XANES analysis of Fe oxidation state in artificially aged Byzantine iron gall inks: a preliminary study

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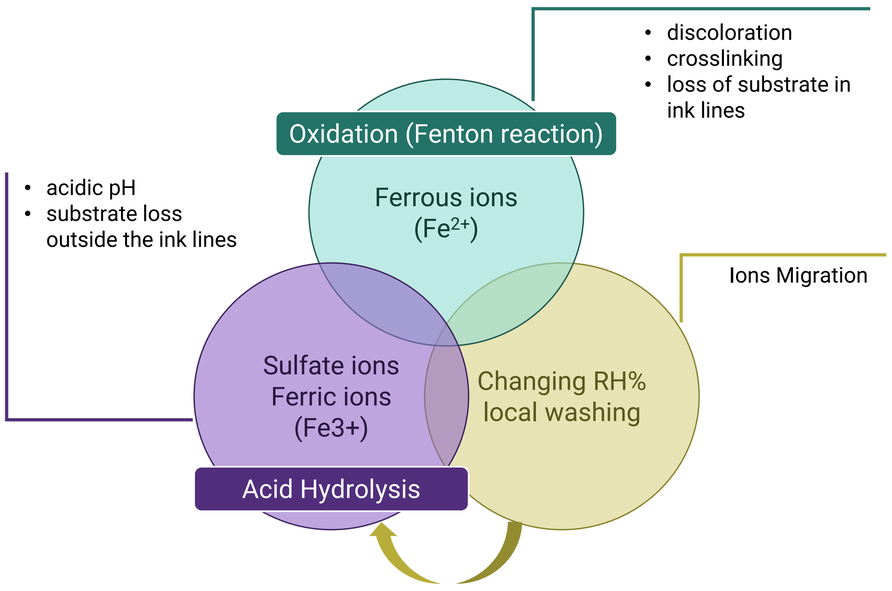
AIM OF THE STUDY

This project aims to study iron gall ink degradation and the corrosive nature of their compounds through thermal artificial ageing. For this purpose, different ink reproductions have been prepared following two Byzantine recipes from MS Vaticanus gr. 914. The samples were characterized before and after thermal accelerating ageing using SEM-EDS, Secondary (SE) and Backscattered (BSE) electrons for elemental and morphological microscopic characterization, whereas XANES measurements were performed at the Elettra XRF beamline to evaluate changes in the iron oxidation states due to the receipt or the ageing process.



CORROSION

Iron gall inks have an acidic pH, due to the production of acidic sulfate ions and ferric ions causing the acid-catalyzed hydrolysis, whereas the ferrous ions catalyze the oxidation reaction of cellulose (Fenton reaction).

These two mechanisms can be transferred to the remaining organic substrate through changing Relative Humidity (RH%) or by local washing, leading to the migration of corrosive soluble iron ions, outside the inked areas.

SAMPLE PREPARATION

Raw Materials

Cooking Method

Results

IA	1.5L 82 g 82 g 82 g 1 cup	H_2O Gall nuts $FeSO_4 \cdot 7H_2O$ Arabic gum Vinegar	**IB**	640 ml 27 g 9 g 45 g 1 cup	H_2O Gall nuts $FeSO_4 \cdot 7H_2O$ Arabic gum Vinegar
IAC	IA + Cypress cone		**IBC**	IB + Cypress cone	

AGING

The ink reproductions were applied on European handmade paper with hemp fibers.

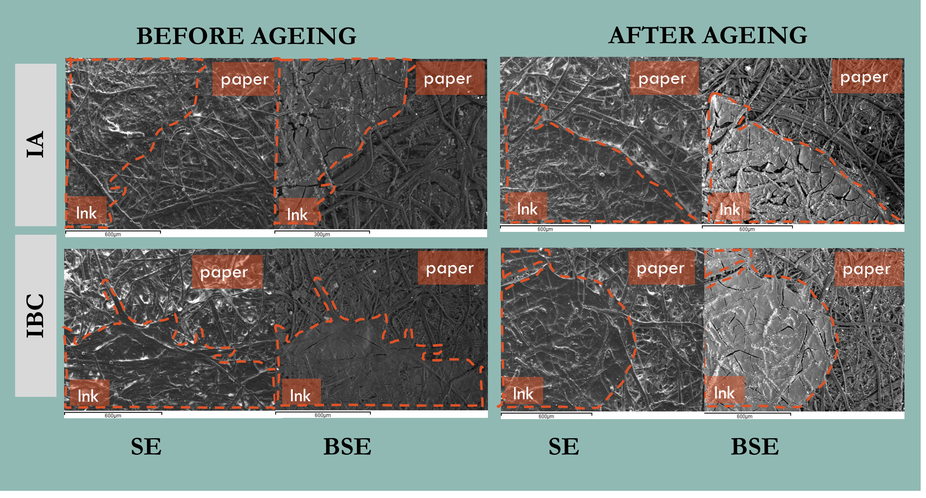
The aging protocol consisted of a change in RH and Temperature respectively from 35% to 75% and from 35°C to 75°C, with a change of 1 unit every 1h 30 min. Each sample has been analyzed in different aging conditions that we call *'new'*, *'fresh'*, and *'aged'*.

- The *new* samples were deposited on the paper two days before the measurements
- The *fresh* samples were deposited two years previous the measurements
- The aged samples were artificially aged following the aforementioned procedure two years previous the measurements

CHARACTERIZATION

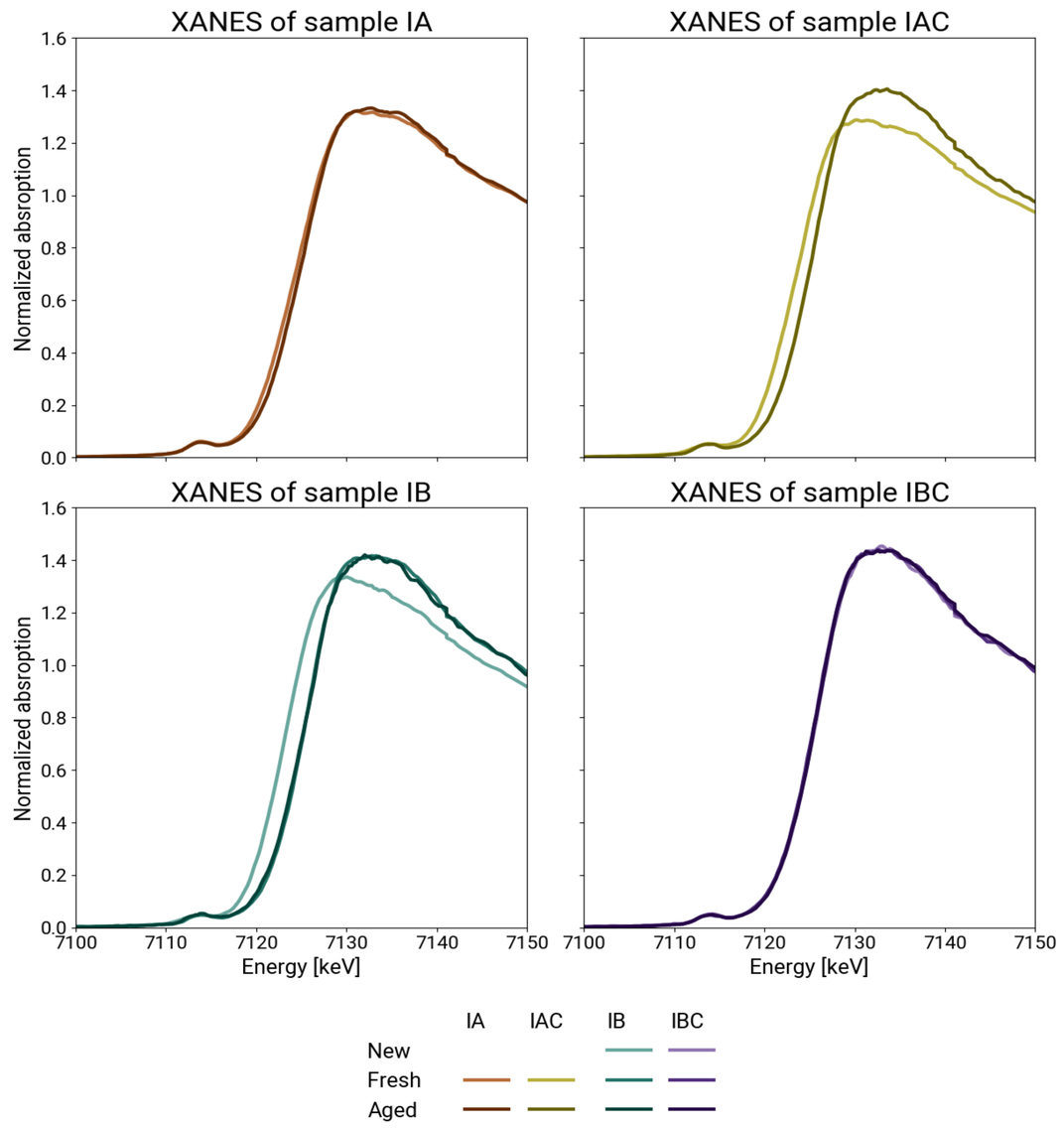
Before aging
IA and IBC inks have penetrated and integrated better within the cellulosic fibers suggesting that the ink shows a greater transparency and thinner fluidity. Also, crystal deposits have not been formed on paper.

After aging
It shows the formation of crystal deposits along the cellulosic fibers, but they are not very intense indicating a better preservation state.

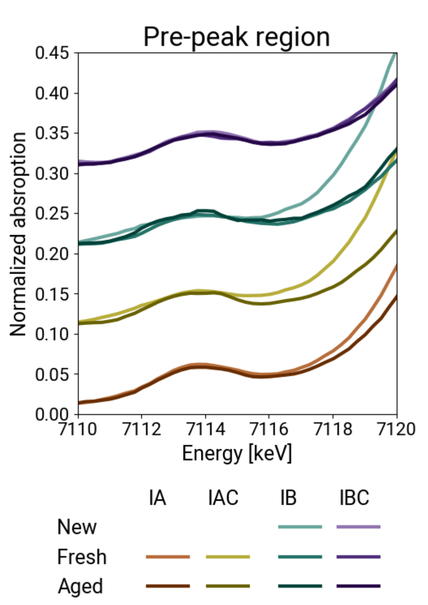


XANES

XAS analyses have been performed at the XRF beamline on the Fe K-edge. For this preliminary study, only the XANES region has been collected from 6.9 keV to 7.2 keV in fluorescence mode. The energy calibration of the Si monochromator was checked using a Fe calibration foil before the ink's measurements.



Fe K-EDGE POSITION



XANES RESULTS

The position of the iron K-edge (inflection point) presents a variation from 7123 to 7126 eV; this can be related to a change of oxidation of iron in the samples, with an increase of Fe^{3+}, while for the pre-edge we observe only a change in intensity. Sample IBC is the sample that shows the smallest variation; indeed, the three spectra do not show any change during the aging process, suggesting that the whole oxidation has occurred during or just after the preparation. Sample IB, instead, displays a change from the new and the fresh version, showing that the oxidation process occurs shortly after the preparation (maybe in some weeks), and then stabilizes. These two inks are made following the same recipe, the only difference is the addition of cypress. Samples IA and IAC, finally, show both a change from the fresh and the aged versions, so a change occurs in this timeframe (from 2 months to different years).

The pre-peaks instead do not show any variation, except for the IAC fresh and the IB new which seem to be more skewed toward the low energies.

CONCLUSIONS AND FUTURE STEPS

These first analyses show an increase in the iron oxidation state during the aging process. Besides, the iron oxidation changes seem to be influenced by the following recipe. Some samples are less prone to degradation after aging (for example IB versus IA) indicating a better-quality ink, with low reactivity. Future XANES experiments will be focused on the investigation of the iron-gall inks degradation excluding any influence of the substrate material using samples prepared on an inert material or by analyzing the inks directly in the liquid form.

References

- Rouchon, Véronique, Eleonora Pellizzi, Maroussia Duranton, Frederik Vanmeert, e Koen Janssens. «Combining XANES, ICP-AES, and SEM/EDS for the Study of Phytate Chelating Treatments Used on Iron Gall Ink Damaged Manuscripts». *Journal of Analytical Atomic Spectrometry* 26, fasc. 12 (2011): 2434–41.
- Xu, Zhi, Qiwen Wang, e Huiming Fan. «Changes in color and iron ions of commercial iron gall inks after artificial aging». *Heritage Science* 11, fasc. 1 (2023): 96.
- Antonio da Costa. et al.. «Scanning Electron Microscopic Characterization of iron-gall inks from different tannin sources, Applications for Cultural Heritage», *Chemistry and Chemical Technology* 8, fasc. 4, (2014): 423-9.

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