, Platinum, Rough* (Hg:Pt = 0.215) and sample 5, *Etching Sepia, Smooth* (Hg:Pt = 0.273). Upon comparison of Pd:Pt values, it is apparent that the Käsebier print does not contain palladium, which is consistent with the sample 5, but not with sample 4.

Spectrophotometric analysis also shows comparable results between the Käsebier print and the Kodak sample 5. There are a number of factors that affect the tone of a platinum print, such as the temperature of developer and the relative humidity of the darkroom. In addition, Käsebier is known to have manipulated materials freely to achieve her artistic vision. Platinum papers were, however, commonly accompanied by specific processing instruction from the manufacturer to achieve the best result, and one assumes that the prints made by Käsebier would have yielded similar tonality to the manufacturer's sample had she wished to do so.

Fig. 8. Gertrude Käsebier, *Lucille Thomajon*, ca.1910 (85.82)

Similarities in surface texture of these two prints may be recognized simply by visual observation. When observed with low angle raking light, the two print surfaces appear very similar; they are smoothest among the study subjects. The sheen is slightly different; Käsebier print appears to have slight sheen (3 out of 5), while sample 5 is dead matte (1 out of 5). The sheen, however, could have been modified by the artist. Comparison of micro-raking images is not possible as neither of the images lack in sufficient highlight area, which is necessary for generating accurate micro-raking image.

The Käsebier print and Kodak sample 5 are also similar based on the information collected during general survey. Although it is not possible to confirm whether or not they are identical papers at this time, this pair may be noted as a possible match for further investigation. One of criteria that may be investigated is presence/absence of image burn on verso of Käsebier print, which is adhered to a mount and currently inaccessible. Kodak sample 5, *Etching Sepia, Smooth* has image burn through to the verso of the sheet, which is unique among all the known Kodak samples. Further examination of XRF spectra, focusing on characterizing factors of the paper substrate itself, such as sizing, may also be beneficial.

5.1.2. Karl Struss, *Nova Scotia*, 1911 (91.1142) and Kodak Sample 7, *Kodak Platinum, Medium, Cream Base*, ca.1909

Among the three prints by Karl Struss, *Nova Scotia* (91.1142) and Kodak sample 7, *Kodak Platinum 1, Medium, Cream Base* share similar characters in all aspects investigated during this study. The relative abundance of mercury to platinum in the Struss print and the Kodak sample 7 are 0.086 and 0.073 respectively, indicating absence of mercury in these prints. Also, the Pd:Pt comparison indicates that neither of the prints contain palladium in image material.

Fig. 9. Karl Struss, *Nova Scotia*, 1911 (91.1142)

The paper surface texture analysis points to their similarity. These are two out of several photographs that have sufficient dimension of highlight areas for micro-raking image capture. Upon the surface-matching test, four out of five participants agree that this pair is a match.

The dates and other physical and visual characteristics are also feasible for the Struss' *Nova Scotia* and Kodak sample 7, *Kodak Platinum 1, Medium, Cream Base* to be a match. Spectrophotometric analysis indicates that they have relatively neutral tonality. Similarities in other characteristics, such as paper thickness, surface sheen, and discoloration pattern are also noted.

5.2. IDENTIFICATION OF MERCURY-SENSITIZED AND MERCURY-DEVELOPED PRINTS

The relative abundance of mercury to platinum in handmade samples yields a unique set of values for mercury-sensitized and mercury-developed samples. The samples that were toned with mercury added to sensitizer only, samples 5, 6, 7, and 8 (mercury in sensitizer) and 13, 14, 15, and 16 (mercury and lead in sensitizer), had Hg:Pt values between 0.2 and 0.3. On the other hand, the samples that were processed with mercury containing developer show much higher Hg:Pt values, ranging between 0.8 and 1.1.

Based on the Hg:Pt ratio of mercury-sensitized and mercury-developed handmade samples, three prints in the MFAH collection may be assumed to be mercury-sensitized and one print to be mercury-developed. *Snake Priest Entering the Kiva* (ca.1902) by Adam Vroman, *Lucille Thomajon* (ca.1910) by Gertrude Käsebier, and *Nude in Forest (Mabel Cramer)* (1909) by Clarence White have the ratio values of 0.241, 0.228, and 0.278 respectively, thus potentially mercury-sensitized. *John Woodruff Simpson* (1903) by Edward Steichen has the ratio value of 0.846, fitting in the range for mercury-developed prints.

Upon identifying mercury-developed platinum prints by Hg:Pt ratio, one should note that this does not excludes the possibility of the photograph having been prepared with mercury containing sensitizer as well as developer. Based on the handmade samples, the prints that are prepared with mercury in both sensitizer and developer have higher net counts of mercury and platinum than the prints with mercury in developer only. Such comparison, however, is possible only when control samples with single variable (mercury-developed and mercury-sensitized-and-developed) are available for comparison, and it may not be a useful method when studying historic prints.

Frederick Evans' *Steps in to Chapter House, Wells Cathedral* (1903) has Hg:Pt value of 0.383. This is the only print that does not fall in one of the three ranges representing no mercury, mercury-sensitized, or mercury-developed, among the ten MFAH platinum prints. There are a number of ways to apply mercury in platinum printing process that were known among the photographers in the early 20th century, and it is easy to assume each processing method would yield different image material composition. In addition, chemical makeup of image material may have shifted overtime. In order to estimate the printing process of Evans' photograph, further investigation that involves fabrication of samples may be considered.

6. CONCLUSION

6.1. COMPARATIVE CHARACTERIZATION OF MFAH PLATINUM PRINTS

Two sets of potential matches are identified between the ten platinum prints in the MFAH collection and the nine Kodak platinum print samples. One of the pairs is *Lucille Thomajon* (ca.1910) (85.82) by Gertrude Käsebier and Kodak sample 5, *Etching Sepia, Smooth* (ca.1909). Among all criteria that are considered, results of XRF analysis, particularly the relative abundance of mercury to platinum in their image material, indicating that they are mercury-sensitized, and absence of palladium, distinguish them from the group. The other pair that is also a close match is *Nova Scotia* (1911) (91.1142) by Karl Struss and Kodak sample 7, *Kodak Platinum 1, Medium, Cream Base* (ca.1909). The main factors considered for nomination of this pair are absence of mercury, absence of palladium, and surface texture.

The above results are by no means definitive, however, each prints may be described to have very similar characteristics to respective Kodak sample. In order to determine whether or not they are actual matches, further investigation of XRF spectra, fiber analysis, and historic literature research regarding the artists' practice should be performed.

During the search for matching papers, a subsequent discovery has been made; mercury-sensitized prints have the mercury to platinum ratio of 0.2 to 0.3, and mercury-developed prints have the ratio of 0.8 to 1.1. Based on these values, *Snake Priest Entering the Kiva* (ca.1902) (79.19) by Adam Vroman, *Lucille Thomajon* (ca.1910) (85.82) by Gertrude Käsebier, and *Nude in Forest (Mabel Cramer)* (1909) (2004.794) by Clarence White are assumed to be mercury-sensitized, and *John Woodruff Simpson* (1903) (2004.669) by Edward Steichen is likely to be mercury-developed.

The ratio values that are associated with the manner of mercury application are calculated using limited number of measurements. Although it appears to be a fair assumption based on the consistency of overall trend, further research to verify the finding is needed.

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