



## **UNDERSTANDING 20TH CENTURY PHOTOGRAPHS: THE BARYTA LAYER SYMPOSIUM**

Organized by the Getty Conservation Institute and Paul Messier Inc., Boston

**Tuesday, January 24, 2006  
The Getty Center  
Los Angeles, California**



The Getty Conservation Institute

## UNDERSTANDING 20TH CENTURY PHOTOGRAPHS: THE BARYTA LAYER RESEARCH SYMPOSIUM

- 8:45am Continental Breakfast: Herculaneum, L3 East Building
- 9:30am Opening remarks  
**Giacomo Chiari**, *chief scientist, GCI*
- 9:45am Photographic Paper Exposed: New Meaning and Possibilities for the Understanding of 20th Century Photographs  
**Paul Messier**, *Paul Messier Ltd. Boston*
- 10:30am Break
- 10:50am Research in the Identification and Provenancing of 20th Century Photographs  
**Dusan Stulik**, *senior scientist, GCI*
- 11:35am Minor and Trace Elements in Photographic Material: Analysis and Meaning  
**David Miller**, *professor of chemistry, California State University Northridge*
- 12:00-1:30pm Lunch (not provided)
- 1:30pm Structural Measurements of DOP Photographic Paper and Particle Size Analysis of Baryta Coating  
**Renaud Duverne**, *Centre de Recherches sur la Conservation des Documents Graphiques, Paris*
- 1:55pm Photographic Paper Musical Chairs: Where Does Each Element Sit?  
**Art Kaplan**, *research lab associate, GCI*
- 2:20pm Practical Demonstration of the Identification of Fiber-Based Black & White Photographs  
**Tram Vo**, *Tram Vo Conservation, Los Angeles*

- 3:30pm Break
- 4:00pm Round Table Discussion of the Next Phases of the Project and Problems of Provenancing and Authentication of Photographs  
**Dusan Stulik** and **Paul Messier**, *moderators*
- 4:45pm Tours of the GCI's Conservation Science Laboratories/Visit to the Getty Museum
- 5:30pm Dinner (provided): Private Dining Room (Food Services Bldg, 2nd Floor)
- 7:00pm Preservation Strategies in a World of Access  
**Anne Cartier-Bresson**, *Director, Atelier for the Restoration and Conservation of Photographs of the City of Paris (ARCP)*  
NOTE: this lecture is located in the Museum Lecture Hall.

For more information on the Symposium, please visit this website:

<http://www.getty.edu/conservation/science/photocon/index.html>

# RESEARCH IN THE IDENTIFICATION AND PROVENANCING OF 20TH CENTURY PHOTOGRAPHS

**Dr. Dusan Stulik** , *Getty Conservation Institute*

Silver gelatin black and white (B&W) photographic paper was by far the most commonly used photographic printing material during the 20th century. Available in many varieties and different grades and produced by a great number of large and small manufacturers in many countries of the world, this type of paper was the medium for millions of art, technical, and documentary photographs now preserved in museums, historical collections and archives as well as in countless private and family collections.

Very few 20th century photographers left detailed information about their darkroom techniques, specifically recording the manufacturer and type of photographic paper used when printing and reprinting photographs. However, even if there is no documentation of darkroom techniques or materials used, there remains the photograph itself. As a very complex material object, a photograph might harbor some important material clues to support its provenancing and authentication.

Scientific investigations conducted independently at the GCI and by Paul Messier have identified a number of chemical and physical markers, or signatures, of baryta-coated B&W photographic paper that could be used in provenancing, authenticating, and in some cases even dating of photographic material and photographs.

Chemical analysis of a large number of 20th century photographs and photographic paper from the GCI's and Paul Messier's reference collections has shown that photographs and photographic papers contain—in addition to silver—several other chemical elements such as barium, strontium, calcium, and very often chromium. These elements are introduced in different stages of the photographic paper manufacturing process as part of the paper substrate (calcium), baryta layer coating (barium and strontium) or gelatin-hardening agent (chromium).

Analytical investigation has further shown that the concentration of these elements is very uniform for any given emulsion run; and this concentration depends on production technology and the purity of raw materials used in the manufacture of photographic paper. Some important physical parameters, such as the overall thickness of photographic paper and partial thicknesses of their individual layers, are also dependent on the technological

parameters and starting materials. At the same time, our investigation has shown that actual concentrations of key chemical elements found in photographic paper and many individual physical parameters of photographic paper differ enough from one type of photographic paper to another and vary enough between different manufacturers to provide the rationale for the development of a scientifically based provenancing methodology for both photographic paper and photographs.

The success of determining a new provenancing methodology and its widespread application depends on both the quality of the analytical and scientific methodologies used for quantitative determination of all key chemical and physical parameters applied in the provenancing methodology and on a quality of a photographic paper database available for parameter matching.

Working closely with scientists at California State University Northridge and the Nuclear Reactor Research facility at the University of California Irvine, we prepared and characterized a series of high quality barium, strontium, calcium, and chromium thin film analytical standards that allow for calibration not only for GCI's analytical instruments but also for any X-ray fluorescence spectrometer that might be now or in the future used in provenancing studies of photographs. These standards will be available to all potential users of this new provenancing methodology to facilitate an easy comparison of data, regardless of type of XRF used or of experimental parameters.

We have also started a systematic analysis and characterization of all samples of photographic paper from the GCI's Reference Collection, and we have already completed analysis and characterization of about 580 well provenanced samples from Messier's collection of historical photographic papers.

The chemical and structural complexity of photographic paper gives us an opportunity to expand a number of measured parameters of each photographic paper; and in turn allows to fine-tune matching an unknown photograph to the photographic paper database. The use of multidimensional data fields calls for the use of advanced "chemometrics" methods to conduct data analysis and aid data interpretation. This part of our research is still in its initial phase but our preliminary results are quite promising and we hope to report on our findings shortly.

With more than one hundred years of widespread use, silver gelatin photographic paper was one of the most longlasting photographic printing mediums, well surpassing the albumen printing process of the previous century. This longevity comes with a great variety of different types of photographic papers from manufacturing companies such as Defender,

AnSCO or Orwo that are now known only by their historical names to leading companies such as Kodak. But in fact, Kodak just announced its closure of their B&W photographic paper manufacturing facilities. Ilford has pledged to be the “last man standing” in the B&W silver halide photographic paper business. Our investigation indicates that there is no comprehensive collection of photographic papers in existence that would allow us to successfully create a comprehensive database of silver gelatin photographic paper.

There is another experimental approach that might be used to build a database for the provenancing of photographs. This approach would be based on the fact that no photographer or printer has had, obviously, the opportunity to experiment with the whole range of photographic papers available throughout the history of the medium. The direct opposite was much more common.

Historically, many photographers and printers tested a limited variety of photographic papers before selecting an even smaller range of papers to satisfy their needs and darkroom technique. Photographers changed their preferences only when their favorite photographic paper became unavailable, or when new technologies delivered substantially better printing materials. Based on this fact, it should be possible to build a series of very specific “individual” database segments of photographic papers used by a particular photographer (based on an in-depth study of his or hers archives); or when archives are not available, on a scientific survey of their well-provenanced photographs.

Dealing with all these various aspects of photographic research, we are convinced that the above-described provenancing methodologies should be used both independently and together to assemble a highly usable reference database of various photographic papers used throughout the history of the silver gelatin photographic printing process.

Of course, the task of building such a database is well beyond the abilities of a single researcher or institution without a broad network of collaborators. At the same time, the potential impact of having a fully developed and scientifically based provenancing and authentication methodology for many aspects of photographic research is too important to leave it untapped.

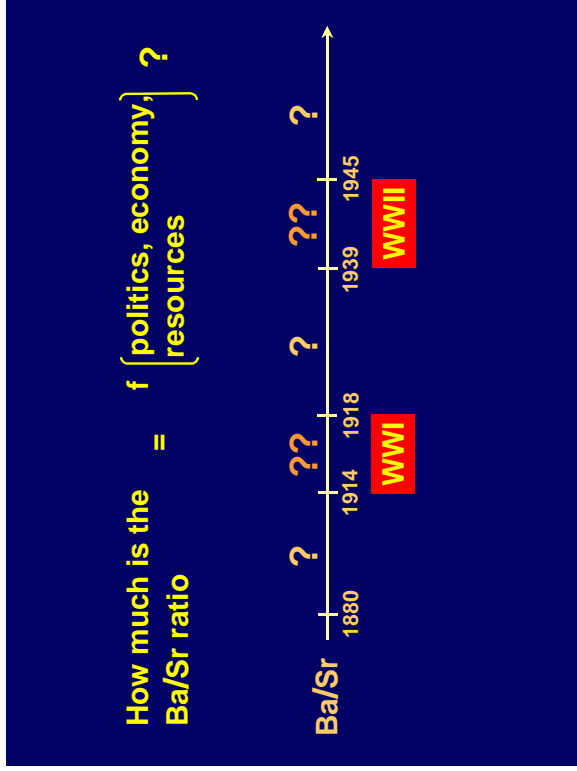
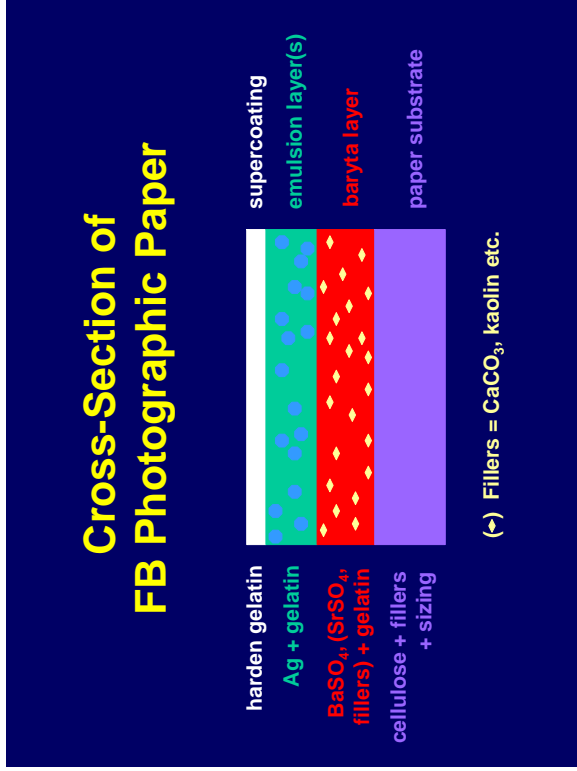
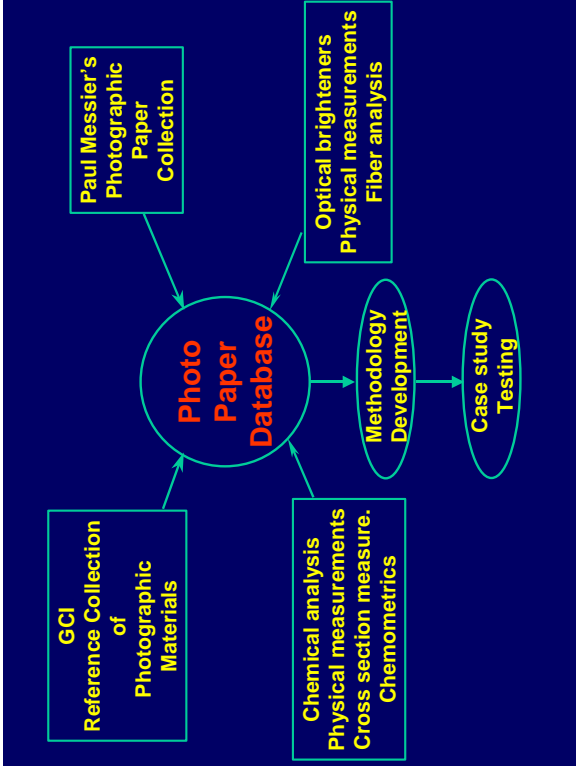
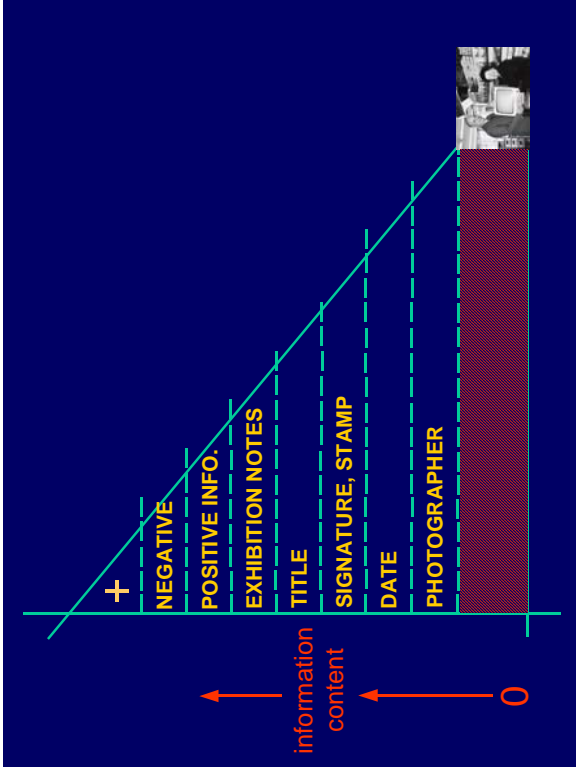
## **Dr. Dusan Stulik**

Dr. Dusan Stulik received his B.S. and M.S. degrees in chemistry at Charles University in Prague and his Ph.D. degree in physics from the Czechoslovak Academy of Sciences.

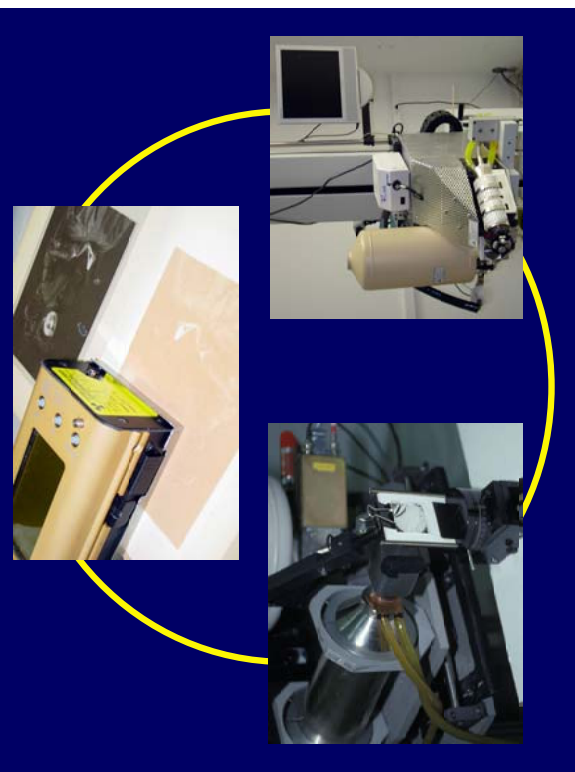
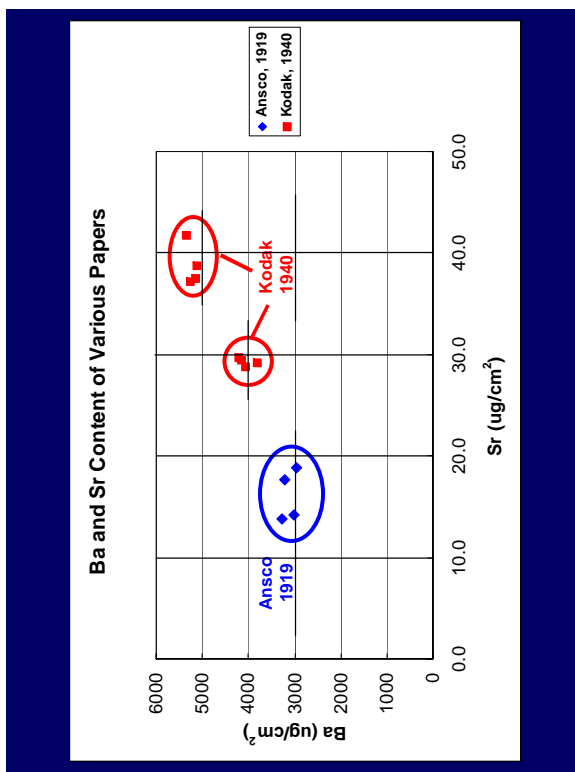
His early research was focused on the application of surface analytical techniques in the investigation of surface chemistry and physics of materials. He was the first chairman of the Surface Analysis Group of the Czechoslovak Spectroscopic Society. After moving to the United States, he taught analytical and nuclear chemistry at Washington State University. After joining the Getty Conservation Institute in 1988, for a number of years he was also a visiting professor of material science at Cornell University, teaching an interdisciplinary course on art and science. His research at the GCI is focused on the application of modern analytical techniques in art conservation and on the development of technical art history as an academic discipline.

For his research relating to the conservation of the St. Vitus Cathedral's 14th-century mosaic in Prague, he was awarded the Medal of the President of the Czech Republic, and together with the project team won the very prestigious Engineering Academy Prize in 2000, presented by the Engineering Academy of the Czech Republic. He is an author and co-author of more than fifty scientific and conservation science articles and several books related to art conservation.

His current research is focused on research on photographic conservation and he is a leader of the GCI's Conservation of Photographic Collections project.







# Expansion of the Data Field

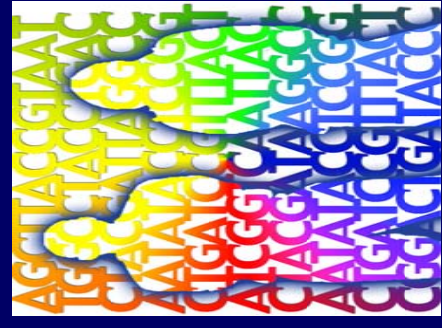
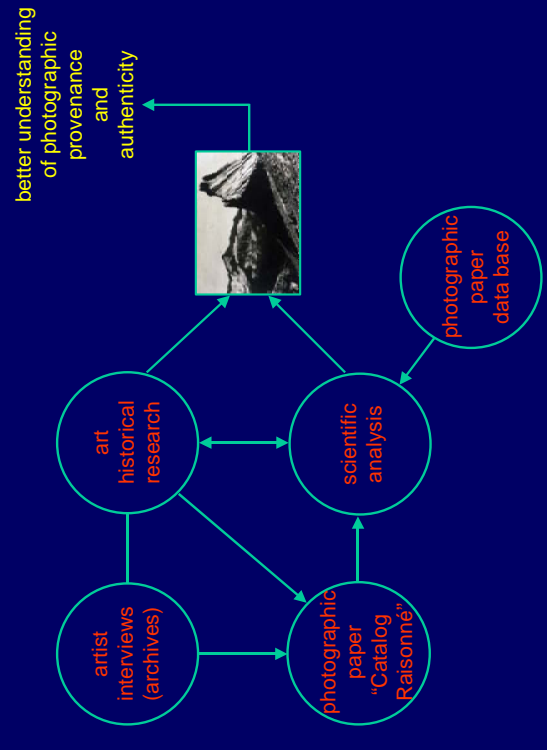
Ba  
Sr  
Ba/Sr

- chemical composition
- physical parameters
- singularities
- other parameters

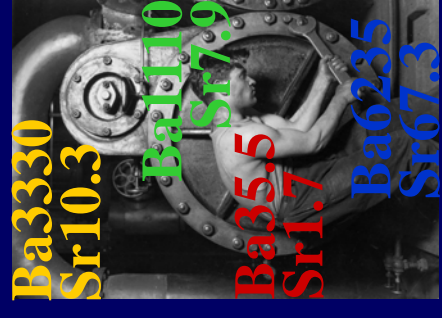
VISUALIZATION

2-3 - Dimensions  
GRAPHICAL

n - Dimensions  
CHEMOMETRICS



Human Genome Project



Barytome Project?

Ba3330  
Sr10.3

Ba1110  
Sr7.9

Ba35.5  
Sr1.7

Ba6235  
Sr67.3

## **PHOTOGRAPHIC PAPER EXPOSED: NEW MEANING AND POSSIBILITIES FOR UNDERSTANDING OF 20TH CENTURY PHOTOGRAPHS**

**Paul Messier**, *Conservator of Photographs in Private Practice, Paul Messier LLC, Boston*

The samples that form the basis of the Getty Conservation Institute's baryta project were selected from a reference collection of photographic papers amassed over the past seven years. The GCI's reference collection contains over 3,000 samples of 20th century photographic paper, and most have been catalogued by manufacturer, brand, surface texture, reflectance, base color, and emulsion grade. The samples fall into two broad categories: books of specimen prints; and packages of unexposed photographic paper. The collection currently contains samples from 57 manufactures covering 369 brands. The collection is particularly strong between 1935 and 1965 with over 1,400 samples included. In fact, of the nearly 900 samples contributed to the GCI as part of this collaboration, most date from this period. Earlier material is much scarcer and is consequentially the highest collection priority. At present the collection contains a limited amount of material pre-dating 1935 (roughly 200 samples). Paper marketed and sold in the United States is most heavily represented. There is moderate western European representation, some papers from Eastern Europe and almost nothing from Russia, East Asia and elsewhere.

The collection began as a direct result of the Lewis Hine authenticity scandal that emerged in the Fall of 1999. The questioned Hine prints exposed the critical lack of objective criteria to categorize, describe and date photographic paper. Early work on the project also exposed the fact that collections of well-characterized photographic paper either did not exist or were not readily accessible to scholars.

Conservators and art historians working with other media have long benefited from the study of reference collections of pigments, resins, gums, paper and textile fibers. In large part, the contemporary field of art conservation, from the standpoint of training, treatment, and scientific research, is based on the methodical study and characterization of these reference collections. The apparent lack of such resources in the field of photograph conservation, coupled with the rapid obsolescence of chemical photography, heightened the perceived need to collect as much as possible as quickly as possible.

Considering the demise of silver-based printing, the collection also serves an intrinsically valuable preservation function, providing a tangible connection to the methods and materials of 20th century photographers.

One of the first research applications for the collection was providing an authoritative baseline documenting the use of optical brightening agents in 20th century photographic papers (Messier, P., V. Baas, D. Tafilowski and L. Varga., 2005. Optical brightening agents in photographic paper. *Journal of the American Institute for Conservation*). The project involved a surveyed of 2,076 black and white, fiber-based papers from the collection for optical brighteners. Very few incidences of brightened paper dating prior to 1955 were found, with no examples pre-dating 1950. The scarce, early incidences of brightened paper were not precisely dated, but packaging, related graphics and image content indicate the papers were manufactured somewhere between 1950 and 1955.

During this early transitional period, the commercial availability of brightened paper was apparently quite limited. The same survey established that the sustained use of brighteners, with widespread commercial availability, began in the latter part of the 1950's, with roughly 33% of all papers from this period showing optical brighteners. The survey found peak use of brighteners in the periods 1960-1964 and post-1980. In the former time frame 55% of papers contained brighteners. In the latter period 78% of fiber-based papers showed brighteners. The survey also concluded that brighteners were found predominantly in the emulsion side of papers produced prior to 1960. After 1960 brighteners were mostly found on both the emulsion side and paper base.

Relatively simple in design and execution, the optical brightener survey nevertheless provides a useful illustration of the purpose and promise of the collection by addressing open questions regarding the material history of photography through objective observation. The "baryta project" is a much more complex elaboration of this same goal.

Baryta papers were introduced in the late 19th century for use with collodion silver printing out papers. Since that time baryta coatings have consisted of predominantly barium sulfate, a white pigment, in a gelatin binder. The surface texture and highlight color of photographic paper are primarily attributable to manipulations made to this coating. On a deeper level, baryta is also a mix of elements, some benign contaminants and some intentionally added to achieve certain functional and aesthetic goals. The hypotheses driving the collaboration with the GCI is that precise measurement of these elements in conjunction with a well-characterized reference collection could provide an important tool to support studies into the origins of significant 20th Century photographic prints, as well as the materials and techniques of the past century's master photographers.

Unlike the optical brightener study, proving this hypothesis required the advanced research capabilities of GCI thus illustrating the importance of collaboration for making

optimal use of the collection. Other collaborative projects, dealing with the permanence of optical brightening agents, paper fiber analysis and surface texture characterization, are currently underway or under consideration. Ideally work on these and other future projects should not only be collaborative but coordinated; involving data sets and samples shared across multiple collecting institutions. To the extent possible, current and future efforts should be complemented with a drive toward building permanent, peer-reviewed, literature dedicated to the material history of 20th century photographic printing.

As developing a shared body of knowledge emerges as a priority, there remains a need for effective forums where the issues of print dating, provenance, technical analysis and catalog raisonné studies can be discussed in a broader context among diverse constituencies including conservators, conservation scientists, dealers, collectors, curators and art historians. And all the while, weaknesses and gaps in the current reference collection should be filled as aggressively as possible through continued active collecting and through the development, and possible integration, of other reference collections of photographic paper.

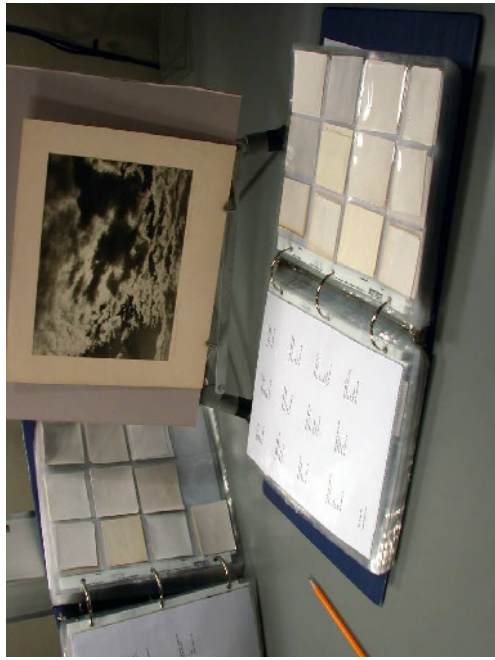
## **Paul Messier**

Paul Messier holds an A.B. cum laude in art history from Vassar College (1984) and an M.A. and C.A.S. in the conservation of works of art on paper from the State University College at Buffalo (1990). Other training includes an apprenticeship in New York City, an internship in Paris, and an advanced research fellowship at the Smithsonian Institutions' Conservation Analytical Laboratory.

In 1995 Mr. Messier established his private conservation practice in Boston. Among his clients are some of the leading museums, private collections, galleries and auctions houses from around the world. He has published widely on the topic of photograph conservation, and has lectured nationally and internationally at venues located in Taipei, Melbourne, Moscow, and St. Petersburg. Recent research projects include the assembly and cataloguing of a reference collection of 20th century photographic papers and the development of an authentication methodology for photographs attributed to Lewis Hine.

This project resulted in a method useful for dating 20th century photographic papers, receiving coverage from publications including *The New York Times*, the *Wall Street Journal*, *ArtNews*, *The Economist* and *The Atlantic Monthly*. Mr. Messier is an elected member of the board of the American Institute for Conservation and has served this organization in various capacities, including chairing the Publications Committee and founding the Electronic Media Group.

Paul Messier, GCI presentation, January 24, 2006



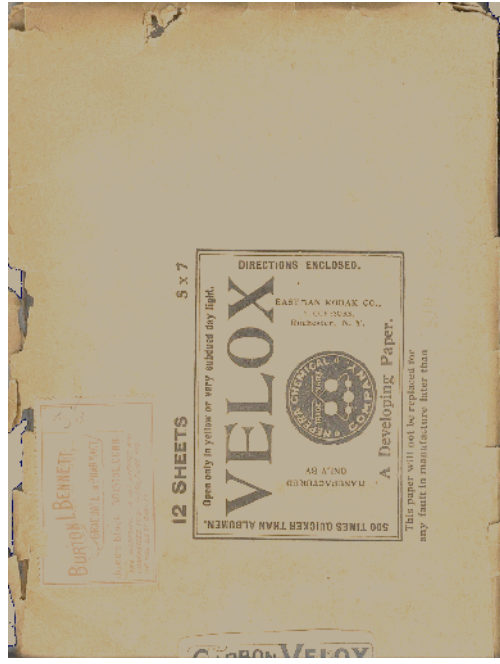
Samples of paper in the collection are organized by date, manufacturer, brand and surface finish. Samples come from packages of unexposed paper (like those in the illustration) and from manufacturer sample books.

Paul Messier, GCI presentation, January 24, 2006



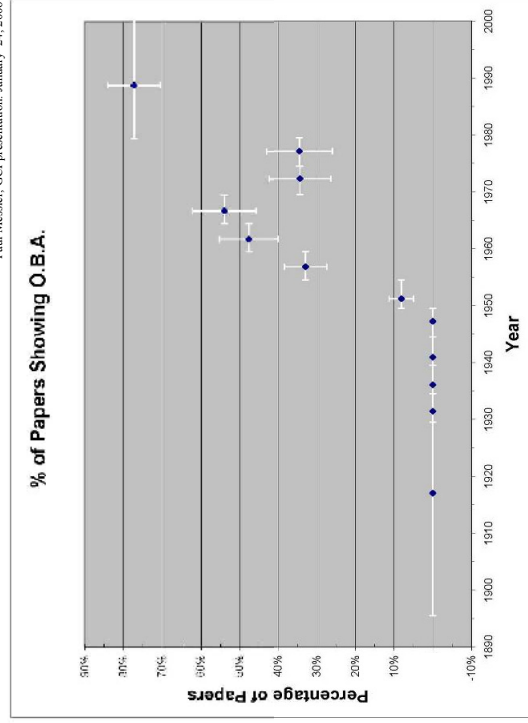
Unbrightened paper, unbrightened paper contaminated with optical brightener; optically brightened paper, photographed using near ultraviolet radiation.

Paul Messier, GCI presentation, January 24, 2006

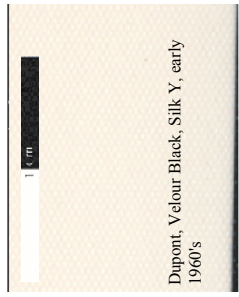
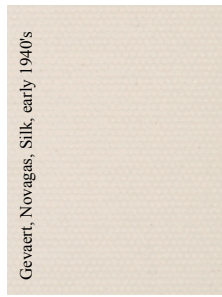


A package of unexposed paper. Eastman Kodak Company, Velox, expired June, 1908

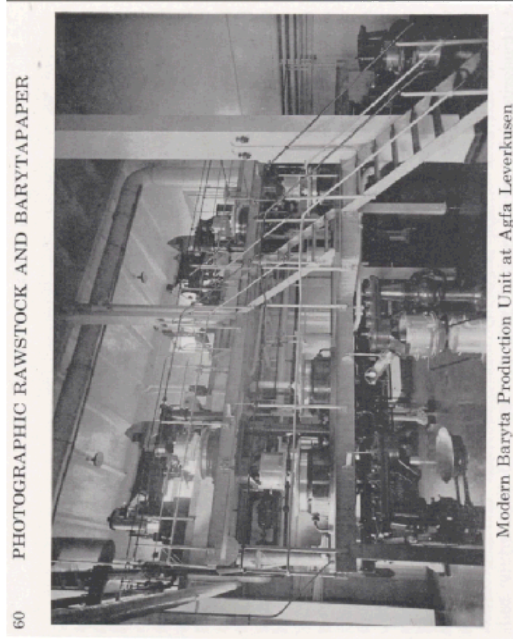
Paul Messier, GCI presentation, January 24, 2006



Paul Messier, GCI presentation, January 24, 2006



Paul Messier, GCI presentation, January 24, 2006



Similar textures applied by various manufacturers to baryta coatings.

Paul Messier, GCI presentation, January 24, 2006

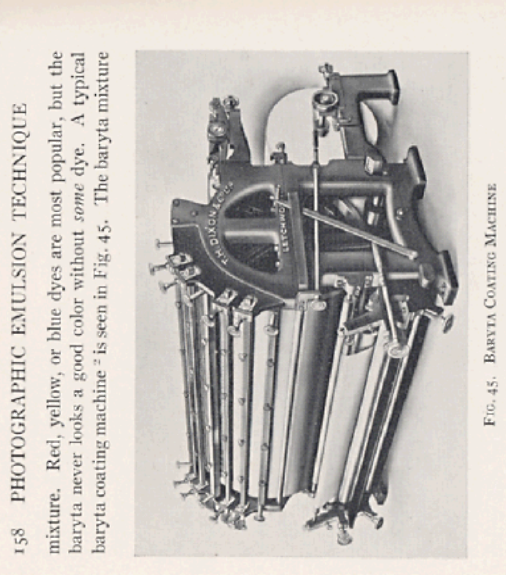


FIG. 45. BARYTA COATING MACHINE

# STRUCTURAL MEASUREMENTS OF DOP PHOTOGRAPHIC PAPER AND PARTICLE SIZE ANALYSIS OF BRYTA COATING

**Renaud Duverne** , (*GCI graduate intern / CRCDG / Université de Paris I – Sorbonne Ph.D. program*)

Besides specific chemical markers such as concentrations of Barium (Br), Strontium (Sr) or concentrations of other major chemical elements in baryta-coated fiber-based (FB) photographic paper, several physical parameters of photographic paper can also be used in characterizing, provenancing and authenticating photographic paper.

An early development of the scientific methodology to determine certain physical parameters related to photographic paper and preliminary tests of this methodology on a small sample set of different photographic papers were conducted at the Centre de Recherches sur la Conservation des Documents Graphiques (CRCDG) in Paris beginning in 2001. This study was continued during my first stay at the GCI in 2002; and elements of this research are the topic of my Ph.D. thesis at the Sorbonne.

A research task for my graduate internship at the GCI is to finalize the development of a working methodology for a) the determination of selected physical markers of baryta-coated photographic papers; b) the measurement of some of these parameters for 550 samples of photographic paper from Paul Messier's Collection of Historical Photographic Paper and the collection of photographic paper in the GCI's Reference Collection; and c) the integration of these measured physical parameters into the existing GCI/Messier Photographic Paper Collection database.

All photographic papers available for our experiments were unexposed photographic papers from original enclosures, or boxes with full manufacturer description and annotation of paper type, surface, thickness (single/double weight) and year of production and/or expiration date. Silver halide components of photographic paper were removed using a standard fixing procedure; and photographic paper was washed, dried and permanently labeled with a database identification number.

Two primary physical markers available for the characterization of photographic paper are the overall thickness (OT) of the photographic paper and its apparent density (AD). Both of these macroscopic physical parameters can be easily determined for all unmounted photographic papers and photographs. In our study the thickness of well temperature and



humidity equilibrated samples of photographic paper were measured using a digital micrometer. The thicknesses of photographic paper in this study of 550 different photographic papers made by 25 different manufacturers varied between 0.066 mm and 0.465 mm. The statistical treatment of thickness data shows a presence of two major groups near 0.17 and 0.36 mm, which, in general, correspond well to the manufacturer's description of the papers as "single weight" or "double weight" photographic papers, respectively.

To obtain a set of samples of calibrated surface area as needed for determining the apparent density of the photographic papers, a 1 5/8" circle of paper was cut of each paper sample using a sharp circular steel punch. Each of the resulting paper discs has an identical surface area of 1338 sq. mm. The exact weight of each disc was determined using an analytical microbalance. The apparent density of all studied photographic papers varied between 0.625 and 1.341 g/sq. mm, showing two major groups with about 0.9 and 1.12 average density, each with no relation to the two thickness groups described above.

To study physical parameters of individual layers of photographic papers, it requires physical sampling. The thicknesses of paper base (TP), baryta layer (TB), emulsion layer (TE) and supercoating layer (TS) were determined after imbedding small samples of photographic papers into Technovit resin and microtoming resulting resin blocks using glass or diamond knives on the precision MT-7 RMC microtome. The thicknesses of individual layers of photographic paper were determined on each 0.6–10 micrometer thick slice of glass slide mounted cross section of photographic paper using a high power optical microscope. Calibrated image-processing software aided the determination of the measured parameters of paper cross sections. There is no simple relationship between the thickness of paper base or thickness of baryta layer and the overall thickness of photographic paper. The thickness of paper base determined so far in this study ranged between 0.065 and 0.45 mm. The thickness of baryta layer for the same set of photographic paper samples ranged between 0.006 and 0.045 mm. Emulsion layer and supercoating are about 0.015 and 0.005 mm thick, respectively.

Our Transmission Electron Microscope (TEM) investigation conducted at the CRCDG in Paris also showed that measurements of particle size and particle size distribution, as well as studies of morphology of barium sulfate particles and the determination of the presence or absence of inorganic fillers in the baryta layer, might provide some additional physical parameters that might be later incorporated into the current version of the photographic paper database to obtain even more precise provenancing and authentication of the 20th century photographic papers and photographs.

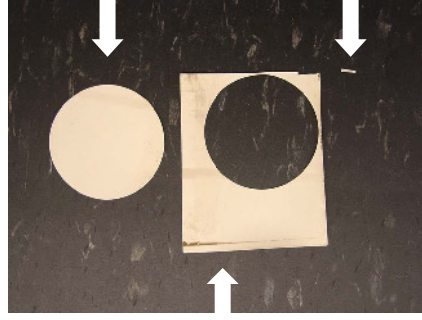
## **Renaud Duverne**

After completing his Master's degree in paper conservation at the University Paris I-Panthéon-Sorbonne (Paris) in 1996, Renaud worked for nine years as a private conservator for some famous French institutions including Bibliothèque Nationale de France, Centre Historique des Archives Nationales, Université Sorbonne, Institut National du Patrimoine). At these prestigious entities he performed treatments on paper works of art as a consultant in preventive conservation; and he also organized academic and professional training.

Renaud joined the Centre de Recherche sur la Conservation des Documents Graphiques in 1999, focusing on photographic material research. His background in conservation of cellulosic material oriented him towards photographic support analysis (e.g., cellulose acetate decomposition survey and DOP identification research). Four years ago, while at CRCDG, he became part of the GCI's baryta analysis project, developing micro-sampling techniques for the study of multi-layer photographic material structure and performing analytical techniques such as chemical spot testing, Micro-XRF, IR spectrometry and atomic absorption spectrometry or PIXE.

Currently at the Getty Conservation Institute as a graduate intern, Renaud is completing his Ph.D. in art techniques history at the University Paris I-Panthéon-Sorbonne.

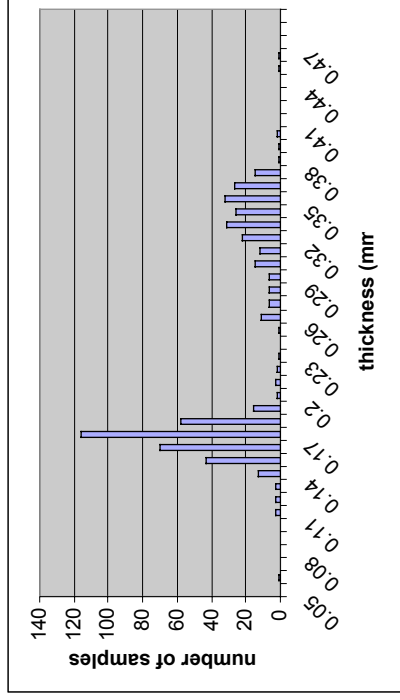
Samples preparation



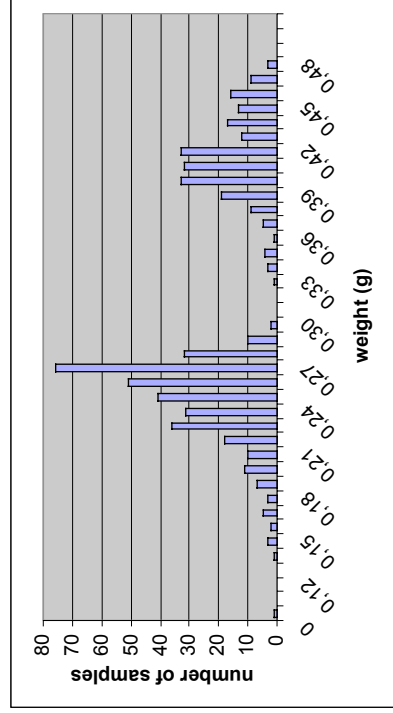
Punched calibrated sample for physical measurement

Fixed, wash and dried non exposed paper, from P. Messier collection

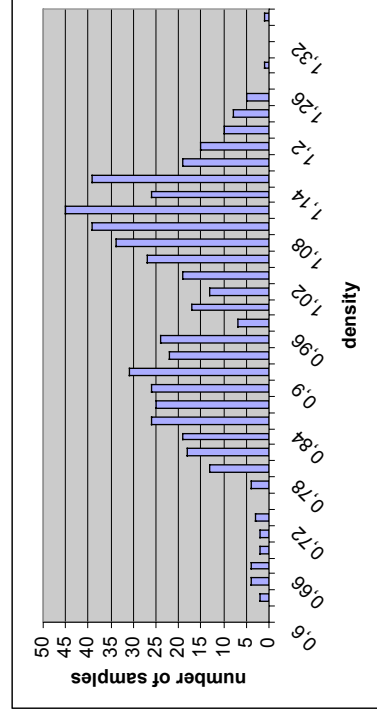
Thickness (mm)



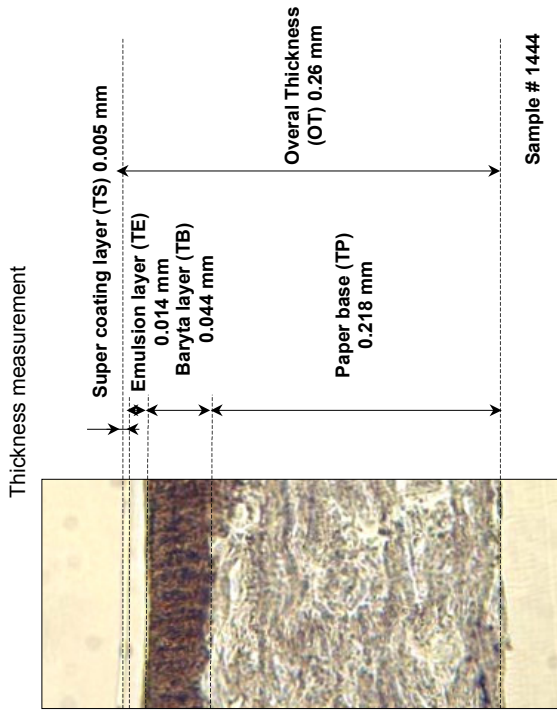
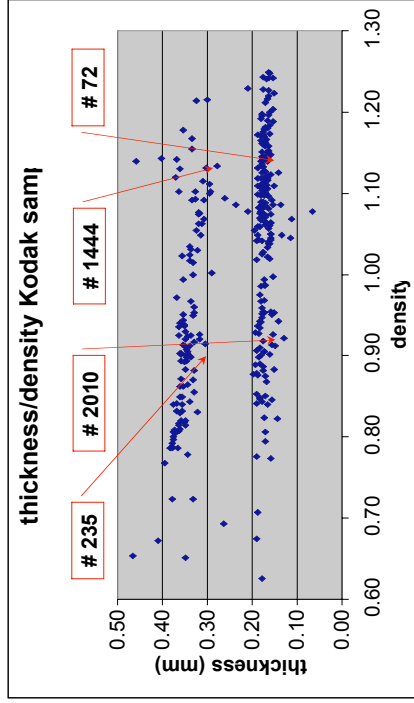
Weight (g)



Density



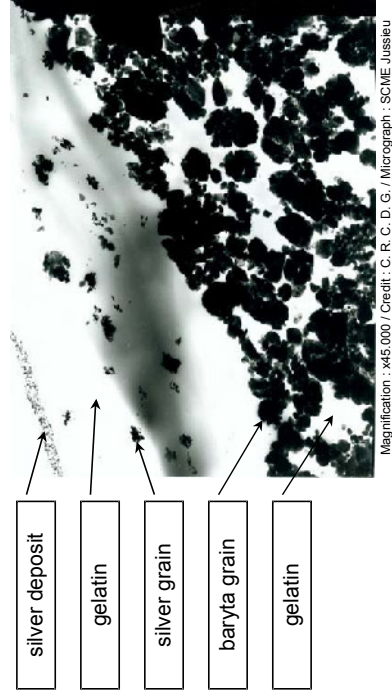
Thicknesses and apparent density comparison



Thickness and specific gravity comparison

Optical Microphoto.	Thickness (mm)	Density
	0.15	0.94
	0.16	1.14
	0.3	0.91
	0.26	1.14

Transmission Electro Photography Baryta and image layer



## **MINOR AND TRACE ELEMENTS IN PHOTOGRAPHIC MATERIAL: ANALYSIS AND MEANING**

**David Miller**, *Department of Chemistry, California State University Northridge*

A common method of analysis for objects of art is X-ray fluorescence spectrometry (XRF). The widespread appeal of XRF stems from the fact that it requires no physical sampling of the object, its relative ease of use and the ability to detect many elements simultaneously. However, the sensitivity of this method is limited, so that it is often difficult to detect minor and trace elements in a sample.

When applied to the analysis of photographs and photographic material, XRF has some specific limitations. First, it is prone to a number of spectral interferences. These interferences result from the overlap of the analytical signals for certain elements and make the interpretation of the results quite difficult. A specific example is the spectral overlap of the X-ray peaks of barium (Ba) and titanium (Ti) that makes it very difficult to detect a low concentration of titanium in a baryta-coated photographic paper. The X-ray peaks of lead (Pb) and arsenic (As) also overlap. Both elements may be present in photographic material, yet it is difficult to determine whether just one or both elements are present in an analyzed photograph based on XRF data alone. A second concern is associated with the quality of quantitative measurements made when analyzing photographs by XRF. The precise measurement of the concentration of different elements in a photograph requires appropriate analytical standards that have been carefully analyzed by methods that are not subject to the limitations of XRF. A cross-calibration approach is an excellent means of validating XRF measurements.

In order to confirm and extend the XRF analyses of photographs and photographic material we have used two additional multi-element techniques: inductively coupled plasma-mass spectrometry (ICP-MS) and neutron activation analysis (NAA). ICP-MS is a modern analytical technique based on introduction of a sample solution into inductively heated argon plasma. In the high temperature of the plasma, compounds are broken down into individual atoms which are then ionized. The resulting ions are extracted into a mass analyzer where they are separated by mass and detected. ICP-MS has the advantages of a general applicability to almost all elements of the periodic table and an extreme sensitivity for most elements, down to parts-per-billion (ppb) or parts-per-trillion (ppt) concentrations. Also, ICP-MS allows for many different modes of chemical analysis, ranging from a simple, rapid semi-quantitative screening of more than 70 chemical elements to a high precision quantitative analysis of selected elements or a measurement of isotopic ratios. Quantitative ICP-MS is subject to errors due to the variation of the sample matrix and great care must be

exercised when preparing standards and samples for analysis. A major disadvantage of ICP-MS when applied to the analysis of photographs and photographic material is that it cannot be performed without physical sampling or micro-sampling. Consequently, ICP-MS is best suited to support all phases of XRF methodology development when: (1) dealing with test materials; (2) screening the presence of different elements in samples of unexposed, unprocessed or fully processed photographic material; or (3) analyzing collections of photographic reference material or samples from collections of study and sacrificial photographs. The application of ICP-MS for the analysis of photographs from a museum or an archival collection of photographs will be always limited to very special cases where there is an urgent need to understand the details of the chemical composition of a photograph in question (due to conservation or authentication reasons) and where the conventional XRF technique does not provide a satisfactory answer.

NAA is also a very sensitive analytical technique. This method has been used to analyze various forms of art including glass, marble and metal objects and paintings. Its major advantages, in comparison with many other analytical techniques, are that it is generally free of spectral interferences, the physics of the process is well understood and little or no sample preparation is required. Consequently, NAA can provide results of high precision and high accuracy that are useful for the development and characterization of analytical standards used to calibrate other techniques such as XRF. A major disadvantage of NAA is that it requires access to a nuclear reactor set up for irradiating samples. All of our NAA measurements were done in collaboration with the Nuclear Reactor Facility at the University of California, Irvine. As with ICP-MS, this method also requires sampling or micro-sampling.

Both ICP-MS and NAA were used to address the question: “In baryta-coated photographic papers, are there any minor and trace elements that can be used as markers or analytical signatures in provenancing and authentication studies of photographs?”.

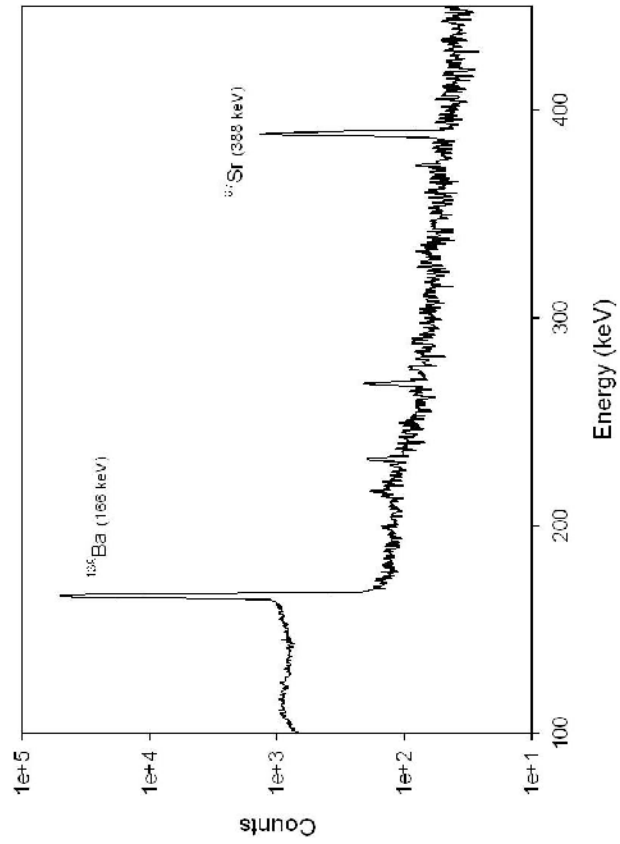
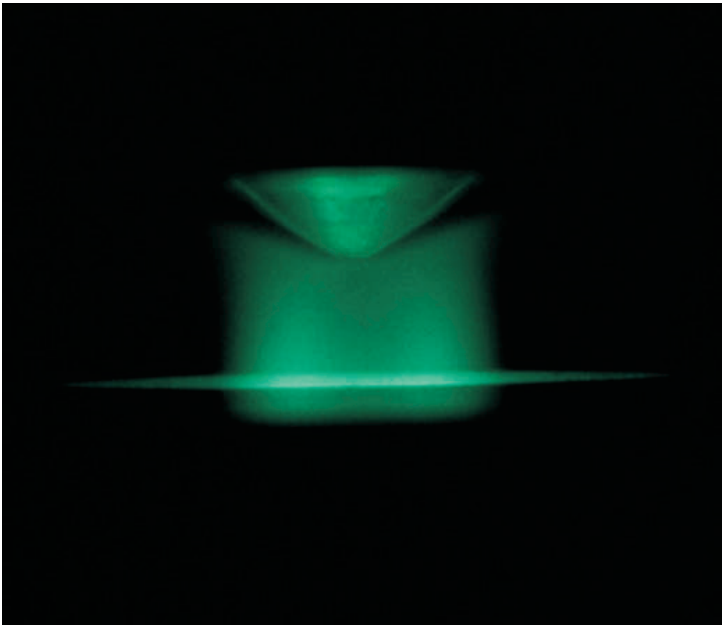
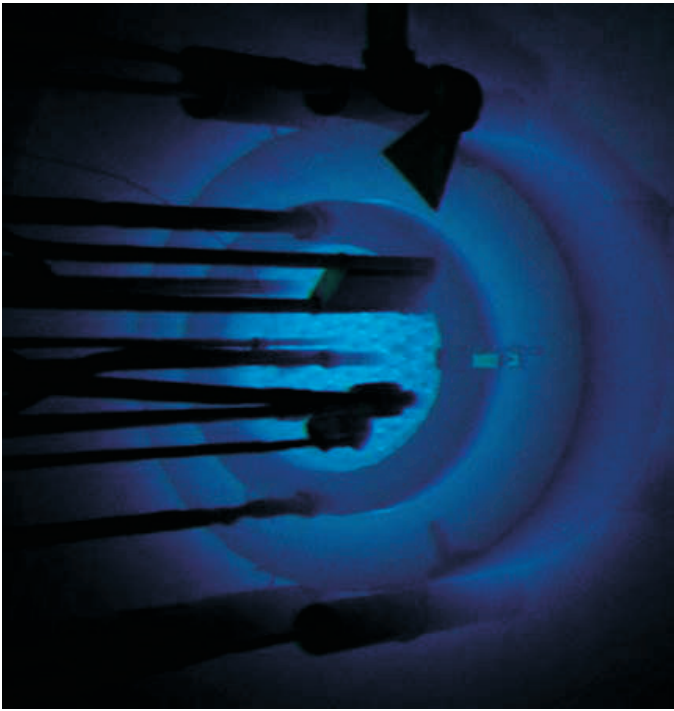
In the quest for an answer to this rather difficult analytical question, we have analyzed a series of photographic papers from the GCI Reference Collection and Paul Messier’s Collection of Historical Photographic Papers that exhibit an unusual elemental composition when analyzed using XRF. We have also analyzed a series of raw materials used in the manufacture of baryta-coated photographic paper and samples of well characterized photographs from the GCI Photograph Study Collection.

This presentation focuses on a very basic introduction to the techniques of ICP-MS and NAA as needed by potential end users of analytical findings (conservators, museum curators and photographic collection managers) who might be new to these methods. The development of a basic methodology for applying ICP-MS and NAA to the analysis of photographic materials will be discussed, together with the first round of our analytical findings. The future direction of our collaborative research will also be presented.

## **David Miller**

David Miller earned his B.A. University of California, San Diego and his Ph.D. in Chemistry from the University of California, Irvine. He is currently professor of chemistry and biochemistry at California State University Northridge.

His research areas include radiochemistry and analytical chemistry. Related experiences include serving as a technical expert for the International Atomic Energy Agency; as an Alexander von Humboldt Fellow at the Technical University of Munich; and as a visiting scientist at the Los Alamos National Laboratory in New Mexico.



Element	Photographic Paper Sample							
	366	971	1497	1693	1962	1976		
Cr	Yellow	Yellow	Yellow		Yellow	Red		
Cu		Yellow						
As	Red	Yellow	Yellow	Blue		Yellow		
Rb	Red	Yellow	Red			Red		
Nb	Blue	Blue	Yellow	Yellow		Yellow		
Mo	Blue				Blue	Yellow		
Cd		Blue	Red		Red			
Ce	Yellow	Yellow	Yellow					
Sm	Yellow	Yellow				Blue		
Pb	Yellow	Red						
Bi	Yellow	Yellow	Red	Yellow	Blue	Red		
Th	Yellow	Yellow	Red	Yellow	Yellow	Red		
U	Red	Blue	Yellow			Red		



# Trace Element Signatures

Photographic Paper Sample						
Element	366	971	1497	1693	1962	1976
Cr	Yellow	Yellow	Yellow	White	Yellow	Red
Cu	White	Yellow	White	White	White	White
As	Red	Yellow	Yellow	Blue	White	Yellow
Rb	Red	Yellow	Red	White	White	Red
Nb	Blue	Blue	Yellow	Yellow	White	Yellow
Mo	Blue	White	White	White	Blue	Yellow
Cd	White	Blue	Red	White	Red	White
Ce	Yellow	Yellow	Yellow	White	White	White
Sm	Yellow	Yellow	Yellow	White	White	Blue
Pb	Yellow	Red	White	White	White	White
Bi	Yellow	Yellow	Red	Yellow	Blue	Red
Th	Yellow	Yellow	Red	Yellow	Yellow	Red
U	Red	Blue	Yellow	White	White	Red

## Color Key

### Concentration in Sample

	same as blank
	3 - 5 x blank
	5 - 50 x blank
	> 50 x blank

## **BARYTA PAPER MUSICAL CHAIRS, WHERE DOES EACH ELEMENT SIT?**

**Art Kaplan**, *Getty Conservation Institute*

One of the major advantages of using X-ray fluorescence analysis (XRF) when analyzing photographs is its ability to provide for both qualitative and quantitative analysis of most important inorganic elements that participate directly in the formation of the photographic image or that are, in a supportive role, responsible for the mechanical, chemical and optical properties of photographs. XRF also allows for completely non-destructive and often even non-contact chemical analysis of photographs, making it a favorite method of collection curators and museum directors. Conversely, there are some disadvantages or limitations to consider when using XRF.

If there is a need to confirm some XRF findings or if the XRF is not providing a clear indication of the presence or absence of certain elements, we often use Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to provide additional information. ICP-MS is capable of rapid multi-element analysis of samples coupled with the ability to detect many elements at the parts-per-billion (ppb) level and some elements down to the parts-per-trillion level (ppt). But of course, there are drawbacks to using ICP-MS, including needing to remove a sample from the material to be analyzed that must then be dissolved in solution. When dealing with photographic paper samples containing high levels of barium sulfate, getting the sample into solution is a difficult process because of the high insolubility of barium sulfate. Both ICP-MS and XRF analysis are very powerful tools in providing information on the chemical elements present in an analyzed photograph, but neither of them allow for an easy determination of where, in a complex internal structure of the photograph, the detected elements are located.

A typical analysis of a 20th century black and white fiber based photographs shows the presence of Aluminum (Al), Silicon (Si), Sulfur (S), Potassium (K), Calcium (Ca), Chromium (Cr), Manganese (Mn), Iron (Fe), Copper (Cu), Zinc (Zn), Selenium (Se), Strontium (Sr), Silver (Ag) and Barium (Ba). The location of some of these elements in a photograph's internal structure can be easily deduced based on a general knowledge of photographic chemistry and technology. Most 20th century B&W photographs are based on silver halide technology, so it is not surprising to find a relatively large concentration of silver in the emulsion layer of dark areas of a photographic image. Many older contact photographic papers were made using silver chloride or silver chloro-bromide emulsion. Most enlarging photographic papers up to the present were produced using silver bromide, silver bromo-iodide or bromo-chloro-iodide emulsions. The photographic gelatin of the emulsion layer acts as a potential sink for halogens (chlorine, bromine, and iodine) produced during the development of the photographic image, and these elements might be detected even in well-processed and fixed photographs.

The baryta layer of most photographic papers contains barium sulfate, with small amounts of strontium sulfate impurities. These two elements together with the sulfate are the main inorganic elements expected in the baryta layer of photographs.

Since the beginning of the 20th century photographers also used a number of different procedures to modify the color of a photographic image or to improve the stability of a silver-based image using both sulfur-based or heavy metal (e.g., Se, Au) toners. The location of these elements in the emulsion layer together with developed silver is also easy to predict.

Locating other elements in photographs can be much more difficult. Chromium alum was sometimes used to harden gelatin; and it can also be found in the gelatin binder of the baryta layer, the emulsion layer and/or in a super-coating layer applied to a top of the emulsion layer to provide protection against mechanical damage. Inorganic fillers of many different kinds were used as additives to the baryta layer, and the same or different fillers were often also added to cellulose mass to modify the properties of paper used as a base for photographic paper. Small amounts of Mn, Fe, Cu as impurities might be present both in the baryta layer or paper substrate.

For provenancing and identification of photographic paper, it is important to understand the location of all major elements detected in photographs. Even if two photographic papers contain identical sets of chemical elements based on both qualitative and quantitative analyses, the distribution of elements within the internal structure of a photograph might be quite different. In some cases it would be very important to understand the location of different elements for interpreting data obtained during analysis. For example, results of quantitative analysis of calcium in the paper base of a photographic image would be different when analyzed from verso or recto side due to the presence of the X-ray absorbing baryta layer.

A study of the locations of different components in a multi-layer structure of a photograph without sampling is theoretically possible, but it would require very special instrumentation, certainly not a practical solution for everyday use by conservation scientists and photographs conservators. At this point of time it seems that the best and most accessible way to study the distribution of different elements is to remove a small sample from a photograph, prepare a cross section and then study the distribution using an Electron Microprobe Analyzer (EMPA) or a combination of a Scanning Electron Microscope (SEM) along with an Energy-Dispersive X-ray Analyzer (EDX) and ICP-MS. These analytical methods provide an opportunity not only for a point analysis of selected areas of the analyzed cross-section but also for obtaining elemental maps of the whole or partially selected area of a cross-section that

show the presence or absence of selected chemical elements in different layers.

These analytical methods require the removal of a small sample. Any removal of a physical sample from photographs should be done only with the approval of a collection curator and only when it is crucial to obtaining information about the internal composition of a photograph and cannot be obtained by any other nondestructive means. Potential damage to a photograph can be minimized by using well-developed micro-sampling procedures that allow the removal of a sample that is not visible to naked eye.

The analysis of photograph cross-sections from the GCI's Reference Collection of photographs, and cross-sections of different B&W fiber-based photographic papers from the GCI's and Paul Messier's collection of photographic paper and an interpretation of analytical results in the light of understanding the internal chemical structure of 20th century photographic material, will be discussed in this presentation.

## **Art Kaplan**

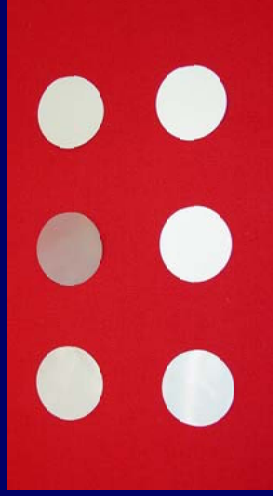
Art Kaplan was born in Bobruysk, Byelorussia. Moving with his parents to Los Angeles in 1980, he graduated from high school in Santa Monica and then enrolled at Santa Monica College. After earning his A.A. degree from Santa Monica College, Art joined the United States Marine Corps where he served a field radio operator for an artillery battalion for several years.

After leaving the Marines, Art returned to school and enrolled at California State University Northridge in the biochemistry program. During his junior and senior years, he worked with Dr. David Miller and the GCI performing Neutron Activation and Inductively Coupled Plasma Mass Spectrometry analysis on glass samples for the GCI's Conservation of the St. Vitus Mosaic project in Prague.

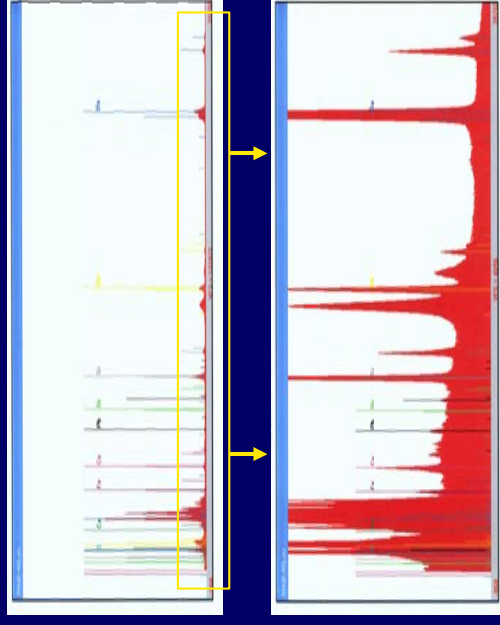
Upon graduating from California State University, Northridge with a B.S. in biochemistry, Art took a position with the Science Department of the GCI. His work centers around the Conservation of Photographs project, while also maintaining the GCI's extensive Reference Collection of artist's materials.

# Papers Sampled

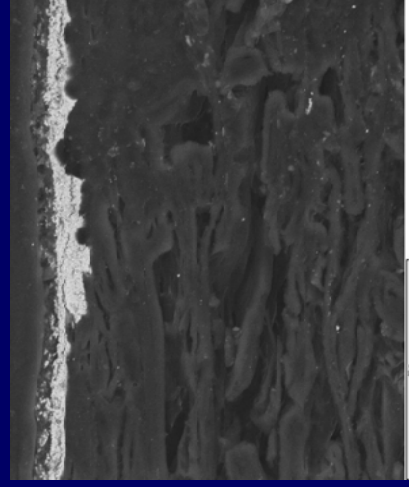
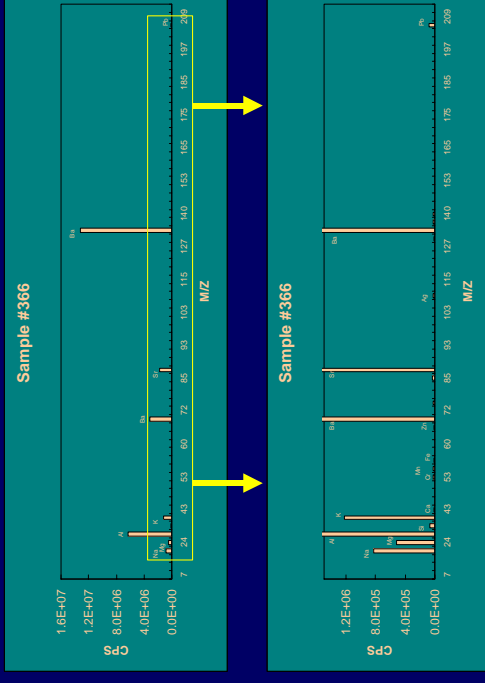
Sample #	Manufacturer	Brand	Year
366	American Aristotype Co.	Aristo	1896
971	Ansko	Cyko	1918
1497	Dupont	Varigram	1959
1693	Ansko	Brovira	1950
1962	Kodak	Ektalure	1976
1976	Agfa-Ansko	Indiatone	1937
DS3019	Kodak	Opal	1952



# XRF Spectra of Sample #366



# ICP-MS Spectra of Sample #366



DS3019



①  
800°C

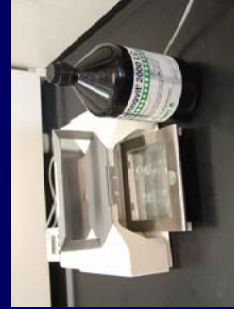
HNO<sub>3</sub> ↓ ②



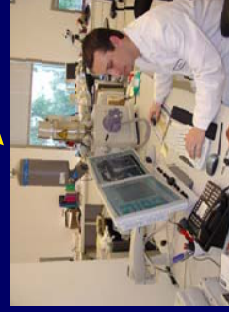
③



Microtoming



Embedding



ESEM