Nondestructive Analysis of Historic Photographs

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Salted Paper Prints

Salt prints were the first negative-to-positive photographic technique. Introduced by William Henry Fox Talbot in 1839, it was the process from which most nineteenth- and twentieth-century photographic formats were derived. Salt prints found in the libraries, archives, and museums at Harvard University include some of the earliest photographic images created.

The Weissman Preservation Center (WPC) has undertaken a university-wide project to preserve and enhance access to salt prints at Harvard. To date over 15,000 salt prints have been located in twelve repositories.

"Articles of China" William Henry Fox Talbot, Salted Paper Print, ca 1844 Harvard Art Museum

The salted paper process is a printed-out process, which means that the image is created from a sensitized paper exposed to the sunlight, with no chemical development. There are many variations on the salted paper print process leading to a diverse range of visual characteristics.

To make a salted paper print in its simplest form, a solution of table salt (NaCl) was applied to a piece of fine writing paper and dried. The application of a sensitizing solution of silver nitrate ($AgNO_3$) produced silver chloride (AgCl), a light sensitive compound. Upon exposure to sunlight silver nanoparticles will form creating an image. The image then needed to be fixed by washing off the unexposed silver chloride with water and fixing the image with sodium thiosulfate.

Coatings

Photographers often coated their salted paper prints. The application of a transparent medium to the surface of the print served both a protective and aesthetic function. Even in the 19th century, salted paper prints were known for their sensitivity to light, humidity, temperature, and pollutants. Characterization of photographic coatings is an important tool for dating and identifying individual photographs, contributing new scholarship to our understanding of the history of photography and making preservation decisions. Correct identification of coatings, which are sometimes be misleading to even a highly trained eye, can thus aid in determining suitable conservation treatment approaches as well as indicate possible deterioration tendencies particular to each coating material.

Gen. Louis [sic] Wallace, Lew Wallace, Author of Ben Hur Harvard Fine Arts Library, Special Collections, 1861-1865

Harvard Class Albums

HUD 253.705, Harvard University Archives.

About 8,000 salt prints are contained in 75 historic class albums dating from 1853 to 1864 in the Harvard University Archives. The use of class albums at Harvard began in 1852, when John Adams Whipple, made 85 daguerreotypes of the class of 1852. The class albums containing salted paper prints were produced annually over a period of 13 years by three prominent Boston photographers; John Adams Whipple, James Wallace Black and George Kendall Warren. Interestingly, the salted paper process was used continuously by these photographers until 1864, which extends the acceptable dates for salt prints well past the mid-1850s and well into the albumen era.

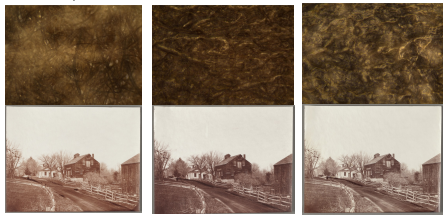
1852 daguerreotypes 1853 1854 1855 1856 1857

Dilute Albumen Prints

Use of the salted paper print process was for a time contemporaneous with albumen prints. The two processes had many variations and could produce prints with similar appearance making correct identification a challenge. Developing non-destructive non-sampling analytical methods for the correct identification of the photographic process used is an important for understanding the process development and for making preservation decisions.

In the Harvard survey, prints with a single layer (including those with additional sizing or coating) were identified as salted paper prints and prints with an albumen binder or so-called emulsion layer were identified as albumen prints. The dilute albumen transitional period has been hard to identify by eye and is a topic of interest and research for conservators, conservation scientists, and curators.

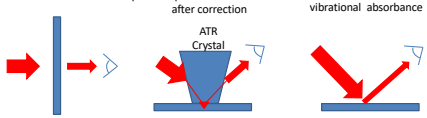
Salted Paper Print | Dilute Albumen Print | Albumen Emulsion Print

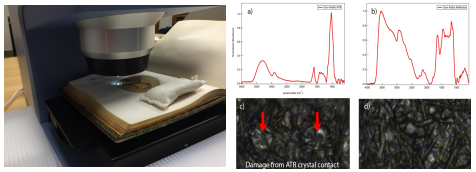


Specular Reflection FTIR

Fourier Transform Infrared (FTIR) spectroscopy is a vibrational spectroscopy technique that provides molecular information about the sample. It can be performed in several different modalities. Specular reflection has been an unpopular mode as the spectra are harder to interpret. Due to its unpopularity as a technique there are few specular reflection FTIR spectral reference libraries. Never the less specular reflection FTIR has the distinct advantage of being a totally non-contact and non-sampling method of chemical identification.

Transmission	Attenuated Total Reflection (ATR)	Specular Reflection
Sample must be thin enough to be transmissive	Contact must be made with object Spectra equivalent to transmission after correction	Signal is convolved reflectivity and molecular vibrational absorbance



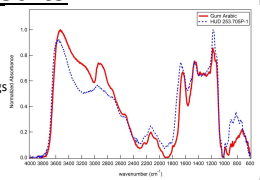


A specular reflection FTIR spectral reference library needed to be created. Reference prints with different coatings were created with a 100% cotton paper and following a historically accurate recipe edited by Mark Osterman. Based on a literature review, the most common nineteenth-century coatings were found to be: bees wax, white wax, gum Arabic, dextrin, albumen, gelatin, casein, dammar, sandarac, shellac, and Canada balsam. To address the issues of how different aging conditions may affect the spectra, two reference sets were made and aged under different conditions. One set was aged outdoors for two weeks (New England sea shore in August) The second set was aged in accelerated aging ovens at the Image Permanence Institute under high humidity testing conditions: 77 degrees F and 85% RH for 4 weeks.

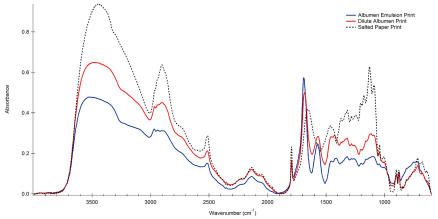
Results

Spectral library matches between the modern reference samples and the historic photographs in the class albums were good providing positive chemical identification of the coatings that were used.

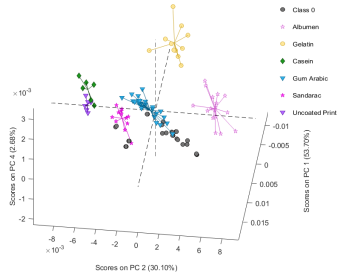
The only data process was a baseline correction to avoid unintentional artifacts and to aid in ease of use of the spectral library.



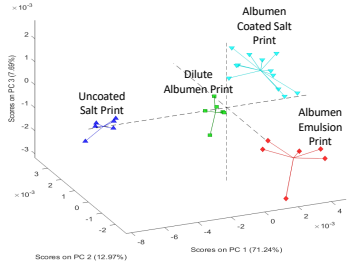
The spectral library correlation search algorithm struggled with differentiating dilute albumen and albumen emulsion prints.



Principal Component Analysis



Applying PCA to the specular reflection FTIR data allows us to use more of the information collected in the spectra. The unknown coatings from the Harvard class albums (Class 0 below) cluster nicely with the spectra from our modern spectral reference library.

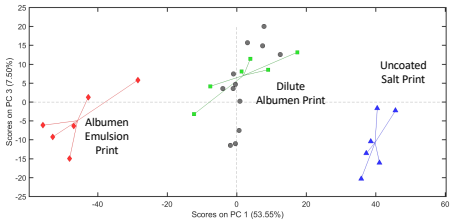


While the spectral library struggled with distinguishing the dilute albumen and the albumen emulsion samples, the PCA model seems to clearly differentiate between the spectra from known modern samples.

James Robertson
AKP045 Rob.P.002,
Fine Arts Library

Theodore Leeuw
AKP 139 Tas.C003,
Fine Arts Library

Suspected historic dilute albumen prints were selected from the Harvard Fine Arts Library collection to test the PCA model. The spectra from the historic samples (grey circles) clustered nicely with the modern dilute albumen spectra in the principal component plot.



Conclusions

Specular refection FTIR is a non-contact non-sampling analytical method for positive chemical identification on cultural objects. A spectral reference library appropriate for coated salt prints on cotton paper was built and was used for positive chemical identification of unknown coatings on the salted paper prints in the Harvard class albums from 1853 – 1864. For the spectral library matching only a baseline correction was applied to minimize possible data processing artifacts and to make the spectral library user friendly. The technique can be extended to other types of objects if appropriate reference spectral libraries are built.

Principal component analysis was also applied to the spectra from the modern reference samples and the spectra from the historical samples. The PCA provides a visualization on how the spectra vary from each other. Similar types of coatings such as the proteinaceous coatings albumen and gelatin can be unambiguously distinguished from each other. The PCA data visualization can also provide some insights into the effects of the aging of the coating on the changes in the spectra.

The correlation functions used in the spectral library searches struggled to distinguish between salted paper prints with albumen coatings, dilute albumen prints, or albumen emulsion prints. The principal component model was able to distinguish between the albumen coated salt prints, the dilute albumen prints, and the albumen emulsion prints. Historic photographs suspected of being dilute albumen prints were confirmed to be dilute albumen prints.

Future directions

Logistics need to be worked out on the best way to share the spectral library and the PCA model with other institutions to extend the scholarship and correct identification of early photographs.

More Information about Harvard Salt Prints:
https://projects.iq.harvard.edu/saltprintsatharvard