

# Title: Chemical Nature And Beam Sensitivity Of Photochromatic Images Investigated By Ag K-edge Quick Spectroscopy

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In 1848 Edmond Becquerel developed the very first colour photographic process and was able to record the solar spectrum with its own colour [1]. The support is a silver plate similar to those used for daguerreotypes that underwent a sensitization step and the positive colour image is directly formed onto the sensitized plate. The exposure times were quite long and the resulting photochromatic images could not be fixed which is why this invention was not widely used. Whilst the origin of colours in these images motivated an intense debate between scientists in the XIX<sup>th</sup> century [2], [3], this issue is still not solved in the XXI<sup>st</sup> century [4], [5]. In order to investigate the nature of these colours, we try to relate the sub-microstructure of the silver and chlorine-based sensitized layer to its optical properties.

We created Becquerel-like samples of photochromatic images and performed X-ray Absorption Spectroscopy (XAS) at the ROCK beamline of the SOLEIL synchrotron around the Ag K-Edge. We chose the single bunch mode of the synchrotron ring to obtain a low photon flux required to measure these X-ray sensitive samples. These samples were analysed as well in reflectance and transmittance UV-visible spectroscopy in the [300 – 800 nm] range.

Thanks to ROCK beamline's Quick-EXAFS monochromator, we were able to study the X-ray sensitivity of our intrinsically photon-sensitive samples. We found safe measurement conditions with a defocused beam ( $3 \times 0,3 \text{ mm}^2$ ) during the single bunch mode (X-ray irradiance:  $8 \text{ W/m}^2$ ) until 5 hours of irradiation, ie. doses up to  $150 \text{ kJ/m}^2$ . We will present the self-absorption issues we had to face when analysing the Becquerel-like samples in fluorescence mode, while working at grazing and normal incidence. We will show how challenging is the measurement of silver chloride standard pellets: we measured metallic silver we identified as photolytic silver [6,7]. Finally, Ag K-edge spectra of sensitized samples are comparable to silver/silver chloride ones. The coloured samples (red, green, blue) spectra revealed the same silver/silver chloride composition which is consistent with UV-Vis results. We will attempt to explain why the XAS spectra of these three coloured samples do not significantly differ one from another whereas their visible absorption spectra show noticeable differences.

We think the contribution of the coloured layer regarding the sensitized layer in the XAS signal could be exacerbated by working with thinner samples ( $\sim 100 \text{ nm}$ ). This will allow us to explore the origin of the colours of photochromatic images in differentiated silver speciations.

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