The investigation of oxidation and migration processes of inorganic compounds in ink corroded manuscripts

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Archives and museums around the world contain a vast number of hand-written documents, music compositions and also drawings that were executed in iron gall ink, the most important in Western history.

Different decomposing reactions with and by the environment (especially with the organic matrix of the paper) are leading to changes in the ink colour and, occasionally, to iron gall ink corrosion. This process consists of two principal mechanisms: the acid hydrolysis by formation of sulphuric acid and the catalytic oxidation by mobile transition of metal ions, above all the major element iron. They end in a complete degradation of the paper. Therefore, non-destructive investigation are of great importance.

We studied the oxidation and migration processes of inorganic compounds in ink corroded material with a combination of micro X-ray fluorescence analysis (micro-XRF) and micro X-ray absorption near edge structure spectroscopy (micro-XANES) on two historical manuscripts in comparison to self-made well-defined iron gall ink samples.

With elemental mapping by micro-XRF of the historical documents, the correlation of the minor elements in the ink (Zn and Cu) to the major element Fe was investigated. It was found that the minor elements occur relatively in higher amounts in the outer regions of the ink spot, indicating that the mobility of non-iron metal ions through the paper is higher than that of iron ions.

Along concentration profiles of Fe, micro-XANES measurements were carried out in order to determine the oxidation state and the local environment. They reveal a spatial dependence of the Fe2+/Fe3+ ratio only in manuscripts in an advanced state of ink decomposition process, whereas the samples with lower degree of corrosion and the model inks showed a nearly constant Fe2+/Fe3+ ratio.

Comparison of the Cu-XANES profiles from an original, a model ink and reference samples (CuSO4 and CuO) showed that Cu is not only present as sulphate but also as oxide in the historical manuscript. The higher hazardous potential for Cu-bearing inks is shown in time-series of micro-XANES measurements.

With micro-XANES it is possible to show in situ the catalytic activity of Cu-ion in iron gall inks as an enforcement of the photo reduction of iron.

The combination of micro-XRF and micro-XANES is a step forward in the understanding of this complicate and complex paper degradation process.

References

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