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LES SCIENCES DE LA CONSERVATION DU PATRIMOINE ET LE DÉVELOPPEMENT DURABLE
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Research on Historical Industrial Photographs

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How to identify prints on paper - the combination of methods of optical microscopy, FTIR / ATR spectroscopy and XRF analysis, by which it is possible to safely distinguish albumin prints, collodion and gelatine process, pigment printing and photos on polymeric underlay.

NTM has a large collection of historical photographs. These are both artistic photographs as well as those that represent important milestones in the development of photographic techniques In addition, there are number of industrial photographs the primary quality of which at the time of their origin was only the documentary value.

Huge amount of photos was taken from the archives of former factories and manufactures, which now no longer exists. They have been kept in substandard conditions for a long time. Now they are cleaned, restored, examined and gradually stored in depositories. There is no information on photographic processes of these images which is necessary before their cleaning and restoration. It was therefore essential to create a simple procedure to credibly recognize historical photographic techniques of positives on paper, using the analytical instrumentation available at NTM.

Tab. 1:
Summary of the essential characteristics of different types of photographs – prints on paper with the naked eye, under a microscope, using FTIR and XRF analyses.

	with naked eye	microscope	FTIR	XRF
Positives on single layer support				
salted paper	matte, brownish	**paper fibres are visible**	sp. of cellulose	Ag
cyanotype	matte, shades of blue		sp. of cellulose + 2170 cm^{-1}(CN^-)	Fe
platinotype	matte, shades of neutral grey	very fine grid of black particles + **paper fibres are visible**	sp. of cellulose	Pt (Pd) *(+ toning)*
Positives on two layers support				
albumin prints	smooth; brown, purple, reddish	**paper fibres are visible** through transparent layer of albumin	sp. of protein (albumin)	Ag *(+ toning)*
gum bichromate prints	matte; different shades	**paper fibres are visible** especially on highlight areas	sp. of gum arabic *(+ sp. of pigment)*	pigment´s elements (C, Fe, Mn,…)
pigment prints carbon prints	smooth or glossy; chocolate brown	clusters of carbon grains and **paper fibres are visible**	sp. of protein (gelatine)	pigment´s elements (C, Fe, Mn...)
Positives on three layers support				
collodion prints	smooth; matte or glossy; warm colours or grey (depends on toning)	**smooth surface; structure of the paper is not visible**	sp. of cellulose nitrate	Ag, Ba *(+ toning)*
gelatine prints	smooth; matte or glossy; warm colours or grey (depends on toning)		sp. of protein (gelatine)	Ag, Ba *(+ toning)*
RC paper	smooth; matte or glossy; grey or sepia		sp. of polyethylene, sp. of brighteners	Ag, Ti

Analyses:

1.Observation under a microscope:
- apparent paper fibres (on the single-layer and double-layer substrates).
- distribution of pigment
- character or type of emulsion degradation

Stereomicroscope Leica M165FC with smooth zoom 16.5:1, digital camera Leica DFC425 and IM50 software were used.

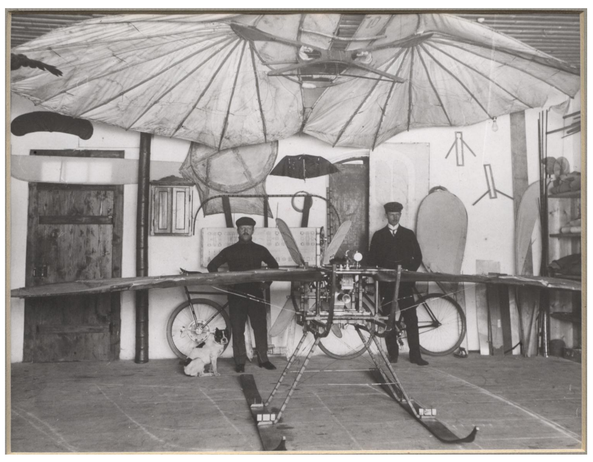
2. FTIR analysis (particularly analysis of organic compounds):
- character of image-carrying layer (albumin, gelatine, collodion, arabic gum)
- some pigments (cyanotype - Prussian blue $Fe_4[Fe(CN)_6]_3$)
- varnishes which may be applied to the surface of the photo
- polymeric base

FTIR spectrometer Nicolet iN10 (Thermo Scientific), ATR/ diamond, 600 – 4000 cm^{-1} and software Omnic were used.

3. XRF analysis:
- metal that forms an image – Ag (Pt, Au, (Pd))
- toning ingredients - Hg (from $HgCl_2$), Cr (from K_2CrO_4) Pb (from $Pb(NO_3)_2$)
- elements of pigments (Fe, Mn in ochers, Fe in Prussian blue,…)
- elements – parts of the support of image-carrying layer – Ba (+ Sr) from baryta layer; Pb from lead white contained in old type of paper or Ti from TiO_2 contained in modern and RC papers.

X-ray fluorescence apparatus built and operated in the Department of Dosimetry and Application of Ionizing Radiation FJFI CVUT, Prague; primary radiation source miniaturized X-ray tube, voltage 30kV; Si-drift detector Amtek X-123 SDD, Al filters 0,25-1,25mm.

These analytical methods must be combined in order to avoid misleading (e.g. FTIR spectra of proteins - albumin and gelatine - are very similar, but the albumin paper from gelatine layer can be easily distinguished by the microscope). On the contrary, gelatine and collodion layer beneath the microscope seem very similarly, but their FTIR spectra are fundamentally different; may be the case that wax or nitrocellulose lacquer applied on the surface of the albumin photo.



Aviation studio of Igo Ettrich in Trutnov, 1905; gelatine print

Harrach glassworks in Nový svět, 1900; toned gelatine print

Vojtěch Ironworks in Kladno,1878; toned collodion print

Vojtěch Mine in Příbram, 1885; albumin print

Prague Metropol Gasworks in Žižkov, 1880; albumin print

Cement factory in Beroun, 1912; gelatine print

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