Identification of Historical Photographic Processes by Non Destructive Physical Methodologies

M. Peres[a], M. L. Carvalho[b], A. Gomes[a], F. M. Costa[a], M. E. Jardim[c]

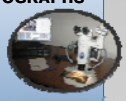
[a]Centro Ciências Moleculares e Materiais, U.L.
[c]Centro de Filosofia das Ciências, U.L.,Campo Grande, 1749-016 Lisboa
[b]Centro de Física Atómica, Dep. Física, FCUL, Av. Prof. Gama Pinto, 1649-003 Lisboa
mariliaperes@ciberprof.com

The old photographic prints show a complex structure, consisting of several inorganic and organic compounds, which results from different photographic used processes, as well as possible molecular changes along time. The knowledge of the structure of a photographic print can allow dating it, knowing its authenticity, identify the technique or processes used and thus allowing us to establish the best conditions for their preservation or disclosure.
Visual methods and microscopic observation associated to non-destructive analytical techniques, such as X-ray fluorescence analysis (XRF), infrared spectroscopy with Fourier transform (FTIR) and scanning electron microscopy associated to energy dispersive spectroscopy (SEM-EDS) have been used in the last decades for identification and preservation purposes.
In this work we present the results obtained by optical microscopy and XRF for some of the 27 photographic samples, mostly from the nineteenth century, obtained by different photographic processes and in various states of conservation.
Using these techniques allowed us to know the stratigraphic structure of photographic evidence and identify the main elements of each layer and the presence of certain elements, such as impurities and draw some conclusions and correlations between the composition and the photographic process.

Early Photographic Process Identification Methodology

1. **Identification of primary visual clues :** name of photographer, date, exhibition or photographic competition labels, logos, etc.
2. **Identification of secondary visual clues:** surface topography (glossy and mate), tonality and colour of the image layer, presence or absence of fading or deterioration.
3. **Microscopic examination of photographs:** microscopic structure, paper fibers, existence of baryta layer.
4. **Identification of photographs using non-contact and non-destructive analytical methods and procedures:**
   . X-ray Fluorescence Spectroscopy (XRF): for identification of inorganic elements
   . Fourier Transform Infrared Spectrometry (FTIR): for identification of organic material.

Microscopic Examination of Photographs
Stereoscopic Zoom Microscope NIKON SMZ1500



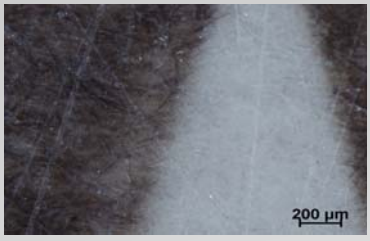
- Magnification: 70x
- Illumination: 45º
- Exposure and Gain: constants for each magnification

Quantitative X-ray Fluorescence Spectroscopy (XRF) of Photographs
Spectrometer for EDXRF analysis

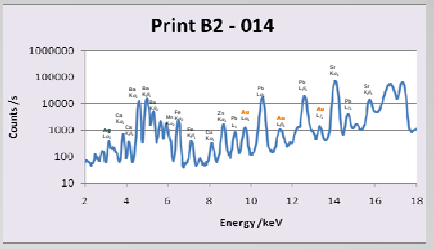
- X-ray tube (PW 1140; 100 kV, 80 mA) equipped with a molybdenium target and Si (Li) detector
- Energy resolution 135 eV at 5.9 keV
- Commercial pulse processor (Oxford).

Photographs

BIEL & Cª; 1874-1890
- Brilliant surface
- Red-brown image



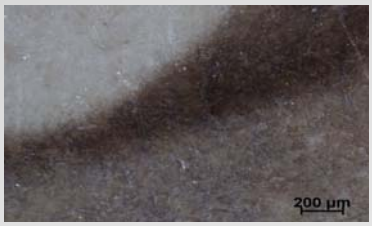
- Paper fibers are clearly visible under magnification
- Tiny cracks overall (binder is cracked)



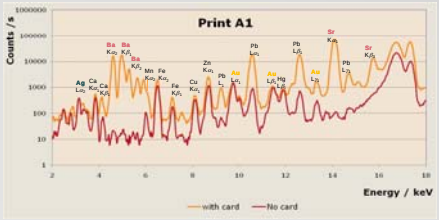
- Silver halide process
- Toning with gold

→ *Albumen*

- Brilliant surface



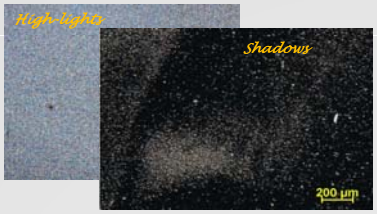
- Paper fibers are visible under magnification



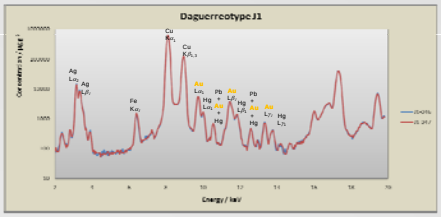
- Silver halide process, toning with gold
- No evidence of baryta layer

→ *Inconclusive*

- The surface is like a mirror



- High density of silver-mercury agglomerates in highlights



- Toning with gold
- High-lights and shadows with the same spectrum!

→ *Gilded Daguerreotype*

Final Notes

- The microscopic essays using Reilly's flowchart (1986) allowed us to do a first characterization of photographic prints.
- Elemental analysis by non-invasive XRF provided us some information about the photographs (presence of baryta layer, toning with gold, the presence of sulfur as degradation agent).
- The use of both techniques gave us some knowledge about the stratigraphic structure of these photographs and identification of major elements present in the samples.
- This type of information is critical to the preservation or restoration and may be useful to identify fakes or reproductions. This is one of the scientists' role: optimizing analytical methodologies and to make the technique available to a wide range of applications for cultural heritage.

Next Steps

- FTIR and SEM-EDS analysis is necessary for a better characterization of photographic processes.
- For inconclusive results we need to repeat with a more energetic X-ray beam (50 keV).
- For better spacial resolution a micro beam (100 µm) will be used.

References

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- Mc CABE, C. & GLINSMAN, L. (1995). Understanding Alfred Sieglitz' Platinium and Palladium Prints: Examination by X-ray Fluorescence Spectrometry, *Photographic Conservation*, pp. 31-40.
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