Monitoring Of Restoration Treatments by Means Of Micro-XRF in Combination with Micro-XANES

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Abstract. This study presents the monitoring of different restoration methods of iron gall ink corroded manuscripts. With a combination of micro X-ray fluorescence analysis (micro-XRF) and micro X-ray absorption near edge structure spectroscopy (micro-XANES) the oxidation and migration processes of inorganic compounds in the manuscripts before and after the treatment are analysed. The corrosion process of iron gall inks induced by Fe^{2+} as catalyst has been described frequently. If the Fe^{2+}/Fe^{3+} ratio may be taken as a proxy for the degradation process, measurements of this ratio allow estimating the degree of decomposition as well as the hazard potential for a given manuscript. Measurements with high spatial resolution localise variations of the oxidation state and correlate these with other minor constituents in the ink. Based on these measurements it is possible to evaluate the results of different restoration treatments. The analyses before and after restoration reveal that the success naturally depends not only on the restoration method. However, in addition it becomes apparent that the state of the historical ink-paper system itself determines the effectivity of the method.

1. Introduction

Iron gall ink was the most important writing material in Europe. It is produced from four basic ingredients: galls, vitriol, a binding material such as gum Arabic and an aqueous medium such as wine or vinegar. It is already known, that reactions between iron gall inks and carrier materials are influenced by storage conditions, that is temperature and humidity and of course by the system itself [1]. The large variety of different chemical compositions leads to a diversity of degradation processes [2] containing changes in colour or resulting in iron gall ink corrosion.
In order to determine the influence of different restoration processes on ink corroded manuscripts we studied historical samples and artificial dummies before and after restoration treatments. Due to the fact that there are two main reasons for the ink corrosion, first of all the acidity of the inks which leads to hydrolytic splitting of the cellulose, and secondary the capacity of soluble iron and other compounds that act as catalyst for the oxidative decomposition of the cellulose, all restoration treatments try to decrease the concentration of acids and/or the concentration of soluble transition metals [3].
Former investigations show that a combination of micro X-ray fluorescence analysis (micro-XRF) and micro X-ray absorption near edge structure spectroscopy (micro-XANES)

is one step forward in the understanding of the complicate and complex paper degradation process in the context of iron gall ink corrosion [4, 5]. With elemental mapping by micro-XRF the correlation of the minor elements such as zinc, manganese and copper in the ink to the major element iron was investigated. Along concentration profiles of iron micro-XANES measurements were carried out in order to determine the oxidation state of iron and its local environment. The first results indicate that non-aqueous as well as aqueous treatments both influence the chemical composition of the inks and therefore change the archaeometrical fingerprint of the historical sample.

2. Experimental

The experiments were carried out at the bending magnet beamline KMC-2 at BESSY (Fig. 1). Final focussing to a spotsize of about 20 µm at the experiment was done by use of a polycapillary half-lens. In order to obtain higher fluorescence intensities and to decrease effects by sample inhomogeneities, the data were collected with a bigger spot size of 30 µm. The elemental mapping was performed with a step width of 50 µm. Micro-XANES spectra at the Fe K-edge were collected in fluorescence mode using an energy step width around the absorption edge of 0.5 eV. Total acquisition time for one absorption spectrum is about 15 minutes.

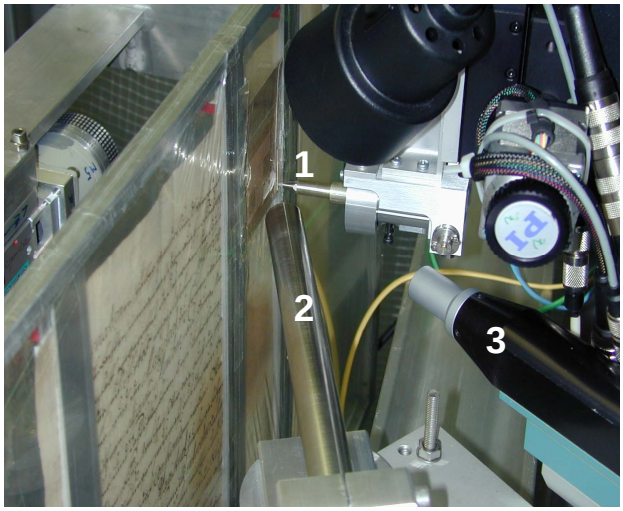

Fig. 1: Experimental set up for the investigation of historical manuscripts [5] with polycapillary lens (1), Xflash-detector (2) and PIN diode (3).

The XANES spectra were corrected for background absorption by subtracting a polynomial function that was fitted to the spectral region before the pre-edge. The spectra were then normalized for atomic absorption by fitting an arc tangent function and a gaussian function to the spectra and setting the arc tangent function to equal step height for all spectra. According to former investigations, we used the inflection point of the absorption edge as a figure of merit for determination of the valence state. The inflection point indicates the energetic shift of the edge position if the bulk chemical composition is not changing. A lower energy position of the absorption edge signifies a higher Fe^{2+} to Fe^{3+} ratio. Hence, the energy shift of the absorption edge to a higher value means the increase of Fe^{3+}. Figure 2 shows an elemental micro-XRF mapping in combination with a micro-XANES linescan.

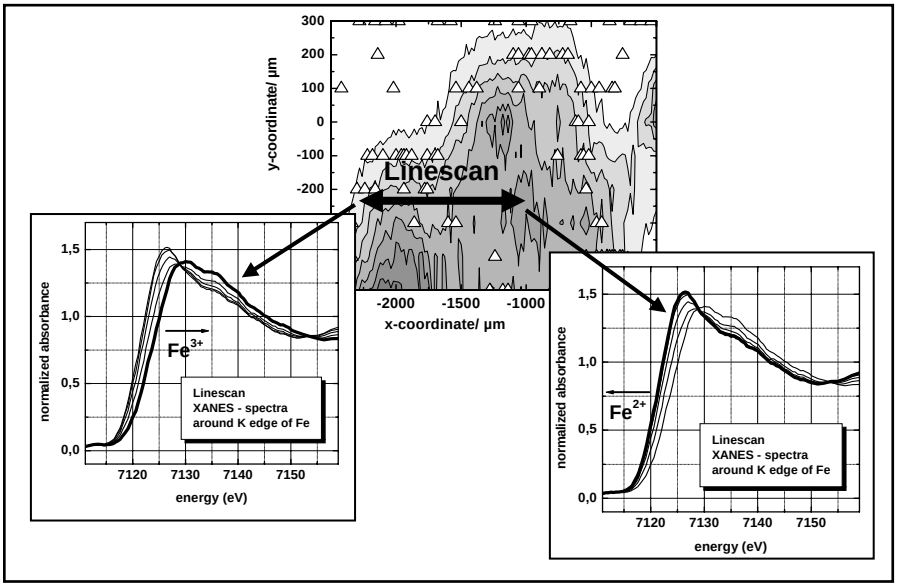

Fig. 2: Elemental micro-XRF mapping in combination with a micro-XANES linescan. The micro-XRF mapping showed here indicates higher relative concentrations of Zn in the edge region of the ink (white triangles plotted in the Fe concentration profile) and therefore a higher mobility of Zn. The micro-XANES line scan indicates an increasing Fe^{2+} concentration with increasing ink area density

3. Results and discussion

Based on two different examples the influence of non-aqueous restoration methods (usually an alkali in an organic solvent) is demonstrated in detail. Due to the fact that this study is still an ongoing project the authors only want to give only a little information concerning the different restoration methods.

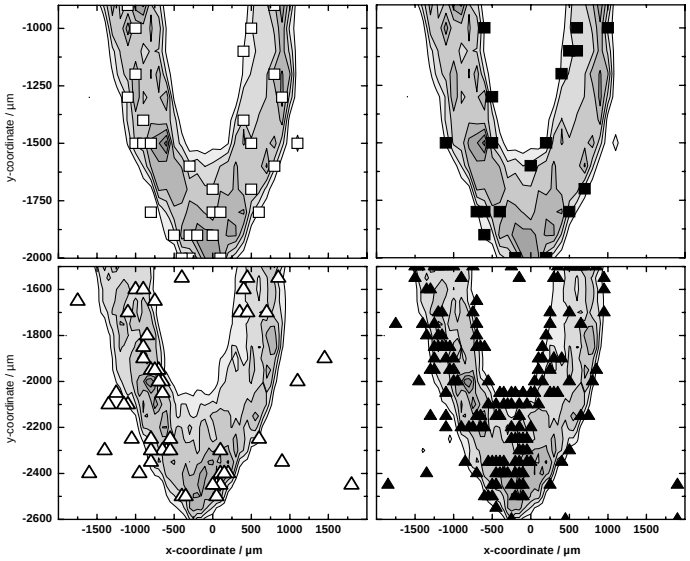

Fig. 3: Comparison of the Zn distribution relative to Fe before and after restoration. Single fingerprint values of Zn are mapped in the Fe concentration profile. White symbols indicate below average values, black ones above average values. Squares symbolise measurements before, triangles after restoration.

The first example is a historical ink with a little amount of iron gall ink corrosion, containing iron, copper, zinc, and manganese. Comparing the distribution of the single

fingerprint values W_{Zn} for Zn to the one of Fe in the ink material it can be seen that there is a quite homogeneous relative distribution of Zn before treatment (Fig. 3, upper part). These fingerprint values were calculated based on a fingerprint model for inhomogeneous ink-paper layer systems (for more details see [6]). Due to the restoration process a significant change took place: the distribution of the element Zn becomes more inhomogeneous (Fig. 3, lower part). The same is true for the other transition metals Cu and Mn.
Concerning the micro-XANES measurements Fig. 4 shows the results of the first measuring series before the restoration process. No significant change of the Fe^{2+}/Fe^{3+} ratio could be observed within measurement uncertainties. The upper curves show the measurements after restoration. Based on these results we can state that no significant changes take place. We might assume a small trend to a more reduced oxidation state. These findings are corroborated by former investigations based on artificial dummies as well as on original documents.

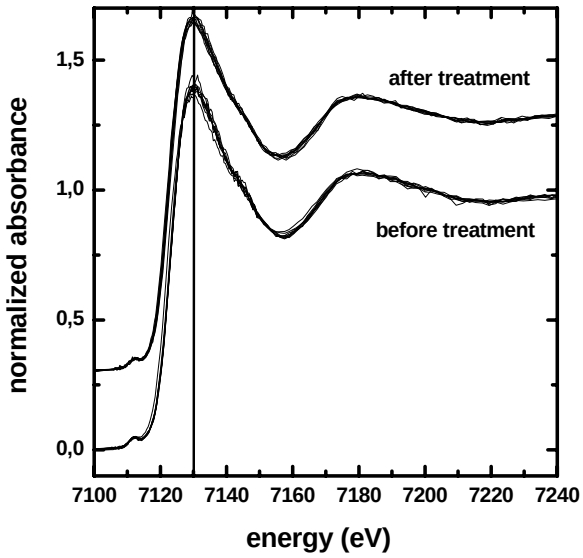

Fig. 4: X-ray absorption profiles around K-edge of iron. The inflection point indicates the energetic shift of the edge position if the bulk chemical composition is not changing. The comparison of the measurements before and after restoration indicates that no change takes place.

However, for another sample the results were quite different. The second sample has revealed an advanced state of decomposition. Figure 5 shows micro-XANES measurements before, a few days after restoration, and after three months. As mentioned before, we used the inflection point of the absorption edge as a figure of merit for determination of the valence state.
In accordance with other investigations (cp. Fig. 2), a significant increase of the Fe^{2+}/Fe^{3+} ratio with an increasing amount of iron in the historical ink can be observed. The present data show that the untreated ink contains more Fe^{2+} in the inner regions than at its rim. After the treatment the Fe^{2+}/Fe^{3+} ratio shifts to higher values - that means an increase of Fe^{3+} concentration. One may conclude that the treatment decreases the hazardous potential of the Fe^{2+}. However, after three months another significant change takes place. The Fe^{2+}/Fe^{3+} ratio shifts to smaller values indicating an increase of the Fe^{2+} concentration. The influence of the restoration process is not very durable. For the validation of these findings we have to establish a more quantitative evaluation of the XANES-spectra.

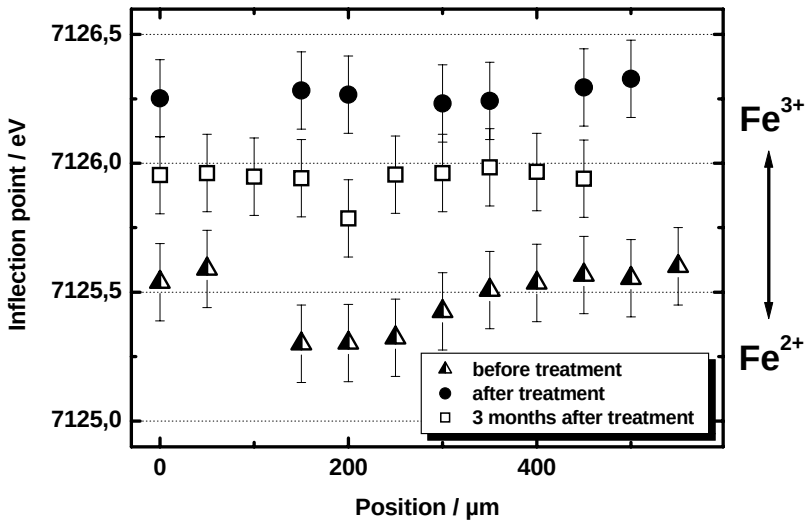

Fig. 6: Inflection points of micro-XANES spectra before restoration, after restoration, and after further three months. The spectra show that the untreated ink contains more Fe^{2+} in the inner regions than at its rim. After the treatment the Fe^{2+}/Fe^{3+} ratio shifts to higher values. After three months the Fe^{2+}/Fe^{3+} ratio shifts to smaller values indicating an increase of the Fe^{2+} concentration. The error estimation clarifies that these changes are significant.

4. Conclusions

The micro-XANES measurements on both original samples revealed characteristic Fe^{2+}/Fe^{3+} ratios. The results agree with former investigations confirming that the Fe^{2+} content is a chemical indicator for the degree of iron gall ink corrosion [7]. We found a nearly constant Fe^{2+}/Fe^{3+} ratio for the first sample with little amount of ink corrosion, whereas the second sample with advanced ink corrosion showed a characteristic spatial dependence between the iron content and the Fe^{2+}/Fe^{3+} ratio. As a consequence, starting from the first sample no significant changes took place after non-aqueous restoration. In contrast we can observe an immediate restoration success concerning the second manuscript, but this restoration treatment seems not to be very permanent.

The results show that the combination of micro-XRF measurements with micro-XANES experiments is a versatile tool to monitor the influence of some restoration treatments of ink corroded manuscripts. In order to test the impact of further conservation treatments, simulation experiments for ink corrosion have to be developed. In addition these results make evident that a continuous monitoring of restoration methods is necessary due to the fact that no standardised treatment method exists [8].

First analyses on artificial dummies treated with aqueous restoration methods indicate that the chemical compositions of the inks change remarkably. However, due to the fact that the significant differences of the varying inks remain stable it seems to be possible to carry out further archaeometrical investigations on the historical documents after restoration treatments.

References

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