



Article: The Atlas of Analytical Signatures of Photographic Processes: Its Past, Present, and the Future

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The Atlas of Analytical Signatures of Photographic Processes: Its Past, Present, and the Future

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*Presented at the 2013 AIC & ICOM-CC Photographs Conservation
Joint Meeting in Wellington, New Zealand*

Abstract:

The idea for the Atlas of Analytical Signatures of Photographic Processes precipitated from a November 2000 George Eastman House expert meeting of photograph conservators, conservation scientists and historians of photography that identified a pressing need for the development of an advanced, more objective methodology for the identification of photographs and photographic material as one of the most important topics of the conservation science field for the photograph research community. GCI scientists prepared the ground for the Atlas work by reviewing, modifying and optimizing the methodology of X-ray fluorescence spectrometry (XRF), Fourier Transformation Infrared Spectrometry (FTIR) and Digital Microscopy for its use in the scientific and analytical investigation of photographs. A critical review of historical literature sources related to the technical history of photography allowed for the identification of over 130 photographic processes that were actively researched and used during the so-called “chemical photography” era. The most challenging part of the Atlas project was, and still is, the locating of well documented and correctly identified samples of important process variants, rare photographic processes and samples of post-processing treated photographs. Only when identifying, confirming and re-confirming recorded analytical signatures were GCI scientists able to describe the morphological qualitative and quantitative signatures typical for each photographic process. Including examples of interpreted XRF and ATR-FTIR spectra for each photographic process, process variant and post-processing treated photograph provides important guidance for conservators and conservation scientists unfamiliar with a particular photograph or photographic process in question when solving difficult and confusing process ID cases. Scheduled to be published in an advanced electronic form the Atlas will serve both as a tool for the systematic investigation of photographs and photographic collections and also as a quick reference for solving targeted ID questions. This paper will provide insight into the multifaceted research towards the publication of the Atlas.

Introduction:

A major goal of the November 2000 expert meeting at the George Eastman House was to discuss and specify research priorities for the scientific research of photographs and photograph conservation and to, even when indirectly, help to delineate several possible directions for, at that time, the new and developing conservation research program at the Getty Conservation Institute. After two days of discussions the need for a new, scientifically based, advanced methodology for the identification of photographs and photographic processes ended up on top of a virtual pyramid of discussed ideas and research topics. That research area also corresponded well with previously developed expertise of GCI scientists in the application of modern scientific

and analytical methods in the analysis and scientific studies of paintings, stone and metal objects and previously conducted targeted studies of photographs.

The idea for the Atlas of Analytical Signatures itself precipitated from a visit to the Logical Image Inc. research facility in Rochester. Working in the dermatology field on site, dermatologists and image scientists created an atlas of dermatologic diseases. A need for such an atlas started to be acute with a heavy increase in international travel and with the import of dermatologic diseases that are very rare in the US and that most practicing dermatologists have had little opportunity to see or diagnose.

That situation is very close to the current situation in the research, conservation and preservation of photographic heritage. Most conservators of photographs, curators and collection managers are well trained in recognizing major and common types of photographic processes but are very hesitant when dealing with unusual or rare photographic processes that do not have clear visual or microscopic signatures to identify them or differentiate them from more common photographic processes. That situation is even more complicated by the fact that often older registrar information attached to collections of photographs often does not contain information on the photographic processes used to create photographs. Even when some process information has been attached to individual photographs in the past, it is not certain that the process information is accurate or complete.

What makes the process identification important for all photograph heritage professionals is that photographs, even when looking rather simple, usually have a complicated chemical and physical internal structure and without understanding the details of the environmental, chemical and light stability of all of the chemical elements and compounds that make up a photograph it is difficult or impossible to specify safe conditions for exhibition, long term storage or active conservation treatment of photographs.

The GCI's research towards the Atlas of analytical signatures started with a "technology transfer" of existing analytical methods already used in the analysis of museum objects and collections and testing and modification of other research methodologies for specific needs of the analysis of photographs. The GCI scientists also developed several new analytical methodologies and analytical procedures to answer some specific problems related to the identification and analysis of photographs.

Once all needed analytical methodologies were developed and tested GCI scientists embarked on a systematic analytical survey of photographic processes. Our visual, microscopic and analytical investigation of thousands of photographs from the GCI's Study Collection and collection of a number of important museum collections of photographs (J Paul Getty Museum, Harry Ransom Center at the University of Texas at Austin, George Eastman House, National Media Museum, Société Française de Photographie, etc.) has shown that the visual observation of a well trained eye can easily identify about 50% of photographic processes with a very high level of accuracy. Using a high power loupe or a quality stereomicroscope to examine the image microstructure and visible layering structure of photographs increases the number of photographic processes that can be securely identified to about 80% of all photographic processes. Non-destructive or noncontact scientific analysis of photographs plays a very important role in providing very objective data

that can be used to validate the results of both visual and microscopic study of photographs and in the identification of the about 20% of remaining photographs that are difficult or impossible to fully identify using their visual or microscopic signatures (Fig. 1).

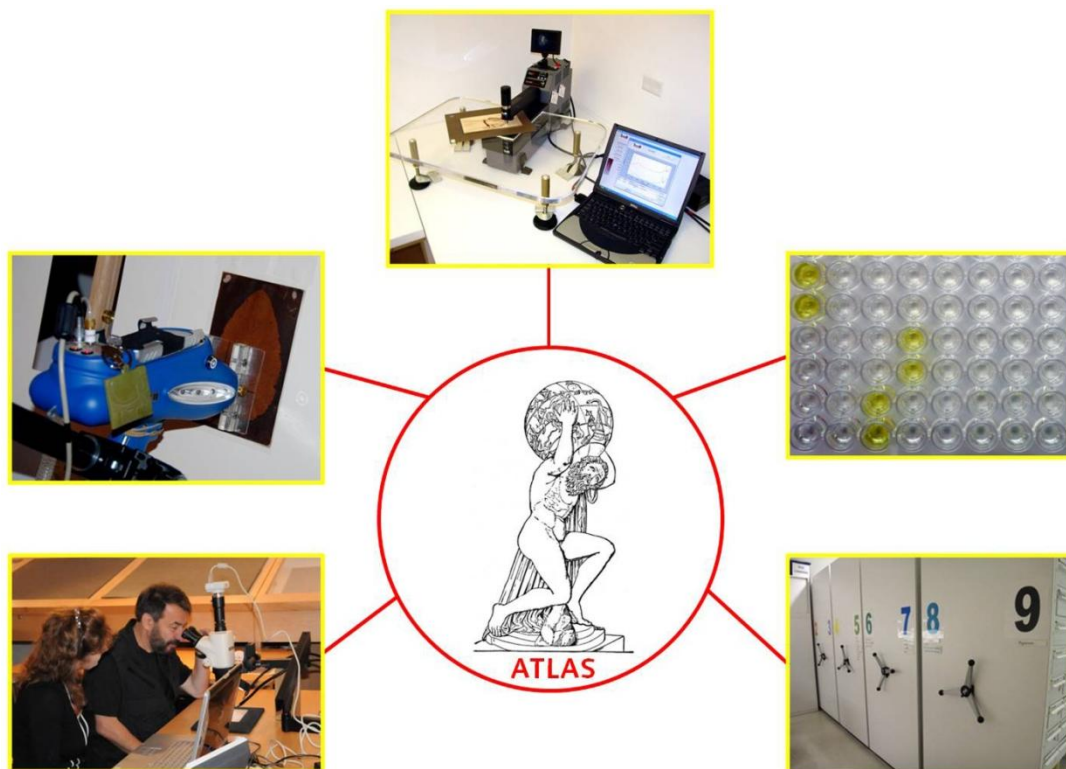


Fig 1. Different analytical tools and the GCI reference collection used by GCI scientists when studying and identifying photographic processes.

Our practical experience, when using our analytical tools and Atlas data when identifying photographs, has showed us that we are able to identify very close to 100% of difficult identification problems. Some of the unresolved ID cases for photographs are mounted in such ways that we have limited analytical access to the image layer. There are also some variants of photographic processes that have almost identical chemical compositions that are beyond the limits of today's non-destructive analytical technology (low concentration of some trace elements in photographic negatives, dye concentration and layer thickness of modern color material, presence of some light elements such as lithium and boron and fluorine in photographic materials). We are very positive that the future development in the sensitivity and resolution of instrumental methods of analysis will allow for even more precise and detailed analysis of photographs and photographic material.

Photographic Processes and Process Variants

In our published articles, lectures and when explaining our research project to visitors of our laboratories we often talk about more than 130 different photographic processes that have been invented, developed, abandoned or replaced since the dawn of photography in early years of the 19th century. This number is based on our in-depth review of photographic literature and several

already published books on photographic processes and their identification (Krivanek 1953; Coe and Haworth-Booth 1983; Reilly 1986; Nadeau 1989; Cartier-Bresson 2007; Lavedrine 2009). The number 130 is more an arbitrary number of the most important and the most common photographic processes. We are well aware that to specify a precise number of photographic processes would be very difficult or impossible and that it is often even difficult to specify what is a true photographic process and what is just a process variant. Figure 2 illustrates just a small number of different photographic processes collected and studied by the GCI Photo Project team that are now an integral part of the GCI Reference Collection / Study Collection of Photographs and Photographic Processes.



Fig. 2. The GCI Reference Collection – A small example of our extensive study collection of photographs and photographic material.

The Current Structure and Organization of the Atlas

Our goal, when developing the organization and structure of the Atlas was to achieve a high level of consistency between individual Atlas chapters that would allow a reader familiar with one part of the Atlas to feel comfortable when moving between all of the Atlas' individual parts. We also wanted to allow for a relatively easy format change between the current and future versions of the Atlas and for easy modification of existing material or for addition of new chapters and the addition of new data, images and spectra and references. The following is a description of the information that makes up each chapter in the Atlas.

Chapter Title

Titles of all individual chapters of the Atlas are based on the common English name of the photographic process used by today’s photograph historians and conservators of photographs. When available or known other English synonyms are also included. Both German and French names of the process are also included together with notes, if needed, on difference between the use and meaning of individual terms (for example: tintype, melainotype, ferrotype, etc.).

Invented by...

When well known the name of the inventor and a known or generally accepted date of invention or known first publication of the process is stated.

Historical Background

Each process chapter has brief historical background information related to the invention or discovery of the process as well as important data on further developments, improvements and modifications of the process, its manufacturing and all available data that would allow for the establishing of exact or estimated “terminal dates” for the use or manufacturing of photographic materials. In some cases a simple or more complex graphical historical timeline is included that allows for quick orientation in the historical aspect of the given photographic process (Fig. 3).

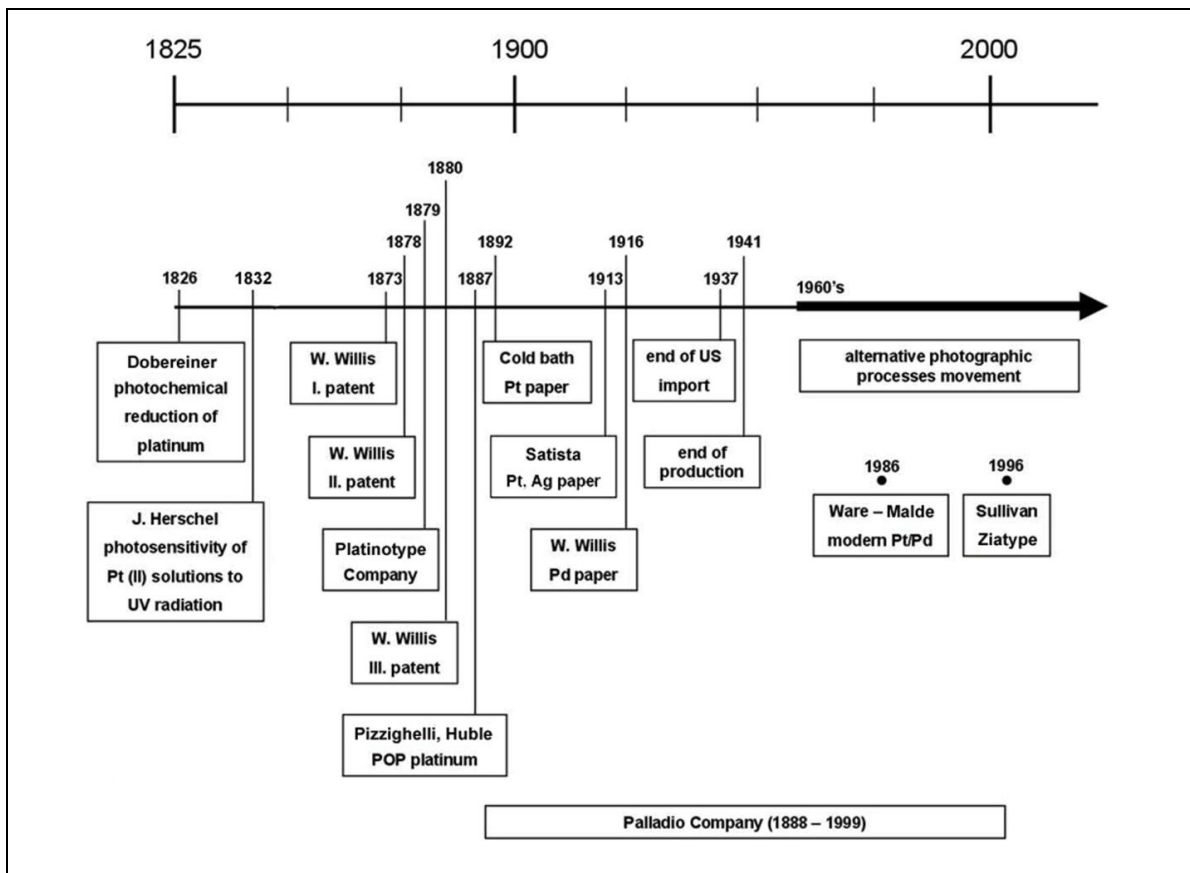


Fig. 3. Timeline of the Platinotype process.

Process Description

The knowledge of all chemicals used to prepare or manufacture photographic material and used during processing or potential post processing of photographs and the knowledge of all individual steps and procedures used to prepare and process photographs is very beneficial when analyzing photographs and interpreting analytical results. The use of some chemicals, directly or indirectly used when making or processing photographs, might leave some detectable traces of material within the processed material that can be used as chemical markers of the photographic process (the presence of iron even in well cleared platinotype photographs, the albumen subbing layer of silver gelatin based glass negatives, the presence of a titanium dioxide filled polymer in RC photographic paper, etc.).

The process description included in the Atlas is based on the most common and highly used procedure known in the photographic literature. Some more complicated process sequences (e.g., different versions of carbon processes) are graphically depicted.

Noted Photographers Using the Photographic Process

A short list of well known photographers that are known for using the process is included. This might be useful for a reader when looking, in literature or on the web, for visual signatures of a process that can be used to aid in the identification.

Important Variants of the Process

A number of photographic processes were often further developed or modified by other researchers. For example the platinotype process was changed and improved several times by its inventor, and further modified by others. The Palladiotype variant of the platinotype process was developed to deal with restrictions on the use of platinum during WWI and the Satista platinum-silver hybrid process was developed in response to the rising platinum prices. Glycerin developed platinotype photographs allowed for localized development of the image according to the fashion of the time. During the revival of the platinotype printing process in the 1960's and 70's artist started to use mixed platinum-palladium chemistry. Several new modifications of the platinotype process were introduced in later part of the 20th century (e.g., Ziatype). When the chemistry of individual variants of a particular photographic process differs substantially, instrumental methods of analysis can be used to identify not only the photographic process but the particular variant of the process as well.

Important Patents

A large number of photographic processes were patented and described in photographic patent literature (Foley 1979; Schimmelman 2002; 13]. The patent literature provides some important data related to many different photographic processes but reading and interpreting patent literature is often difficult and sometimes rather confusing. Contemporary patent literature and patent search sites provide, too often, too many patents with small variants in process chemistry or material processing to be beneficial in photograph ID studies. Only the key patents for each photographic process, if any, have been included in the Atlas.

Photographic Process ID Tools

Each chapter of the Atlas contains information on all important visual characteristics of a photographic process or useful hints that can be used to aid the process identification. Some examples include how the RC photographic paper feels between fingers; that the typical topography of carbon prints can be observed under raking light or that localized darkened areas of older platinotype prints may indicate the use of the glycerin development method (Fig.4).

Microscopic Signatures

The microscopic signature part of each chapter of the Atlas contains several microscopic details recorded from a typical example of a photograph of the particular photographic process. Recorded under a range of different magnifications the microscopic images can be used directly for process identification based on a side by side image comparison. When useful for process identification, some typical examples of photograph damages (e.g., emulsion abrasion of glossy collodion photographs) are also recorded and provided as identification tools. Microscopic images also show images areas (usually photograph edges or corners that might help to identify the layered, internal structure of the photograph). When available some SEM images (even though these are not non-destructive) are included to demonstrate or explain the image layer structure that might be typical for a given photographic process (Fig. 5).



Fig. 4. Some typical visual characteristics (signatures) of photographic processes.

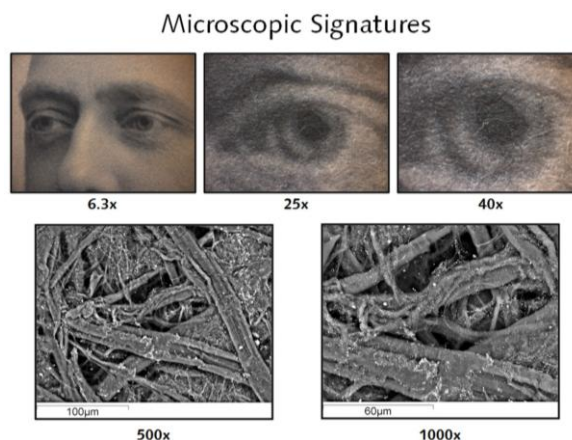


Fig. 5. Typical Microscopic Signatures of Photographic Processes.

XRF Analytical Signatures

The XRF analysis of photographs provides important information on the presence or absence of about 25 different chemical elements that have been identified by GCI scientists when analyzing thousands of historical and modern photographs (Stulik and Kaplan 2012). Besides the simple presence or absence of certain chemical elements the simultaneous presence of several elements in a photograph provides very important information that can be used when identifying a photographic process (e.g., the simultaneous presence of both platinum and iron and the absence of silver would strongly indicated that the analyzed photograph belongs to the platinotype category of photographs. XRF spectra recorded both at the maximum image density (D-max) and minimum image density (D-min) areas of the photograph and sometimes also spectra recorded

from the back of an unmounted photograph and mounting board or mounting substrate might be used to understand both the elemental composition and sometimes also the layering sequence within a photograph or mounted photograph package (Fig. 6).

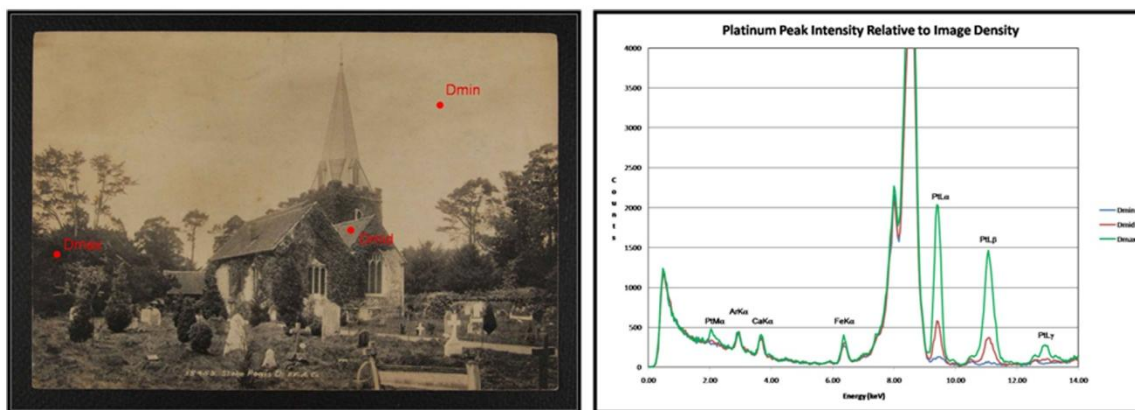


Fig. 6. XRF analytical signatures showing a difference between spectral intensity of key elements in the D-max and D-mid and D-min areas of the photograph.

FTIR Analytical Signatures

The identification of the organic components within an analyzed photograph is a very important step when identifying photographs. Organic material (gelatin, albumen, collodion) are major binders of imaging metals and compounds within the image layer of a photograph. Paper and organic polymers (cellulose nitrate, various cellulose acetates, polyesters, etc.) are important components of both negative and positive photographic materials. Identification of a polyethylene layer on the back of a B&W or color photographic paper allows one to identify a modern RC photographic material. Many different organic coatings and varnishes have been used during the almost 200 years of photography in order to protect the image layer against environmental effects or to modify its appearance (glossy, matte, semi-matte, etc.). More detailed and semi-quantitative analysis of photographs can also provide some important information on the presence of external or internal sizing material within a paper substrate of a photograph. By sampling several layers of a photograph ATR-FTIR analysis can also provide some information on the internal layering structure of a photograph (e.g., simultaneous detection of paper substrate, albumen in the image layer and thin organic varnish of many 19th century albumen photographs).

ATR-FTIR analytical signatures

Peak Location (approximate)	Identification
3330 cm^{-1}	OH - free
2900 cm^{-1}	C - H, CH_2 , CH_3 stretching
2850 cm^{-1}	C - H, CH_2 , CH_3 stretching
1635 cm^{-1}	adsorbed water
1420 cm^{-1}	C - H
1315 cm^{-1}	C - H
1200 cm^{-1}	C - OH, C - CH
1155 cm^{-1}	ring breathing
1105 cm^{-1}	C - O - C glycosidic
1050 cm^{-1}	C - OH (2° alcohol)
1025 cm^{-1}	C - OH (1° alcohol)
895 cm^{-1}	C - O - C in plane

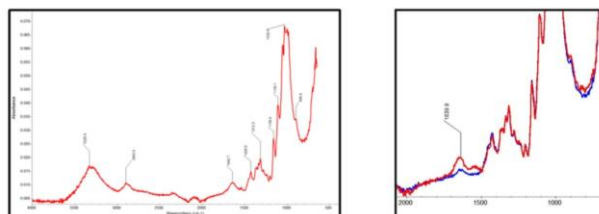


Fig. 7. ATR-FTIR analysis of a photograph showing a portion of a spectra interpretation table from the Atlas.

All modern FTIR instrument in conservation laboratories use different commercial spectra libraries when aiding analysis and interpretation of FTIR results. Most of these industrial spectra libraries contain information on a large number of different single species and pure organic materials and such spectra libraries have limited use in conservation science practice which, usually, deals with the analysis of impure and often well aged and deteriorated organic materials and material mixtures. This was the main reason why conservation scientists at the Getty Conservation Institute initiated the work on an art conservation library of infrared spectra that later morphed into the current IRUG spectra library (IRUG 2013). Even the IRUG library of FTIR spectra is limited when dealing with the identification of the complex, multi-component layered structures of many photographs and photographic materials. FTIR spectra included in the Atlas typical for all of the main photographic processes and many process variants will aid greatly in the FTIR analysis of photographs (Fig. 7).

Other Analytical Signatures

The analytical methodology covered in the Atlas focuses namely on utilizing non-destructive methods of analysis that do not require any physical sampling. There are many instances, in conservation science investigations, when small samples of analyzed objects are available for analysis and some other (very often more sensitive) methods of chemical analysis can be used (e.g., the analysis of traces of iron based developer on micro flakes of collodion emulsion found on the bottom of a negative container or sample of varnish material flaking from the back side of a photograph). Some information on other analytical methods for further and more detailed analytical investigation of photographs is also included in the Atlas.

Post Process Treated Photographs

Many existing photographs have been post process treated (a treatment that is not an integral part of the photographic process). In many cases such a treatment was done as part of the processing of a photograph or it could have been done later on. Some examples of post-processing treatment include the archival selenium toning of photographs or varnishing of photographs for an exhibition. The identification of the post-process treatment of photographs provides valuable insight into the darkroom technique of a photographer, photograph printing laboratory or studio (Fig. 8).

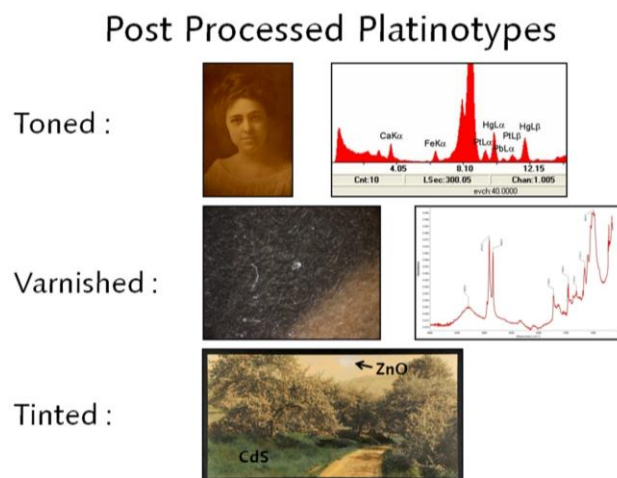


Fig. 8. Examples of various post-process treatments of photographs.

Identification Table

Identification tables included at the end of each individual chapter of the Atlas might be the most important tools for the advanced identification of photographs and photographic processes. The identification tables provide summaries of all visual, microscopic and analytical clues obtained during the investigation of a photographic process and allow one to compare these clues with other photographic processes and process variants that are easily or often misinterpreted during process identification. Tables indicate both key and supporting clues needed to identify and confirm the identification of a particular photographic process or a photograph (Fig. 9).

Tonality	Process	Surface Coating	Paper Fibers	Pt	Pd	Fe	Hg	Ag	Au	Ba	Cellulose	Gelatin	Collodion	Others
black	platinotype	-	X	X	-	X	-	-	-	-	X	-	-	-
	Pt / Pd	-	X	X	X	X	-	-	-	-	X	-	-	-
	varnished Pt	X	X	X	-	X	-	-	-	-	-	-	-	X*
	matte collodion	X	-	<X	-	(X)	-	X	<X	X	-	-	X	-
	Gevaluxe	-	X**	-	-	-	-	X	-	(<X)	X	-	-	-
	Satista	-	-	X	-	X	-	X	-	-	-	<X	-	-
	palladiotype	-	X	-	X	X	X	X	-	-	X	-	-	-
brown	hot dev. Pt	-	X	X	-	X	-	-	-	-	-	-	-	-
	Pt / Pd	-	X	X	X	X	-	-	-	-	X	-	-	-
	Hg toned Pt	-	X	X	-	X	X	-	-	-	X	-	-	-
	matte collodion	X	-	<X	-	(X)	-	X	X	X	-	-	X	-
	silver gelatin	X	(X)	-	-	<X	-	X	-	(X)	-	X	-	-
	kallitype	-	X	-	-	X	-	X	-	-	-	-	-	-
	tannin toned cyano	-	X	-	-	X	-	-	-	-	X	-	-	X***
	U toned Pt	-	X	X	-	X	-	-	-	-	X	-	-	X†
Ziatype	-	X	-	X	X	-	-	(X)	-	X	-	-	X#	

X – present
 - – absent
 (X) – may be present
 X* – often wax or linseed oil
 X** – unique image structure under a microscope
 X*** – presence of a very characteristic CN spectral peak

Fig. 9. The Identification table for a family of platinotype and platinotype-like photographic processes.

The Targeted Audience for the Atlas

The Atlas was developed, planned and written for practicing photograph conservators, conservation scientists and curators and managers of collections of photographs who might need to identify more unusual photographs. The Atlas would also aid individuals studying the darkroom techniques of a photographer’s work or changes in his or her darkroom techniques due to different available photographic technologies or the outside influences of other photographers. Students of photograph conservation will also benefit when from the Atlas as an information resource on past photographic processes, their chemistry and identification.

Not all photograph conservators or curators have easy access to a well equipped conservation science laboratory and staff with an in-depth knowledge of the technical and chemical aspects of photography. At the same time, many photograph conservators or curators have access to art conservation laboratories experienced in analyzing paintings or other objects along with conservation scientists well familiar with XRF or FTIR analysis but often without experience in

the analysis and interpretation of analytical data obtained from the analysis of photographs. Many local or accessible universities or industrial laboratories may have well equipped analytical laboratories and scientists proficient in the general aspects of chemical analysis but without any experience and knowledge needed to successfully interpret analytical data obtained from analysis of photographs.

The main purpose of the Atlas is to help a conservator and curator formulate analytical questions related to a particular photograph and at the same time to assist a scientist that is not familiar with analysis of photographs when interpreting the analytical data with examples of well characterized and identified photographs for needed spectra matching or comparison. The Atlas also contains a number of interpretation tables that provide help when dealing with photographs of similar analytical signatures, with the identification of overlaps of spectral peaks and with warnings against potential misidentifications or misinterpretations of analytical results.

By combining the individual expertise of a conservator or curator with the analytical expertise of a scientist and utilizing the Atlas as a communication tool between very different professional specializations, many difficult photograph identification problems can be successfully solved.

General Guidelines for the Use of the Atlas when Identifying Photographic Processes:

There are several working strategies on how to use the Atlas when identifying photographs or photographic processes.

- Collect all visual and microscopic signatures of a given photograph. If you are still not sure what photographic process you are dealing with try to identify the imaging metal or imaging compound in a given photograph using XRF spectrometry. The XRF analysis will provide you with information not only on imaging material but also on the presence of toning metals and on inorganic elements contained in the substrate of the photograph.
- Using FTIR spectrometry attempt to detect and identify the presence of an organic binder in the photograph. Beware that the top layer of the photograph might be coated with an organic coating or varnish that might shield the analytical signal from the organic binder!
- Compare all of the collected visual, microscopic and analytical signatures for a photograph in question with the interpretation tables located at the end of each process chapter which may pertain to the work in question. Work first with all interpretation tables that contain a combination of the imaging metal and organic binder detected in the photograph under question. This comparison will help to narrow down your search further.
- Compare all visual, microscopic and analytical signatures of a preselected group of photographic processes (those containing identical imaging metals and organic binder), looking for the best signature match between the photograph in question and a set of photographs with similar signatures.
- In most of the cases the above described procedure yields an accurate and reliable identification of a photograph or a photographic process. If even after recording and

interpreting all signatures the nature of the photographic process is still not certain, there might be a need for using methods that would require micro-sampling to resolve the remaining identification issues. These steps should be very rare and they should not be taken without the approval of a conservator and curator or without consultation with experts in advanced methods of photograph identification.

How will the Atlas and its content be further developed, updated and expanded?

We are expecting that the Atlas will be “live material” that will be periodically modified and upgraded whenever new quality data on signatures of photographic processes will be well researched and confirmed.

The Atlas is projected to be available first in PDF form (Stulik and Kaplan 2013). At the same time we are developing its e-book (iBook) version with enhanced functionalities that would greatly aid a reader or researcher when using the Atlas in their everyday work. Including high resolution images within the iBook version of the atlas, downloaded on today's widely used iPad platform would allow the reader to enlarge all individual images within the Atlas as needed for detailed inspection or comparison with observed or recorded images (Fig. 10). The same type manipulation will be available when working with XRF spectra (Fig. 11).

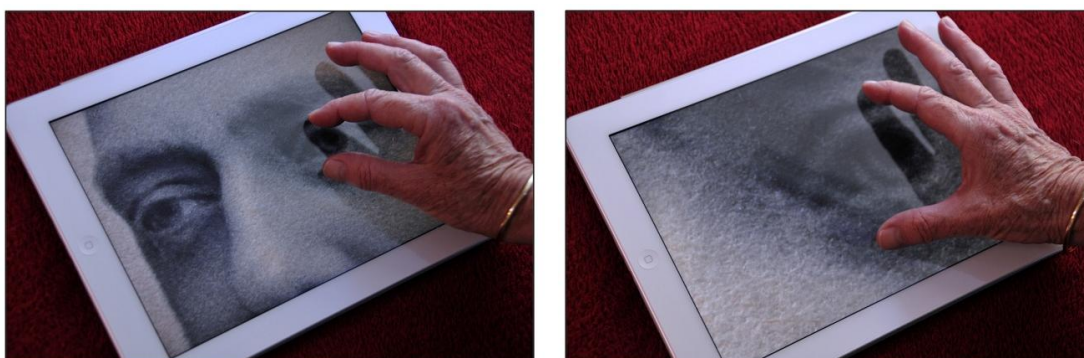


Fig. 10. Finger assisted manipulation of high resolution images of the Atlas.

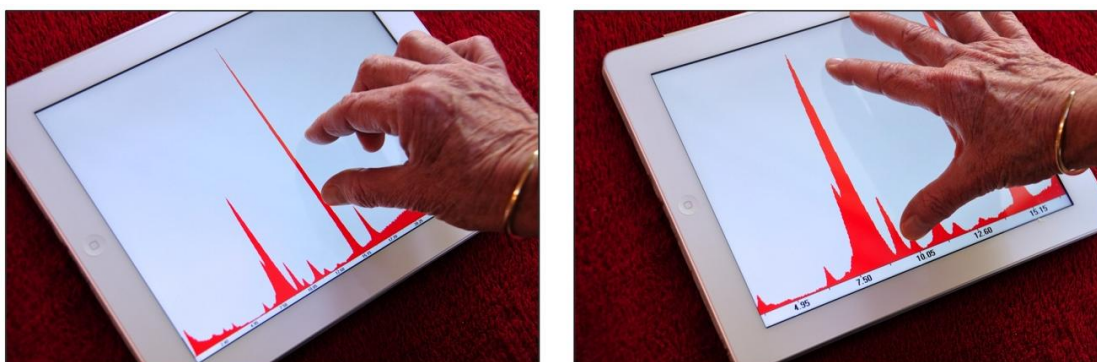


Fig. 11. Horizontal and vertical expansion of an XRF spectrum allows for easier reading and interpretation of analytical results.

Both XRF and FTIR spectra will also provide functionalities that will aid when reading spectra included in the Atlas. Touching a given spectral peak will provide information on chemical elements (XRF) or chemical compounds (FTIR) associated with it, provide warning on potential spectral overlaps and explain different spectra features in the light of the chemistry and internal structure of a photographic process (Fig. 12).



Fig. 12. The interpretation aid shows a typical assignment of a selected spectral peak together with potential spectral interferences.

We have also already started to prepare the ground for the future development of the Atlas. Using advanced methods of photography tailored, computer aided, library searches, chemometric tools and dedicated expert systems (Cartwright 2008) will allow for machine aided interpretation of analytical results and photographic process identification (Fig. 13).

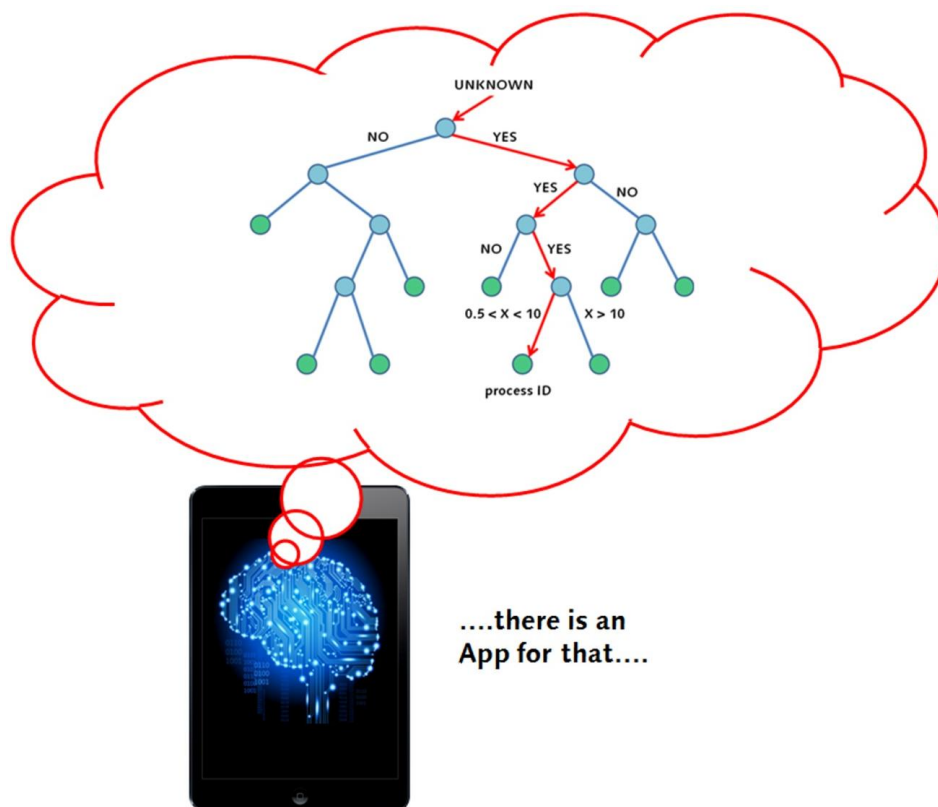


Fig. 13. A vision of computer assisted photograph process identification.

We hope that once all the current uncertainties related to different formats, standards and platform availabilities will be resolved that the Atlas will also be available in additional, fully functional tablet and/or mobile platform versions.

The electronic form of the Atlas should allow for easy additions, corrections and amendment of its content.

The most important and the most difficult part of our Atlas project has been and always will be the identification of well characterized and well identified examples of photographs and photographic processes. Our experience has shown that this part of the project is even more difficult than we could have imagined. Most photographic material in many museums, archives, libraries and private collections is not well identified and in some cases incorrectly identified. Photographs or photographic processes that were not well identified are practically “invisible” to search inquiries of registrar databases or collection records.

Our project experience also shows that the most valuable information leading towards the identification of unusual or uncommon photographic processes in collections is via the personal memory of collection managers, curators, conservators or registrars with an in-depth knowledge of their collections who often remember unusual photographs or photographs that need further investigation.

We hope that besides the continuous, long term support of our current project collaborators our Atlas work and research will generate interest and support from other researchers interested in old or unusual photographic processes. We hope that these researchers will help us locate well identified examples of different photographic processes that should be included in our further analytical investigation. With input and active collaboration of other researchers, the Atlas can be a very important resource of information and analytical data on different photographic processes that will serve the entire photograph research and conservation community well into the future.

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