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Pushing the Limits of the Identification of Photographs: Variants of the Gum Dichromate Process

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Abstract:

Advanced methods of non-destructive chemical analysis of photographs have been developed and tested for identification of all major photographic processes used during the era of so called "chemical photography". Using visual and microscopic clues in combination with the identification of inorganic material using X-ray fluorescence spectrometry (XRF) and organic material using attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy (ATR-FTIR) and enzyme-linked immunosorbent assaying (ELISA) allows for highly reliable identification of almost all photographic processes used in the past. Many major photographic processes described in photographic and technical literature had many different variants and modifications introduced by photographers or researchers to achieve certain visual or textural qualities of resulting images or to simplify or speed up darkroom processing. A reliable and clear identification of these process variants is possible only when the resulting photographic images have substantially different chemical composition or a specific image structure characteristic only for a given variant of the photographic process. Photograph conservators as well as collection curators and managers need to know what the current, scientifically based process identification methodology can do and what are its' current limits. Researchers in photographs also need to know the limits of current, non-destructive analytical procedures and which identification questions might be answered by analysis requiring micro-sampling (ELISA). The experimental photographic process album created by the photographer Ted Jones, from the collection of Alex Novak, contains a number of different variants of gum dichromate pigment prints re-created using published historical recipes. The analytical (XRF/ATR-FTIR/ELISA) investigation of all gum dichromate prints in the album that included modified recipes, multiple and tri-color pigment gum photographic prints as well as some special variants of the gum pigment process (glue as gum, gum using acrylic paint, etc.) provided interesting insight into variants of the gum dichromate process and their identification.

Introduction:

In November 2000 the GCI organized an international expert meeting of conservation scientists, photograph conservators, photography art historians and educators working in photograph conservation at the George Eastman House in Rochester. The goal of the expert meeting was to identify several important research ideas that were needed by the photograph conservation field but that were not sufficiently covered by other sister photograph conservation research institutions worldwide. Following the discussion several research ideas were identified as high priority needs that also corresponded well with the existing expertise of GCI scientists and equipment available for the project at the GCI scientific and analytical laboratories. At the end of

the meeting participating experts identified advanced research in the scientifically based identification of photographs, photographic materials and photographic processes as one of the most important research topics needing to be fully developed. Without knowing the photographic processes used when making a given photograph it is very difficult to work out the environmental conditions needed for its long term preservation as well as proper display or exhibition conditions. A detailed knowledge of the process chemistry, its' processing and post-processing treatment and its' potential deterioration pathways are critical in developing strategies for its conservation and preservation treatments.

For this work the GCI began developing a methodology and assembling a portable scientific laboratory (fig. 1), composed of a digital microscope, UV lamp, micrometer, caliper, XRF, ATR-FTIR and several computers, that could be moved between collections to identify and analyze examples of various photographic processes and materials (Stulik 2005). The portable laboratory is already in its third iteration and is constantly being upgraded with well tested and rugged portable instruments. One of the major goals of the project was to publish an *Atlas of Analytical Signatures of Photographic Processes* that would document the analytical signatures (microscopy, XRF, FTIR, SEM) of all of the processes and process variants of the chemical photography era. When work began on documenting the analytical signatures of historic photographic processes it quickly became clear that the identification of well characterized and well identified examples of all photographic processes would be a significant hurdle. Most photographic material in museums, archives, libraries and private collections is not well identified and in some cases incorrectly identified. Since the beginning of the project the GCI photo project team has contacted a large number of collections of photographs regarding access to examples of unique and often difficult to find and identify photographic processes.

Fig. 1. The GCI portable scientific laboratory.

In 2008 a frequent collaborator of our project, the photography dealer Alex Novak, contacted us in regards to a process album he had obtained from his friend, photographer Ted Jones. Jones spent a significant portion of his career working in TV production, editing, producing and directing various shows and received numerous awards for his work. In 1977, Jones began freelancing making videos, films and photographs. His photographic work focused on 19th century non-silver photographic processes with a particular focus on the gum dichromate process. A retrospective traveling show of his gum dichromate prints was exhibited throughout Scandinavia during a two year period and his photographs are in the collections of the St. Louis Art Museum, the University of New Mexico Art Museum and the James A. Michener Museum of Art. Jones passed away quietly at his home in August of 2007.

The Jones process album was created in the early 2000s and is composed of 43 prints all made using different photographic processes. The process used to create each print is described in the text accompanying the album with the amount of information ranging from only a reference to the published recipe to having a complete list of chemicals, processing steps and materials used to create a particular print. Of particular interest to us were 10 variants of the gum dichromate process (Table 1) that were included in the album and created using historical recipes (Maskell and Demachy 1897; Eastman Kodak 1898; Richards 1905; Scopick 1978; James 2000). These examples were ideal for inclusion in the Atlas of Analytical Signatures of Photographic Processes.

Inventory Number	Process Description
TPB001	Demachy gum process
TPB002	Multiple gum printing
TPB003	Gum printing in color (three color)
TPB004	Albumen-gum dichromate process (Renger-Patzet 1904)
TPB005	Gum process (Sawyer 1933)
TPB006	Gum dichromate (Richard's process 1896)
TPB007	Photo aquatint (Demachy postscript)
TPB026	Casein printing
TPB028	Glue as gum
TPB033	Gum using acrylic as pigment

Table 1. Inventory of gum dichromate process variants in the process album of Ted Jones.

The gum dichromate process is very flexible and two individuals producing prints using the exact same recipe can achieve very different results, primarily because the process relies on the hand coating of paper and the personal pigment preparation and application technique of the artist. The development of the print can also greatly affect its appearance and analytical signature depending on the water temperature, length of development and the use of localized development. This inevitably results in a non-uniform application of material to the paper and as such the quantitative analytical results are expected to vary even between two examples of the exact same process created by the same individual.

Each print was analyzed using XRF, ATR-FTIR and ELISA in an attempt to identify all of the inorganic elements and organic components of each print as well as to determine the capabilities

of the methodology and instrumentation in differentiating variants of the gum dichromate process.

Determination of Elemental Composition Using X-ray fluorescence Spectroscopy:

X-ray fluorescence spectroscopy (XRF) is a non-destructive, non-contact technique that is often used in photograph conservation to determine the elemental composition of a photograph and its support. The technique makes use of the ability of high energy x-rays to ionize atoms by the ejection of inner shell electrons from the sample being analyzed. As the excited atoms de-excite they generate fluorescence x-rays which are then detected by the instrument and sorted based on their energies. The energies of the fluorescence x-rays are characteristic of the particular elements in the sample and can provide both qualitative and quantitative data. XRF analysis has been widely used in the study of cultural heritage primarily due to its portability, ability to perform non-destructive/non-contact analysis, and ability to provide elemental information on all elements in the periodic table with an atomic number greater than sodium (Potts and West 2008; Stulik and Kaplan 2012). Numerous studies of photographs and photographic materials related to authentication, provenance, identification and artist techniques have been performed using XRF analysis (McCabe 1995; Stulik 2008, 2011; Grieten 2010; Stulik and Kaplan 2012).

The XRF analysis of the gum dichromate pigment prints in the Ted Jones album was performed using a Bruker Tracer III-V air path portable XRF spectrometer with an approximately 1 cm spot size, with a Rhenium x-ray tube, Si-PIN detector, and a Yttrium foil internal standard. All analyses were carried out using an Al/Cu primary beam x-ray filter, operating at 40 kV and 15 μA for 300 dead time corrected seconds at a distance of approximately 3 mm from the sample. To obtain information on the presence of elements with an atomic number lower than potassium the analyses were performed with a vacuum attachment, without an x-ray filter, operating at 15 kV and 12 μA for 300 dead time corrected seconds at a distance of approximately 3 mm. Each print was analyzed in the maximum image density area (D-max) and minimum image density areas (D-min), both in the ambient environment and under vacuum, in order to identify the elements present and their location in the print (image area, paper support, or both).

The goal of the XRF analysis was to identify any elemental differences between the different variants of the gum dichromate process present in the album including detection of chromium from the sensitizer or other sources, detection of any fillers, buffers or opacifiers in the paper base, identification of any additional inorganic elements added during the processing of the prints, any inorganic pigments used, and to identify any elements present in the prints that are inconsistent with the historical recipes.

The major differences between the different variants of the gum dichromate process present in this album primarily have to do with differences in the concentration of the sensitizer, the choice of ammonium or potassium dichromate, the amount of gum arabic and pigment used, with the one exception being the Renger-Patzet variant which utilizes manganese sulfate in the sensitizer (Wall 1931).

The typical XRF spectrum for a gum dichromate print (TPB001) showing analysis of both the D-min and D-max areas is shown in figure 2. The print was created using Robert Demachy's

French formula (Eastman Kodak 1898) and utilizing an unknown pigment. Elements detected include calcium, titanium, chromium, manganese and iron. When comparing the spectra for both the D-max and D-min areas it is observed that the levels of calcium, chromium, manganese and iron are significantly higher in the higher density image areas of the print while the amount of titanium detected is lower in the D-max area of the image. From this information we can state that the titanium is from the paper substrate, most likely as titanium dioxide (TiO_2) whitener in the paper. While the presence of calcium, chromium, manganese and iron are all from the image areas. The most likely source of calcium, manganese and iron is from the pigment used to create the print, most likely umber, a brown toned pigment composed of manganese and iron oxides which may also contain other material such as calcite or silicate (Eastaugh et al. 2008). The higher titanium signal in the D-min area of the print is due to the fact that there is less material between the paper base and the instrument to attenuate the titanium signal from the paper.

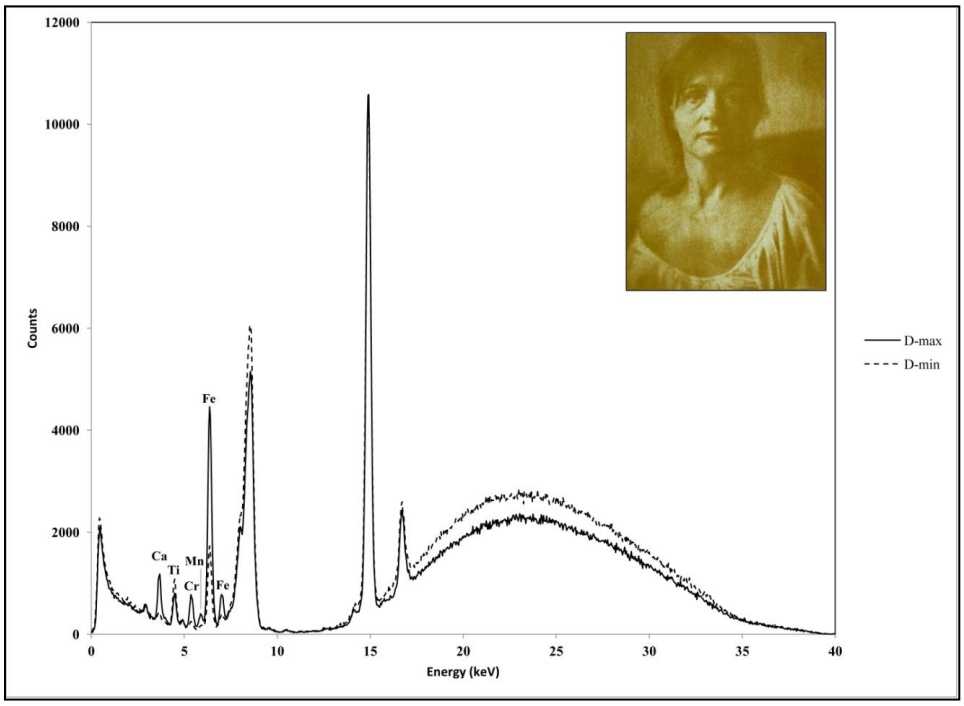

Fig. 2. XRF analysis of the D-max and D-min areas of print TPB001.

The chromium is present from the dichromate in the sensitizer. There are other possible sources of chromium that could account for its presence either as a pigment or as a hardener (chrome alum) in the sizing of the paper. In order to compare the chromium signal from gum dichromate prints created using a chromium based pigment as opposed to those where the sensitizer is the only source of chromium we compared the XRF analysis from the Sawyer variant print of the gum dichromate process in the album, which was created using a chrome oxide pigment, to the chromium signal from the other 9 variants in the album, none of which utilized any chromium based pigments. The analysis of chromium in the 9 prints where the sensitizer and possible sizing agent were the only sources of chromium found that the peak area for Cr Kα ranged from 1741 to 8648 counts while the peak area for the Cr Kα in the Sawyer process gum print using a chrome oxide pigment was found to be 20041, a value two and a half times that of the highest chromium signal observed for any of the other prints. From this comparison it can be seen that

the signal observed for chromium in chromium pigment based prints is significantly higher than when the sensitizer and sizing agent are the only sources of the chromium signal. An exception to this may be seen with pigment processes where a very small amount of chromium based pigment was used, e.g., mixed with other pigments in order to create a specific hue in a particular layer or in a layer containing a very small amount of chromium based pigment to enhance particular image details or for other aesthetic reasons.

In researching the historical recipes for the 10 variants in the album it became clear that the only print exhibiting any changes in the elemental composition, excluding pigments, in its recipe was the Renger-Patzet (TPB004) variant. The recipe for the variant calls for the addition of manganese sulfate to the sensitizer. The process claimed to be an improvement over the gum dichromate process especially in the rendering of half-tones (Wall 1931). The recipe calls for the use of 5 grams of manganese sulfate in 12 mL of sensitizer, a relatively small amount of manganese. Figure 3 shows the XRF spectrum for the print analyzed in both the D-min and D-max areas and the detection of the manganese signal. The manganese signal is low but is still well above background to be able to positively identify its presence and suggest the possibility that the print may be the Renger-Patzet version of the gum dichromate process. One caution in regards to this interpretation is that in addition to the presence of manganese in the sensitizer there are also a number of manganese based pigments (Eastaugh et al. 2008) that could have been used. Since the manganese is carried in the gum layer of the image it's XRF signal varies with the thickness of the gum layer which can lead to difficult interpretation problems, in particular that the XRF signal would behave the same as it would for a manganese based pigment in that the amount detected varies in proportion to the amount of gum and therefore pigment in the layer. In this case the artist listed bone black as being the pigment he used and so we know that the only likely source of the manganese signal is from the manganese sulfate in the sensitizer.

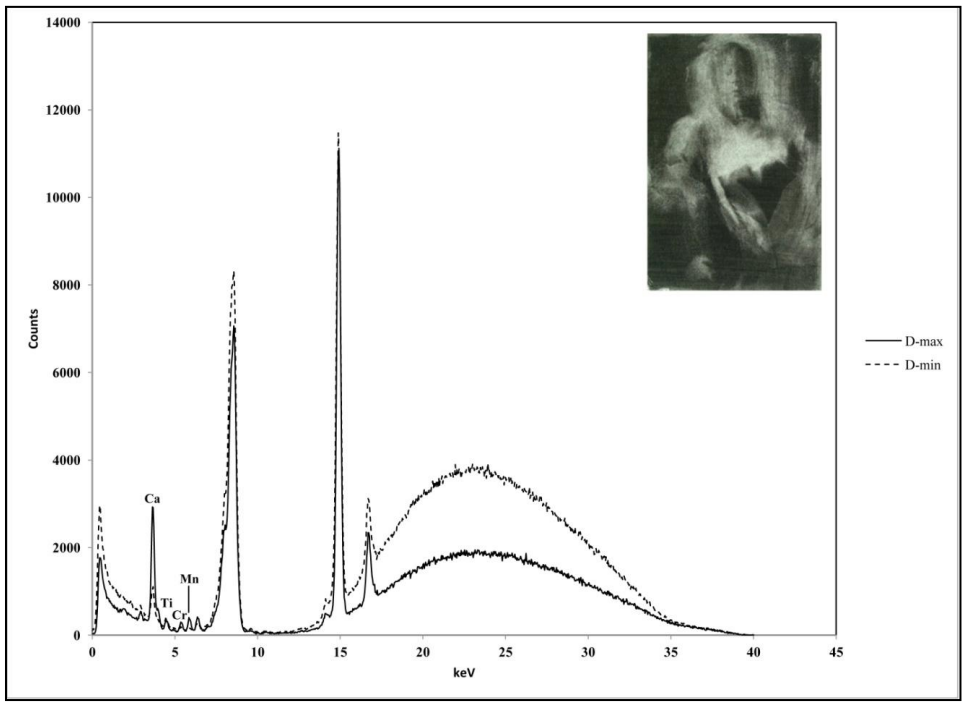

Fig. 3. XRF spectrum of the analysis of the D-max and D-min areas of TPB004.

One of the most useful aspects in using XRF to analyze gum dichromate prints, or any pigment prints, is the ability to identify inorganic pigments in the prints and provide information as to the prints long term stability and aid curators, conservators, archivists and collectors in determining proper storage and exhibition conditions for the print. It has long been known that pigments vary greatly in terms of their light stability and environmental susceptibility and as such it is critical to properly identify the pigments used to create the prints in order to properly exhibit, conserve and store them without causing any damage.

Of the ten prints in the album eight of them had the pigments used to create the prints listed (Table 2). Because some of the variants in the album where from multiple printings the number of pigments actually described was 13 with 2 of the pigments used not identified. Of the pigments listed 3 were organic and undetectable using XRF analysis while 2 others were described but the manufacturer did not provide any information as to their composition and XRF analysis did not detect any inorganic components.

Inventory Number	Manufacturer	Pigment Used	Elements ID'd
TPB001	None listed	None listed	Fe, Mn
TPB002	Winsor & Newton	Cadmium red deep	Cd, S, Se
	Winsor & Newton	Golden yellow	Cd, S, Se
TPB003	Grumbacher	Cadmium red light	Cd, S
	Winsor & Newton	Golden yellow	Cd, S
	None listed	Rembrandt blue	None
TPB004	None listed	Bone black	Ca, P
TPB005	Winsor & Newton	Chrome oxide	Cr
TPB006	None listed	None listed	None
TPB007	Van Gogh	Permanent red light	None
TPB026	Winsor & Newton	Spectrum red	None
	Winsor & Newton	Permanent yellow deep	None
TPB028	Winsor & Newton	Chinese orange	None
TPB033	Utrecht	Acrylic red oxide	Fe
	Utrecht	Gold ochre yellow	Fe

Table 2. XRF identification of pigments in gum dichromate prints

The XRF analysis confirmed the presence of four cadmium based pigments, both in the form of cadmium sulfide, a yellow colored pigment, cadmium selenide, a red colored pigment, and cadmium sulfoselenide, a mixture of the two, which can vary in color from yellow to orange to red, and is identified by the presence of cadmium, sulfur and selenium in the spectrum.

The XRF analysis was able to confirm the presence of iron based pigments in two of the prints and also identified an iron and manganese based pigment, possibly umber, used to create one of the images (TPB001) for which no pigment was listed. The identification of bone black pigment in TPB004 was confirmed by the detection of elevated calcium and phosphorous in the D-max area of the spectrum obtained under vacuum as compared to analysis of the D-min area (Fig. 4).

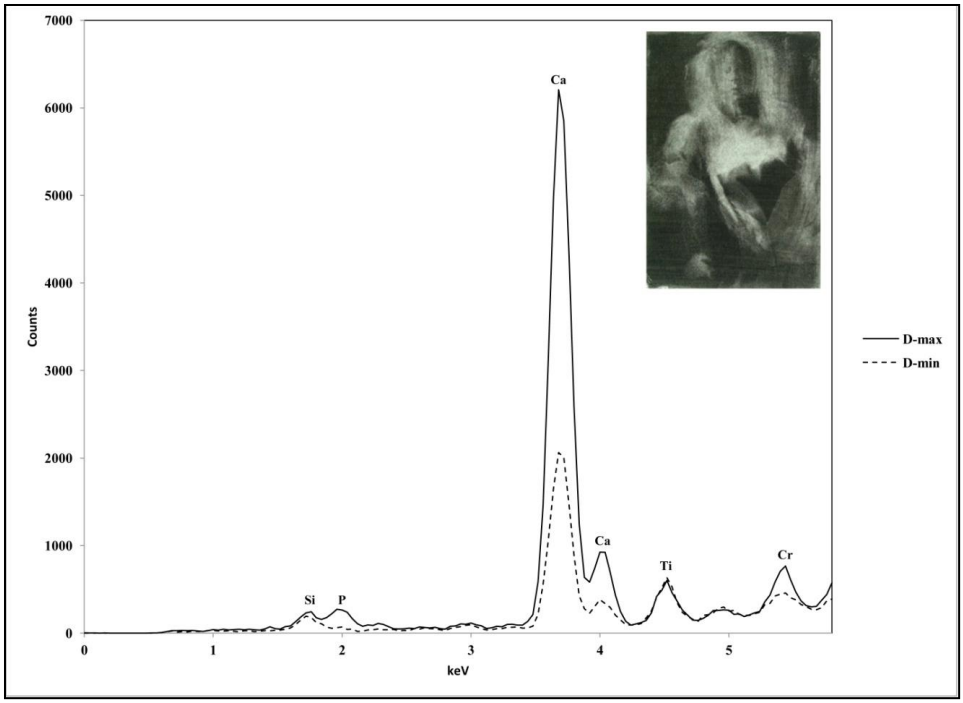

Fig. 4. XRF analysis using vacuum to identify low Z elements in the D-max and D-min areas of TPB004.

Identification of Organic Components by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy:

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) is an important tool in the examination of historic art materials. The technique provides information about the bonding features between atoms or functional groups in a molecule and can also provide important information about chemical changes in a sample following aging or chemical treatment through the appearance of new bands, band shifts or changes in the intensity of existing bands in the spectrum. The technique is ideal for the study of museum objects because it requires no sampling or sample preparation and is an ideal complement to XRF analysis in the study of photographs and photographic materials because it can provide objective analytical information on the presence of organic materials in the photographic support, binders in the image layer and coatings and varnishes that may have been applied to a photograph print, film or negative post processing (Derrick et al 1999; Khanjian and Stulik 2003).

The technique makes use of the ability of infrared radiation to cause rotational, translational and vibrational motion within molecules. As the infrared radiation is absorbed by the sample the instrument generates a spectrum depicting the absorbance or transmittance of the sample versus the wavelength or wavenumber. The spectrum for a particular molecule is unique and is often called a “fingerprint”. Unknown materials can be matched against a spectral library of well know and well characterized materials to identify it. This can be done because the position of particular absorption bands in a spectrum are often unique to particular functional groups and occur at or near the same wavelength regardless of the composition of the material.

All of the prints from the Jones album were analyzed using a SensIR *TravelIR* ATR-FTIR, with a HeNe laser, DTGS detector and a single bounce diamond crystal mounted on a stainless steel DuraDisk. The instrument performs 64 scans at a 4 cm^{-1} resolution through a spectral range of 4000 to 650 cm^{-1}. The results were matched against a custom built library created from the analysis of over 15,000 photographs and photograph components.

The identification of gum dichromate prints using ATR-FTIR analysis has one significant deficiency and that is the composition of the gum arabic. Gum arabic, or acacia gum, is a natural plant gum harvested in Africa and Western Asia. Gum arabic is a polysaccharide composed of long-chain polymers of sugars and falls into the same group of molecules as cellulose, a monosaccharide and the primary component of most papers. As such the ATR-FTIR spectrum of gum arabic and cellulose are very similar, both exhibit two broad bands at ~1000 and ~3300 cm^{-1} along with a band at ~1300 cm^{-1} and ~1625 cm^{-1}, (Fig. 5) and it can be easy to mistake one for the other, the one significant difference being that the ~1625 cm^{-1} peak is typically more pronounced in gum as opposed to cellulose but this can vary depending on the particular sample. Although difficult it may still be possible to differentiate the spectra of cellulose and gum arabic by either looking at differences in some of the minor bands in the sample or, in the case of gum dichromate prints, comparing the spectrum of the image area to the spectrum of the paper base to see if they differ (Fig. 6). Unfortunately, in most cases, the spectrum of gum arabic prints and the paper material on which they sit are almost identical, with the exception of a situation in which a sized paper was used where the amount of sizing agent was high enough to be detected by ATR-FTIR thereby providing some indication of a difference in composition between the paper and the image layer. Any differences would most likely be minor and it is important not to over-interpret the spectrum and mistake something like sizing in the paper for some indication of a particular photographic process. This can be additionally difficult because the 1625 cm^{-1} peak for gum arabic and cellulose overlaps the Amide I protein peak (~1650 cm^{-1}) that is present in gelatin and albumen photographs as well as in protein sized paper.

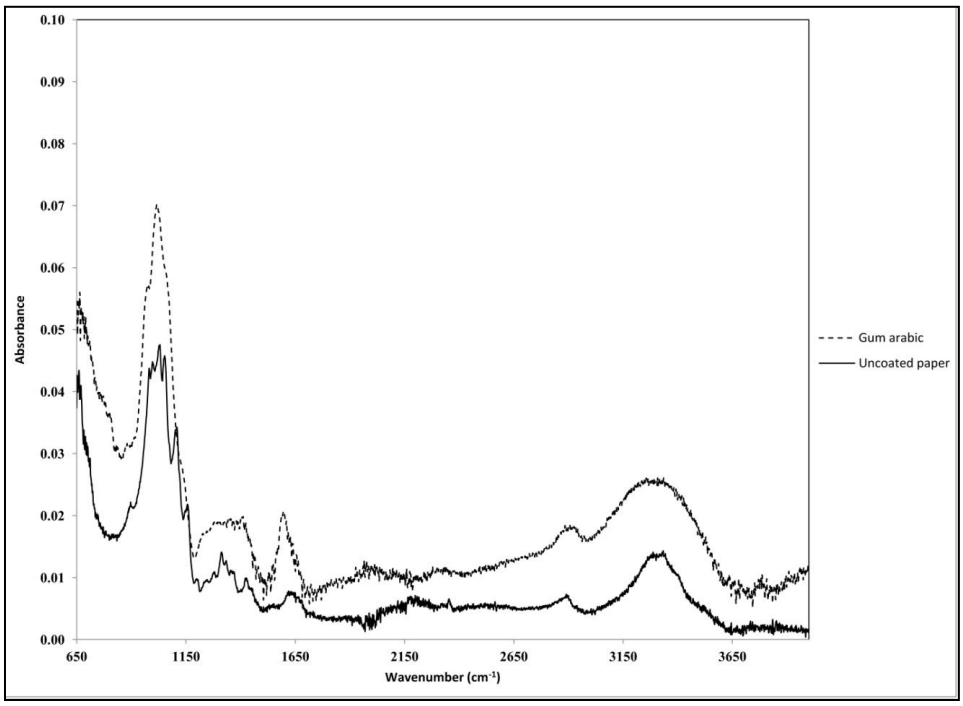

Fig. 5. FTIR spectrum showing the analysis of gum arabic and plain paper.

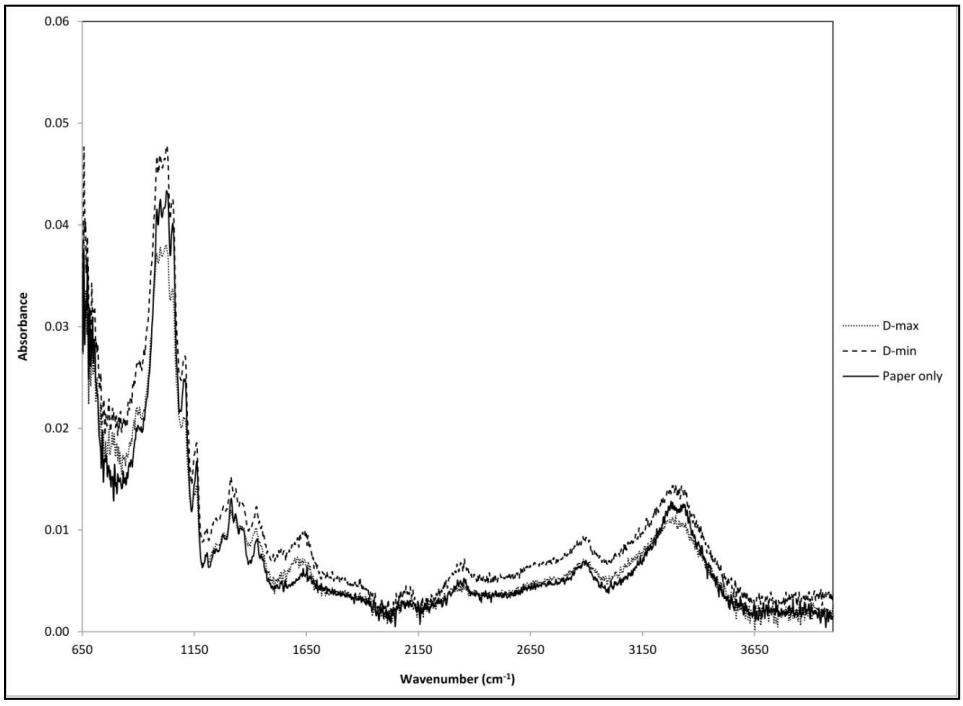

Fig. 6. FTIR spectrum of the D-max, D-min and paper only areas of print TPB001.

Several variants of the gum dichromate process that were included in the Jones album were of particular interest to us in testing the limitations of our instrumentation and methodology. Among these were the Renger-Patzet albumen gum dichromate process (TPB004) and the glue as gum (TPB028) variant. Figure 7 shows the ATR-FTIR spectrum of TPB004 and the Amide I (1633 cm^{-1}) and Amide II (1537 cm^{-1}) peaks are clearly visible along with the 1021 cm^{-1} peak. Only the 1537 cm^{-1} gives any indication that the material being investigated is something other than cellulose or gum, since we know the variant used to create the print we can clearly identify the peak as being the Amide II peak of the albumen protein. However without this additional information there is nothing in the spectrum alone that would lead one to suspect that the print was created utilizing gum dichromate unless you had additional information (e.g., XRF detection of chromium, ELISA detection of plant gum) from other analyses.

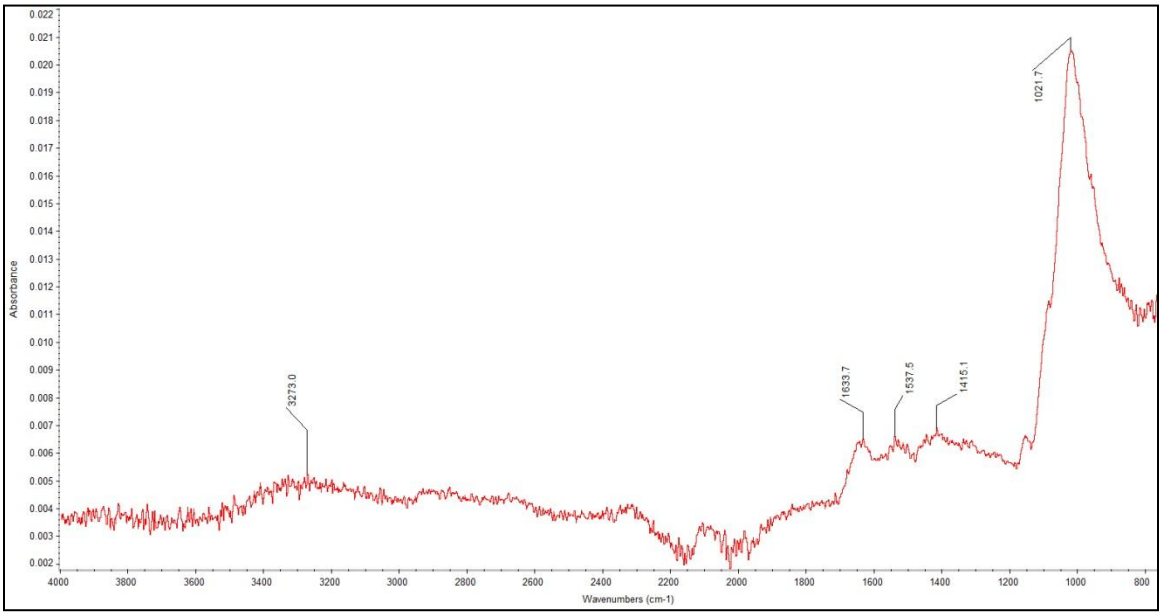

Fig. 7. ATR-FTIR spectrum of the albumen-gum dichromate print (TPB004).

The ATR-FTIR analysis of print TPB028 (Fig. 8) illustrates the importance of building comprehensive spectral libraries. The print is the glue as gum variant of the gum dichromate process and has no gum arabic, rather the pigment is mixed with animal glue and potassium dichromate before exposure. The XRF spectrum clearly shows the presence of chromium and can lead one, based on visual and microscopic examination, along with XRF analysis to identify it as being gum dichromate, carbon or some other photographic process based on the ability of dichromate to harden organic colloids upon exposure to light. Fortunately for us the artist listed the specific adhesive he used for the glue component of the print, Lineco adhesive, which we were able to acquire. From the ATR-FTIR spectrum we can see that all of the spectral peaks from the adhesive are also clearly visible, at the same position with changes in intensity, in the analysis of the print. This example clearly illustrates the benefit of having a comprehensive spectral library of materials as well as a comprehensive analytical methodology for the analysis of photographs and photographic materials.

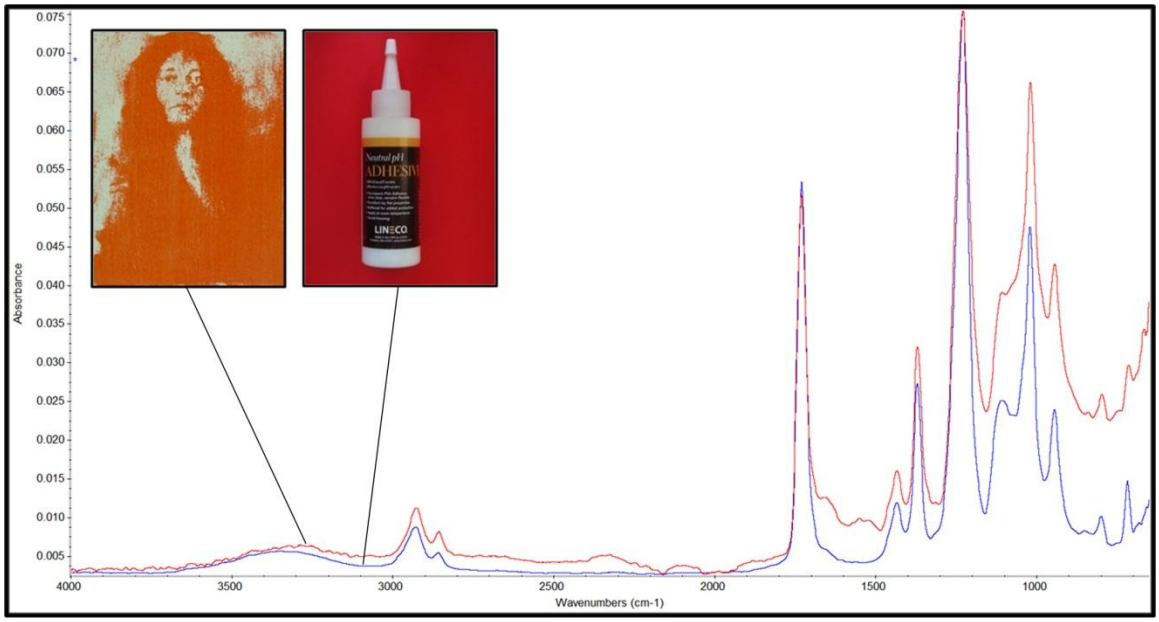

Fig. 8. ATR-FTIR spectrum of a glue as gum print (TPB028) and the glue alone.

Identification of Gum Arabic in Photographs by Enzyme-Linked Immunosorbent Assay:

Enzyme-linked immunosorbent assaying (ELISA) is a technique used for detecting and quantifying the amount of various substances (proteins, antibodies, hormones, etc.) in a sample. The technique is able to identify and quantify a number of substances used in photographic processes including albumen, casein and plant gums (Mazurek 2008, 2010). The technique works by using antibodies specific to the substance of interest, which are bound in the wells of a microplate. Once sampled, the substance being investigated will bind to the antibodies on the plate and the bound sample-antibody complex with either directly cause a color change in the solution or a secondary antibody is added that binds to the sample-antibody complex and causes a color change. The absorbance of the solution is then measured at an appropriate wavelength using a UV-Vis spectrophotometer. The color change is compared to a series of standard solutions to determine if the solution contains the substance of interest. The amount of substance present in solution can be determined based on the absorbance of the solution as compared to the absorbance of standard solutions. ELISA was used to test the prints in the album in order to identify the presence of gum arabic as well as to test the application of the technique for use in the identification of variants of the gum dichromate process through the detection of albumen and casein as well as to test the methodology for possible false positives from the improper binding of antibodies to other materials.

For the analysis a dry cotton applicator was used to swab the surface of a photograph. Dry swabbing works because the typical surface of a gum dichromate photograph has no coating and the gum arabic is exposed and fragile enough that lightly dragging something across the surface of the print removes material. Swabbing the surface of the photograph with a dry swab and very light pressure, similar to dusting, can remove enough material for analysis yet leaves no visible evidence of the sampling. The swabbed sample was then prepared and analyzed using ELISA. The detection limits for gum arabic are typically in the range of ~1 ng/ml but vary based on the

manufacturer of the product. Because the amount of material removed from the surface varies based on several factors (pressure applied during swabbing, surface condition, gum arabic concentration, etc.) quantitative results are not possible unless the amount of material removed can be standardized. A negative result is not a confirmation that there is no gum arabic in the photograph rather the amount of material removed during the dry swab procedure may not contain enough gum arabic to obtain a positive result.

For the ELISA analysis each sample was swabbed and tested for casein, albumen and plant gum in order to confirm the presence of gum and to identify evidence of possible variants of the gum dichromate process in the cases of TPB004 and TPB028. After swabbing all visible sample material was removed while keeping the amount of cotton removed from the swab to a minimum. The samples were prepared for analysis according to Mazurek (2010). The absorbance of each solution was measured at 405 nm using a Finstruments model 341 microplate spectrophotometer.

The results from the analysis are shown in figure 9. A positive result is one where the absorbance of the solution is above 0.3, a value well above what was measured for the blank. Each of the prints tested positive for the presence of plant gum with the exception being TPB028 which came in just below the cutoff for a positive test. TPB028 is the glue as gum variant of the gum dichromate process and uses no gum arabic. The elevated signal for the presence of gum arabic may be due to some cross contamination during the ELISA procedure from other samples or it may be due to something else in the sample that could lead to a false positive for plant gum. One additional aspect of the ELISA analysis of TPB028 was that it also came close to testing positive for the presence of casein. This should not be unexpected since this print contains pigment mixed with glue as opposed to gum. Casein based adhesives exist and have been used in everything from wood glues, canvas sizing and pigment binding (Tracton 2006). This close positive may be an indication that some component of the glue may be close in structure to what the antibody used typically binds to in plant gums. Further evidence to suggest the possibility of this "improper" binding of the antibody to the incorrect target molecule is that the antibody itself doesn't exhibit strong specificity to gum arabic but rather binds to a whole range of plant gums (Mazurek 2008) thereby increasing the likelihood of false positives.

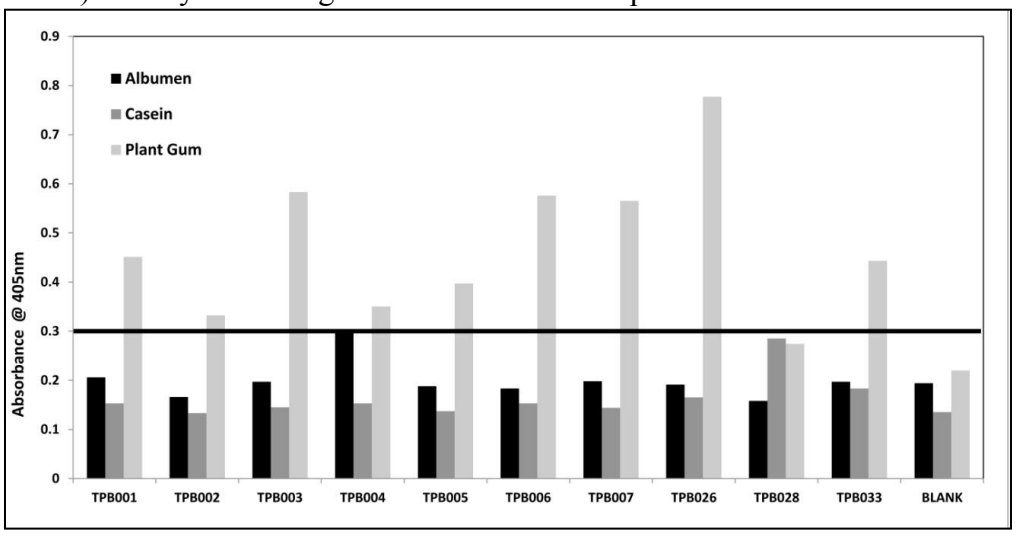

Fig. 9. Results of ELISA analysis for the gum dichromate variants in the album.

The other variant of the gum dichromate process that was interesting to test using ELISA was TPB004, the Renger-Patzet albumen-gum print. TPB004 tested positive for the presence of both plant gum and albumen which would indicate that the dry swab sampling was able to remove enough gum and albumen from the surface of the print for the ELISA analysis to detect both.

The greatest advantage of ELISA as opposed to ATR-FTIR analysis is in the fact that unlike ATR-FTIR which has a hard time positively identifying the presence of gum arabic in a gum dichromate print because of the similarities in the spectrum to cellulose, ELISA analysis can positively confirm the presence of a plant gum in the print, making it a useful tool when either confirmation of FTIR results are desired or if positive identification using other methods aren't possible.

Conclusion

The identification of gum dichromate prints using noninvasive analysis works well when identifying gum dichromate prints in general but the identification of different process variants requires the existence of clear chemical signatures (markers) that are unique for a given variant of the process. XRF analysis is a particularly useful tool when analyzing the majority of inorganic pigments that contain heavier chemical elements (e.g., different variants of cadmium pigments). Vacuum XRF even allows one to differentiate between lamp black and bone black pigments based on the detection of phosphorous and calcium in the pigment. The absence of metal elements in an XRF spectrum of color monochrome or tri-color pigment prints clearly indicates the use of organic pigments or dyes. In the analysis of the Ted Jones album confirmation or identification of 9 out of the 15 pigment used was possible and the presence of chromium was identified in each of the prints where it was present.

FTIR analysis can provide information on organic binders and coatings or varnishes present in many photographic processes as well as chemical changes that may occur due to aging or chemical treatment of a photograph. Analysis of all the prints in the Ted Jones album using ATR-FTIR showed that regardless of the variant of the gum dichromate process used all of the ATR-FTIR spectra were very similar with the one exception being the albumen-gum variant which had some indication of protein being present, however the amount detected was so low that it was difficult to determine the source (e.g., binder, paper sizing, etc.). FTIR detection of gum arabic is complicated by the fact that both gum arabic and the paper substrate contain polysaccharide backbones.

In cases where the identification of the presence of gum arabic as part of the photographic process is found to be critical and sampling of the material has been authorized other analytical techniques can be used. One such analytical technique is ELISA and it requires minimum sampling due to its high sensitivity. Utilizing a cotton swab and extremely gentle pressure we were able to remove enough material to positively identify the presence of plant gum in all of the samples in the album where it was used. We were also able to show that the analysis of certain variants of the gum dichromate process may benefit from the use of virtually nondestructive ELISA testing for the detection of gum, glue, casein or albumen when used as a pigment binder. The establishment of a more consistent sampling procedure that could also determine the mass of material removed would be a necessary step for the use of ELISA for quantitative analysis.

Since 2000, the development of an objective scientifically based methodology for the identification of photographic processes and materials has been a focus of the GCI photo project team. In order to achieve this goal the GCI team assembled a portable laboratory of non-destructive scientific equipment. While the laboratory was a great start its capabilities, along with the developing methodology, could not be fully tested without having the proper material to analyze and it quickly became clear that the existence of well characterized and accurately described photographs are rare in collections. The photographic process album of Ted Jones was an ideal example of well characterized and described photographs that served as a test case to examine the capabilities of the GCI's constantly evolving portable laboratory and to provide some insight into the identification of numerous variants of the gum dichromate process. The scientific investigation of the album also demonstrated the strong advantages of a comprehensive scientific investigation of photographic prints in order to gain a more complete understanding of the composition of a particular print. Our future collaborative work with current alternative process photographers (Stulik and Kaplan 2010) working and experimenting with different pigment dichromate processes will be very beneficial to conservation scientists when pushing the envelope of current limits of the identification of pigment process variants.

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