

# A NEW SCIENTIFIC METHODOLOGY FOR PROVENANCING AND AUTHENTICATION OF 20<sup>th</sup> CENTURY PHOTOGRAPHS: NONDESTRUCTIVE APPROACH

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## ABSTRACT

*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 photographic paper was the medium for millions of art, technical, and documentary photographs now preserved in museums, historical collections and archives.*

*As a very chemically complex material object, a photograph might harbor some important material clues to support its provenancing and authentication. Scientific investigations conducted at the GCI 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.*

*The X-ray fluorescence spectrometry (XRF) 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 and calcium. These elements were introduced in different stages of the photographic paper manufacturing process as part of the paper substrate (calcium) and baryta layer coating (barium and strontium).*

*The XRF investigation has further shown that the concentration of these elements is very uniform for any given emulsion run; depending on photographic paper production technology and the purity of raw materials used in the manufacture of photographic paper. Our investigation has shown that the 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.*

## INTRODUCTION

The authenticity of any art object can be described as the correct attribution of its origin and authorship. The provenance of the art object deals with records or documents authenticating the art object or providing information related to the history of its ownership. Art forgery refers to creating and selling works of art that are falsely attributed to be the work of other, usually more famous artists [1]. Art forgery dates back several thousands years [2, 3] but the forgery of photographs is a more recent phenomenon. Photography had its origins in the early 19<sup>th</sup> century but photographs became the target of forgers only during the second part of the 20<sup>th</sup> century when the market value of art photographs increased dramatically [4]. Well publicized cases of forged Man Ray's [5] and Luis Heine's photographs [6] infiltrating the art market clearly document this phenomenon. Today when a single photograph can sell at auction for almost \$3,000,000 [7] and when the auction prices of a number of individual 20<sup>th</sup> century photographs reached over the \$500,000 level [8], it is safe to predict that the photograph art market will have to deal with more cases of forgeries of photographs in the foreseeable future.

The detection of forgeries of art objects is always a difficult task but the detection of forged photographs is particularly difficult. In the detection of forgeries of paintings, sculptures or drawings the art expert can look for differences in painting or carving techniques, stylistic or iconographic inconsistencies, and materials (pigments, binders etc.) that were not available during the time when forged pieces of art would have been created could be also investigated [9].

Photography is a medium of multiple originals. The photographer selects and records a photographed scene on a piece of film (in “classical or chemical” photography). From this moment the creation of a developed negative and the creation of a final photograph(s) can be performed by the photographer him or herself, photographer’s assistants or printers, or by commercial photographic laboratories. The time period during which a photograph was printed is also important for the art market. As “vintage prints” are usually considered photographic prints made at the same time as the negative or within the next several years or so. So called “printed later or modern prints” were printed later by the photographer, his assistants, or printers under the direct supervision of the photographer. So called “posthumous prints” were made by a technician who never worked with the photographer, but still from the original negatives [10]. At the same time all of the above mentioned types of photographs could be printed in different formats using different types of photographic papers (Fig. 1).



*Figure 1. Henri Cartier-Bresson himself or his printers printed several versions of his “Quai de Javel” photograph during his lifetime.*

Some photographers put a complete ban on the printing of any “posthumous prints” [11] while some allow only some limited printing of selected photographs, often with specific instructions as to how the prints should be processed and printed [12]. Many photographers did not provide detailed instructions about how to deal with their artwork and so the printing of their negatives might be at the will of their heirs or owners of their negatives. All of the above mentioned factors make the provenancing and authentication of photographs very difficult and challenging.

Some curators, art dealers, and art collectors have developed a high level of connoisseurship that helps them deal with some more obvious forgery issues but the previously mentioned forgery cases have shown that connoisseurship alone cannot solve all forgery authentication and provenancing problems. Many problems related to forgeries of paintings, sculpture, drawings and other art and archaeological objects have already been solved using the methods of technical art history, conservation science, and forensic science [13].

The research in photographs conducted at the Getty Conservation Institute during the last several years focused on the development of advanced and more objective methodology for

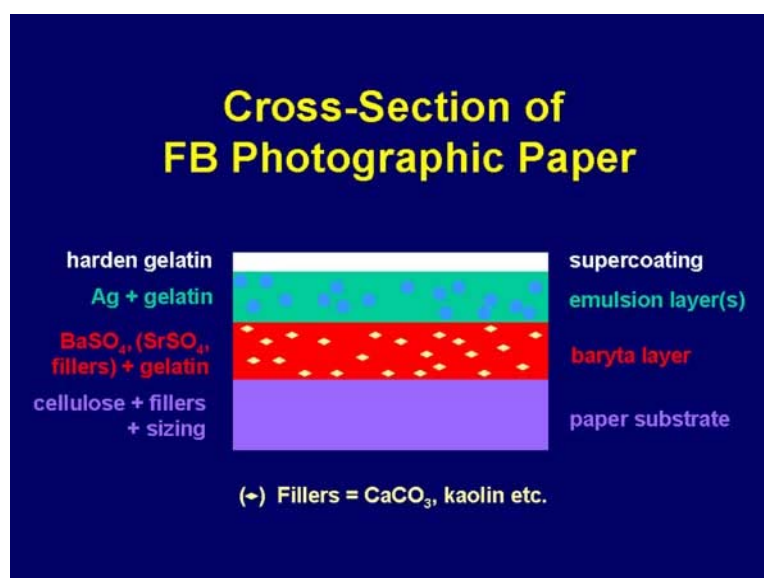
the identification of photographic processes and process variants using both nondestructive and non-contact methods of chemical analysis and on applications of quantitative methods of non-destructive chemical analysis in the development of new scientific methodologies for provenancing and the authentication of photographs.

Our early analytical research focused on answering questions asked among practicing B&W photographers about the relationship between the “silver halide loading” of different commercially available photographic papers and of the “depth” of attainable blacks in fully B&W processed photographs. Our quantitative XRF results have shown that the concentration of silver in a studied set of unexposed and undeveloped photographic papers ranged between 120 and 230  $\mu\text{g}$  of silver per  $\text{cm}^2$  (Table 1).

<b>Bergger (Prestige)</b>		<b>Forte (Elegance)</b>		<b>Agfa (Classic)</b>	
<b>Ag</b>	<b>120.0</b>	<b>Ag</b>	<b>227.0</b>	<b>Ag</b>	<b>189.0</b>
Ba	3590	Ba	2460	Ba	3950
Sr	8.3	Sr	5.8	Sr	9.7
Cr	49.1	Cr	40.5	Cr	56.2
Mn	11.6	Mn	9.4	Mn	12.0

*Table 1. Concentrations of major chemical elements determined in three samples of photographic paper.*

The same analysis also showed that the concentration of some other elements (such as barium, strontium, chromium, and calcium) present in the analyzed samples of fiber based (FB), baryta coated photographic papers varied substantially for different photographic papers (Fig. 2).



*Figure 2. Internal structure and chemical makeup of a typical silver gelatin fiber based photographic papers.*

Discussing our findings with conservator of photographs Paul Messier (Paul Messier Ltd. Boston) we embarked on a pilot collaborative project between our two laboratories to test if differences in the concentrations of barium and strontium between different papers produced by different photographic paper manufacturers differ enough to serve as a basis for the development of a new, scientifically based methodology, for provenancing and authenticating

20<sup>th</sup> century silver gelatin, fiber based, baryta coated photographs and photographic papers. The results of this pilot project have been presented at the Baryta Layer symposium that took place at the Getty Conservation Institute in January 2006 [14].

## PRELIMINARY TESTS

In order to develop the encouraging results of our pilot project into a fully developed and practical methodology of provenancing and authentication of photographs it was necessary to prove that the baryta layer for each analyzed photographic paper is chemically and physically uniform for each emulsion run. These test were conducted by quantitative XRF analyses of a number of analytical spots across a single photographic paper, and by comparing multiple analyses conducted on the first and last photographic paper of a large volume packaging of the photographic papers (250 sheets of the 8x10” photographic papers) and on several packages of photographic papers of the same and different emulsion runs (different emulsion numbers) (Fig. 3). The second battery of analyses tested the accuracy and reproducibility of XRF measurements. A series of consecutive analyses were conducted on a single sheet of photographic paper analyzed under several different operating conditions (accelerating voltage and emission current of the X-ray tube) without changing the geometry of the experiments. The identical analyses were repeated several times across several days after complete shut down and re-start of the XRF spectrometer. To conduct each of these measurements, the X-ray tube was warmed up and equilibrated for more then twenty minutes. We have also studied the effect of the sample-XRF spectrometer geometry. These experiments have shown that even a small (1mm) increase of distance between the analyzed sample and the “nose” of the XRF spectrometer decreases the intensity of measured X-rays by about 15% (Barium La peak) and that the well defined and highly reproducible experiment geometry is critical for the success of actual measurements on real photographs. Our preliminary test led us to to modify the XRF instrument and to develop a standard operating protocol for the quantitative analysis of the baryta layer of photographic papers.



Figure 3. Several experiments were conducted to determine the uniformity of mechanically coated photographic papers.

## STANDARD OPERATING PROTOCOL

Our laboratory has at its disposal several laboratory grade and portable XRF spectrometers that are used for different aspects of GCI conservation science research. In our research in photographs our main tool for the inorganic analysis is the Keymaster TRACeR III XRF

spectrometer equipped with a Rhenium anode X-ray tube and an aluminum/copper sandwich primary beam X-ray filter. We have modified the instrument for the quantitative analysis of photographs by attaching a 4x 4" square 1mm thick geometry restrictor plate made of Lucite. The geometry restrictor plate, when slightly touching an analyzed photograph keeps constant distance between a photograph and the XRF instrument. The geometry restrictor plate also allows one to keep the spectrometer perfectly perpendicular to the analyzed photograph as needed for the quantitative analysis (Fig. 4). The X-ray tube is operated at 40kV at 12  $\mu$ A emission current in the air and at 15kV at 12uA under vacuum. Due to the low concentration of key elements in photographs we are collecting spectra for 300 seconds. The longer analysis time also provides for good statistics when interpreting the quantitative results of the analysis.

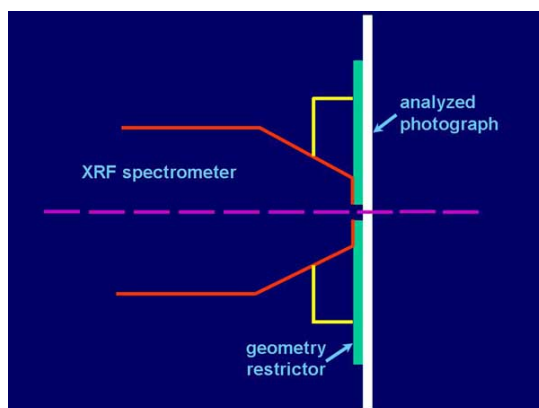


Figure 4. Simple modification of the XRF spectrometer allows for well defined and reproducible analysis of photographs.

## CALIBRATION STANDARDS

The new scientific methodology for the provenancing and authentication of photographs will have an impact on research in photographs and on the photograph art market as well as on solving important problems related to forgeries of photographs only when it would provide means for other photograph experts to adopt our methodology in their work. To achieve that goal it is important to prepare a set of high quality quantitative calibration standards that would allow for the identical calibration of all XRF instruments around the world that may be used in such tasks.

We have prepared and analyzed a set of analytical standards containing barium sulfate and strontium sulfate in different concentrations and in concentrations covering the whole range of concentrations of barium and strontium previously determined in samples of photographic papers from both the GCI and Paul Messier's collection of baryta coated photographic papers [14]. Because of already proven macroscopic lateral homogeneity of baryta coating on photographic papers we have selected a number of existing photographic papers with different concentrations of both elements. Each photographic paper was thoroughly fixed to remove silver halide components of photographic emulsion, leaving behind a paper substrate covered with a baryta layer and a thin layer of gelatin. Out of each fixed photographic paper we cut a circular (1-5/8" diameter) target for the XRF using a 1-5/8" metal punch. Five smaller samples, 5/16" diameter, were removed from the area surrounding the larger target for the Neutron Activation Analysis (NAA). The NAA analysis was selected because of its high sensitivity, high precision and low level of spectral interferences. The fact that samples of photographic papers could be analyzed without any chemical treatments and preparation was also an important factor for the selection of the NAA analysis. Samples were sealed into special ultrapure polyethylene vials designated for NAA analysis and were loaded into the rotary rack of the nuclear reactor together with a number of NIST trace element standards and

blanks. Samples were irradiated in a Triga nuclear reactor at 250kW of power which generated a thermal neutron flux of  $10^{12}$  neutrons/cm<sup>2</sup>sec. Samples were irradiated for 30 minutes and allowed to decay for 30 min. prior to counting. The samples were counted for 4 minutes using a Camberra gamma ray spectrometer. The resulting barium and strontium analytical standards (Fig. 5) can be used to calibrate any current or future XRF spectrometers that are or will be used in the provenancing and authentication of baryta layer based photographs.



Figure 5. GCI-Messier barium and strontium standards for the quantitative XRF analysis of baryta coated photographic papers.

## TEST OF WORKING METHODOLOGY

To test the new authentication and provenancing methodology on real photographs we printed nine identical 8x10" photographs on several well known and widely used photographic papers that were commercially available in the year 2000. A randomly selected print from this test set was printed twice and it was used as an "unknown" for the test. Even when we tried to print all of the photographs to achieve identical contrast and tonality, there were some slight contrast and tonality differences between several prints in the sample set. These differences are "engineered" into different photographic papers by the manufacturer and can serve as clues in the identification process to knowledgeable experts. To prevent any contrast or tonality clues when comparing the "unknown" with a set of different photographs, the "unknown" print was toned dark brown using a selenium toner. A group of leading photography conservators, museum curators, dealers of photographs, auction house experts and photography appraisers attending the Baryta Layer symposium [14] was asked to identify the "unknown" visually but none of whom were able to correctly identify the paper the "unknown" photo was printed on. All of the photographs in the test set were previously analyzed using XRF spectrometry following the above described standard operating protocol. Six consecutive analyses were performed on selected D-min areas of all photographs in a test set and spectral intensities for both barium and strontium in each photographic paper were plotted on an X-Y graph together with corresponding standard deviation fields. The "unknown" sample was analyzed only once (during a live demonstration) using the identical experimental conditions of previous measurements conducted on the test set of samples. The quantitative XRF analysis for barium and strontium in the "unknown" photograph when compared with analytical data of the test set of photographs allowed for the correct identification of the "unknown" photograph as being made on Forte Elegance Glossy FB Grade 2 B&W photographic paper (Fig. 6). We have also shown that the inclusion of other quantitative chemical analysis data (concentration of calcium) or physical measurements of photographic paper or photographs (overall thickness of a photographic paper) would provide means for confirmation of the XRF results.

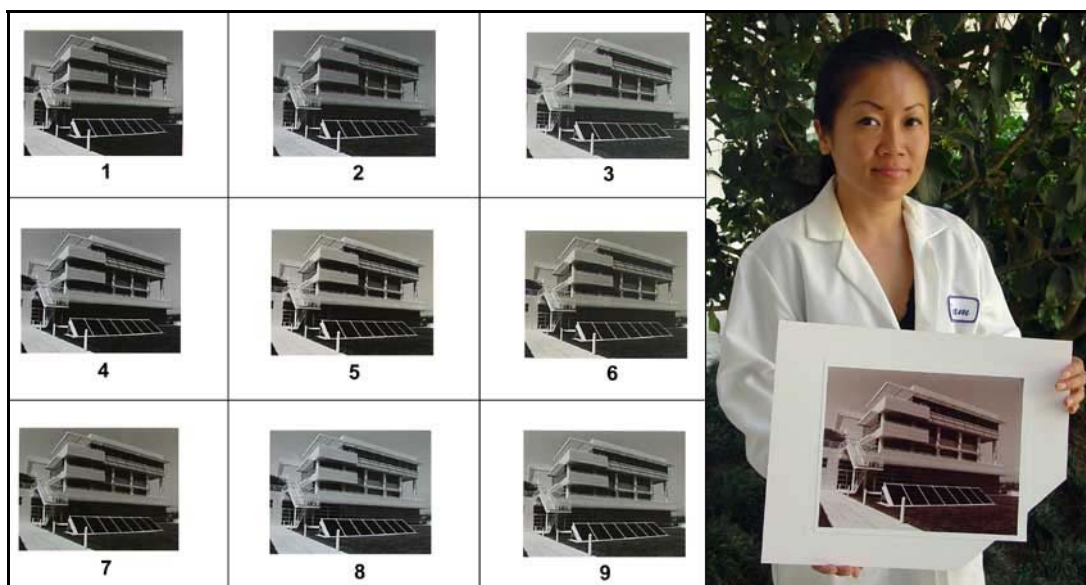


Figure 6. Nine photographs were printed on different photographic papers. XRF analysis correctly identified the selenium toned "unknown" photograph on the right as being printed on paper #8 from the test set.

## REFERENCE MATERIAL DATABASE

All the preliminary test of our methodology indicated its great potential when dealing with many important questions related to provenancing and authentication of photographs. At the same time the ultimate success and the broad application of the new methodology depends on access to a high quality database of analytical data obtained from the analysis and characterization of numerous historical and current samples of photographic papers.

Silver gelatin photographic papers were first introduced during the late 1880's, first as "printing-out papers (POP)" and later as "developing-out papers (DOP)". We do not know too much about early baryta coating technology but by the beginning of the 20<sup>th</sup> century, silver gelatin photographic paper was prepared mechanically and contained a very uniform and homogeneous baryta layer. Besides the major manufacturers of photographic papers such as Kodak in the US, Ilford in the Great Britain, and Agfa in Germany who produced photographic papers throughout the 20<sup>th</sup> century there were many other smaller manufacturers in many countries of the world producing photographic paper during a limited periods of time. Each manufacturing company produced a number of different types of photographic papers and introduced or changed their product lines often. For example in the year 1947 the Kodak company offered several basic and specialized photographic papers (Athena, Azo, Velox, Velox Rapid, Opal, Platino, Kodabromide, AD Type, Illustrators' Azo, Illustrators' Special, Royal Bromide, Resisto, Resisto Rapid, Studion Proof, and Portrait Proof). These photographic papers were available in several different contrast grades, with different surface textures and coated on paper stocks of different tints [15].

Working with samples of historical photographic papers from the Paul Messier collection of photographic papers and with more then 500 different photographic papers from the Getty Conservation Institute (GCI) Reference Collection we were able to plot the concentrations of barium and strontium in analyzed photographic papers into an X-Y graph (Fig. 7). The graph illustrates the range of concentrations of both elements in frequently used photographic papers. The same type of photographic paper produced in different years might have different chemical composition or its composition might change due to changes in technology or due to changes in the sources of raw materials.

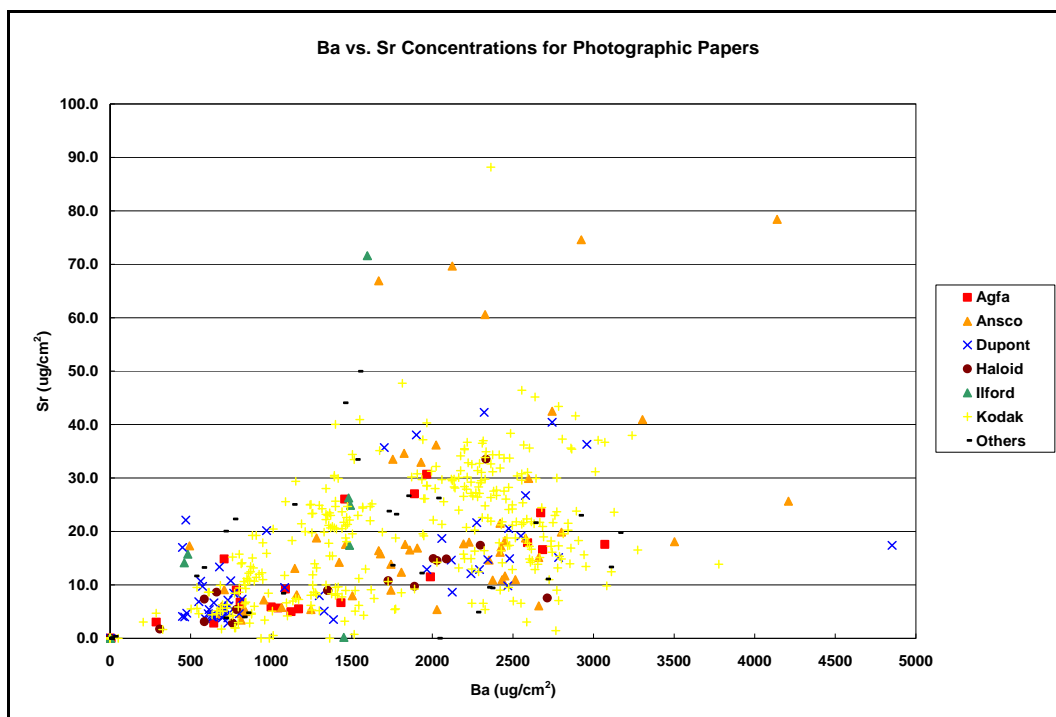


Figure 7. Results of the XRF analysis of more than 500 different 20<sup>th</sup> century photographic papers.

To use our methodology for the identification of photographs without limitations (not counting concentration overlaps due to similar composition for both elements) would require access to the ultimate database of all photographic papers ever produced by all manufacturers during their manufacturing periods. A general strategy that can be applied in order to match analytical data from the analysis of an unknown photograph with analytical data from a database of “all” photographic papers is schematically depicted below (Fig. 8).

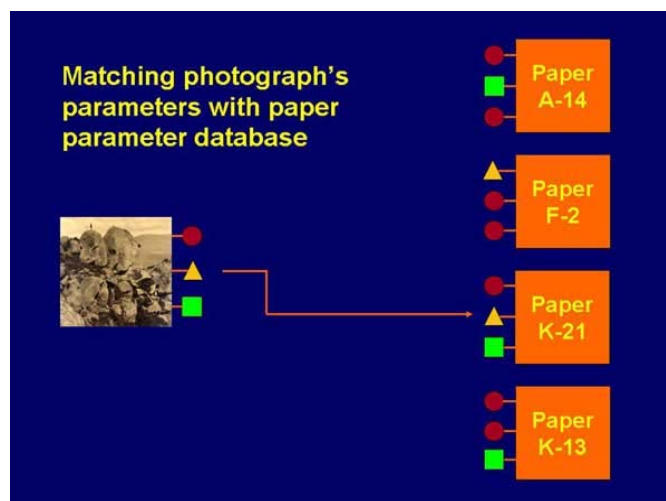


Figure 8. General strategy for matching analytical parameters of unknown photographs with analytical parameters of the photographic paper database.

When we started our systematic analysis of photographic papers (summer 2000) it was our hope that many samples of historical photographic papers would be available from well organized and preserved archives of the major photographic papers manufacturing companies still in business. It was a very disappointing when we found that such archives do not exist now and if some of them were in existence in the past they do not exist now. The situation is

even more critical now (2008) when a number of photographic paper producing companies stopped the production of silver gelatin photographic papers [16].

There are several museums of photography and museums of science and technology that keep some materials related to the development of the photochemical industry and there are some collectors of “photographica” interested in collections of historical photographic papers. As far as we are aware there are only two major photographic paper collections (the GCI Reference Collection of Photographic Material and Paul Messier’ Collection of Historical Photographic Paper [17]) in existence now that actively collect historical and still available photographic material and are engaged in the scientific analysis and characterization of photographic papers.

It seems to us that a chance to build up a very comprehensive database of analytical data on photographic paper is very slim and that the only chance to even approach that ideal collection would need to be based on a very broad and active international collaboration of many institutions and individuals interested in advancing research in photographs. An appeal for help to build such a collection of photographic papers addressed to the broader public has appeared on the Getty Museum Web page and resulted in a substantial increase in the number of photographic papers in the GCI collection [18].

#### **WORKING WITH “INDIVIDUAL DATABASE SEGMENTS” (IDS)**

Reading about the virtual impossibility to build up a comprehensive collection of photographic papers as need for the provenancing and authentication of photographs might be rather discouraging but our research has indicated a possibility to use our methodology even when there is no comprehensive and complete collection of analytical data or photographic paper available.

Many photographers and printers liked to experiment with different photographic papers but many of them also developed a close attachment to certain kinds and types of photographic papers. That was the reason why most art photographers opted for working with a small number of photographic papers and changed their selection only with changes of their “print aesthetics” or when their favorite papers were not available or did not provide good and consistent results. This observation, supported by our own photographic experience, has led us towards a working concept of the so called “Individual Database Segments (IDS)”. Instead of having available a database of all photographic papers ever produced, to solve targeted provenancing and authentication problems dealing with the body of work of an individual photographer, the researcher can work only with a segment of a comprehensive paper data collection that relates to an individual photographer (Fig. 9). For example if there would be a questionable Man Ray photograph on the market or in a museum collection, a researcher dealing with the authentication task would need to conduct the XRF analysis of the photograph using a properly calibrated XRF instrument and to compare analytical results with Man Ray’s IDS. The Man Ray IDS would be created by analyzing many well authenticated and provenanced Man Ray photographs created throughout his photographic career. Some important information about the use of photographic paper by an individual artist could be also obtained in collaboration with art historians or historians when consulting photographers’ records, business documents, photographer’s writings or his/her darkroom notes.

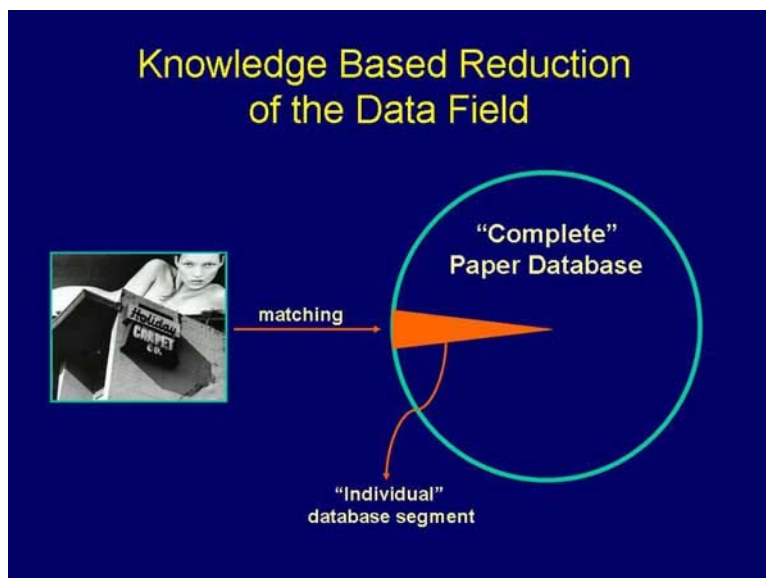


Figure 9. Authentication of photographs using the Individual Database Segments (IDS).

## CONCLUSIONS

Our preliminary tests and small scale real photograph provenancing tests have proven the viability of our original idea that the quantitative analysis of silver gelatin, baryta coated, fiber based photographs might be used to develop a scientifically based methodology for the provenancing and authentication of 20<sup>th</sup> century photographs. Our follow up research and experiments targeted the preparation of high quality barium and strontium XRF standards that can be used in the quantitative calibration of any XRF instrument. We have also developed a standard operating protocol for the highly reproducible quantitative XRF analysis of photographs. Our large-scale analysis of more than 500 photographic papers from the GCI Reference Collection and from the Collection of Historical Photographic Papers of Paul Messier has shown a range of concentrations of barium and strontium in different types of photographic papers manufactured by more than twenty different manufacturers throughout the 20<sup>th</sup> century and the beginning of the 21<sup>st</sup> century. A small-scale test of our methodology, when applied to identification of real samples of photographs, has shown that the quantitative XRF analysis can be used in the identification of photographs. Our investigation also showed that the inclusion of another quantitative parameter related to a particular photographic paper can increase the quality of a match between the unknown photograph and data from the photographic paper database.

The future success of our methodology for provenancing and authentication of photographs and its application in research of photographs depends on the availability of a large database of analytical data related to photographic papers produced during the era of silver gelatin, baryta coated photographic paper. We have also developed a working strategy on how to use our analytical methodology when dealing with provenancing and authentication of photographs of an individual photographer. The art historical research and analysis of photographs representing all known photographic papers used during a lifetime of a photographer, so called "Individual Database Segments (IDS)" can be built that can be used to solve important provenancing and authentication problems related to a particular photographer (L. Heine, Man Ray etc.).

Our current research is focused on testing of different aspects of our methodology when working with collections of photographs and when developing IDS's for pre-selected

photographers. We are also exploring the possibility of expanding the photographic paper database to include additional quantitative chemical and physical parameters of photographic papers and photographs that would improve matches between unknown photographs and the photographic paper database or photographer's IDS.

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