Characterization and state of preservation research of an 18-century manuscript

NACIONALNA I SVEUČILIŠNA KNJIŽNICA U ZAGREBU

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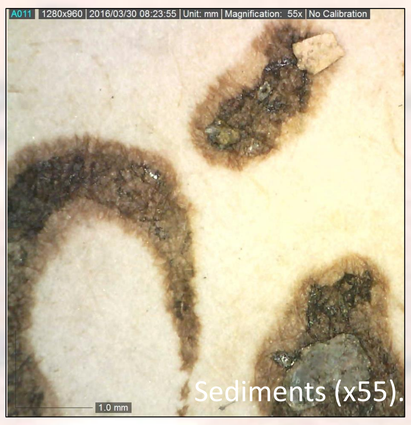
INTRODUCTION

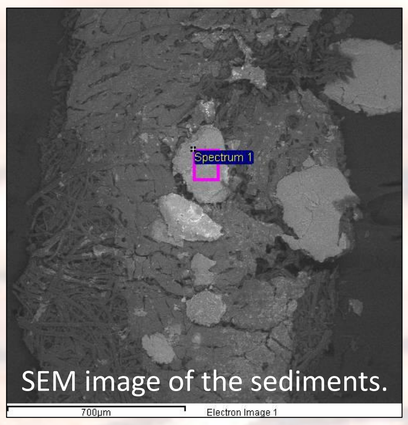
A study combining different microscopic, spectroscopic and photographic techniques has been done to characterize original materials and asses the state of preservation of an 18-century iron-gall ink manuscript. A letter that Andrija Bahunek send in 1747 to Baltazar Adam Krčelić (1715-1778), a renown Croatian historian, theologian and lawyer, is kept at the Manuscripts and Old Books Collection of National and University Library in Zagreb. Krčelić left his entire private library, together with his personal correspondence to then Royal University Library and his bequest became the basis of todays Manuscripts and Old Books Collection. The research was done to aid conservation decision making and to choose the most suitable conservation-restoration method for the manuscript.

Sediments on the surface of the ink.



Sediments (x55).

Sediments (x230).



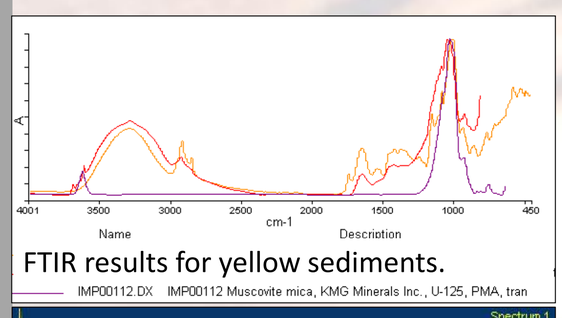
SEM image of the sediments.

METHODS

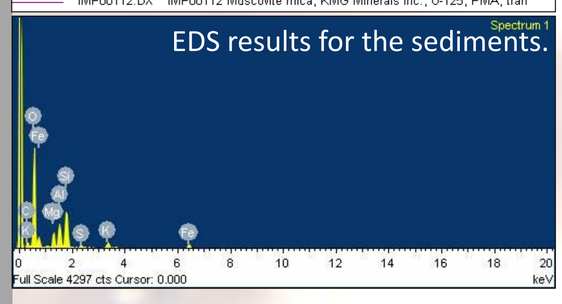
The manuscript was in a very poor state of preservation. The surface of the ink was full of sediments. They were different in shape, color and were all firmly attached to the surface of the ink. It was not possible to determine the source of the sediments, and therefore the most adequate conservation method, without conducting a broad interdisciplinary research. Techniques used included light and SEM microscopy, XRF and EDS elemental analysis, FTIR molecular analysis and VIS/UV/NIR photography.
The crystals were studied under light microscope to document their morphological features. Size varied between 0.5 and 1 mm in diameter. They were roughly divided into three categories according to their dominant color: yellow, black and translucent. XRF, EDS and FTIR analysis were done for each category separately.

RESULTS

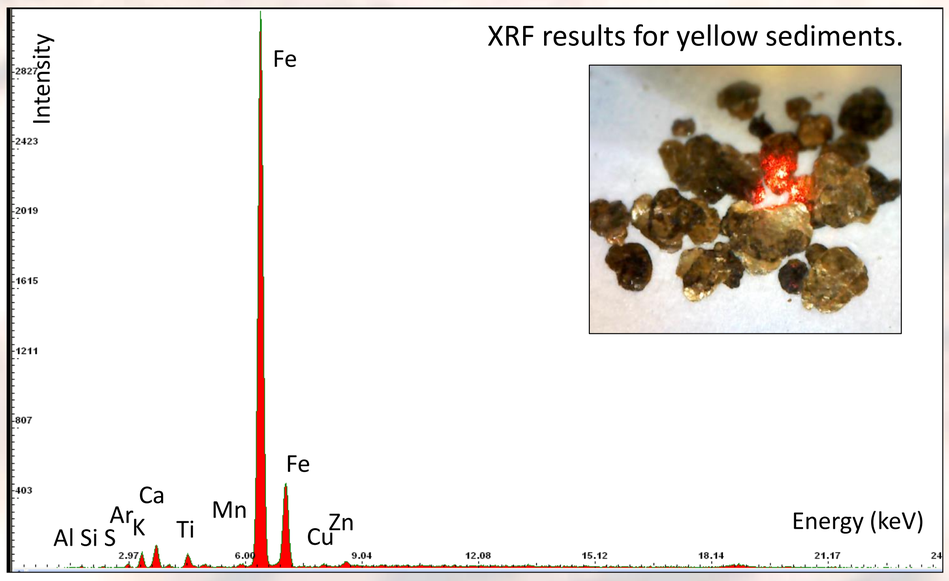
Results show that the ink used on this document was of a poor quality which is the main reason of such preservation state. The ink corroded severely, Fe^{2+} ions migrated far from original pen strokes (best visible on infra-red photography, $\lambda = 950$ nm), and vast majority of paper was irreversibly deteriorated (visible as complete light absorption on ultra-violet induced visible fluorescence photograph - UVF).
Paper was machine-made out of natural fibers and traces of protein binder was detected. Its quality did not play a significant role in this deterioration.
Elemental and molecular analysis indicated that the crystals were predominately muscovite with traces of other materials, such as bitumen, probably from degraded organic compounds. The ink was characterized as iron-gall ink with a lot of trace elements in its composition (dominant elements Fe, Ca, Cu, Zn, with traces of Al, S, K, Mn). Detected elements indicate impure vitriol used in ink production (Cu, Zn) with different compounds added. Previous research repeatedly linked the presence of Cu in iron-gall inks to faster and more severe deterioration of manuscripts.



FTIR results for yellow sediments.



EDS results for the sediments.

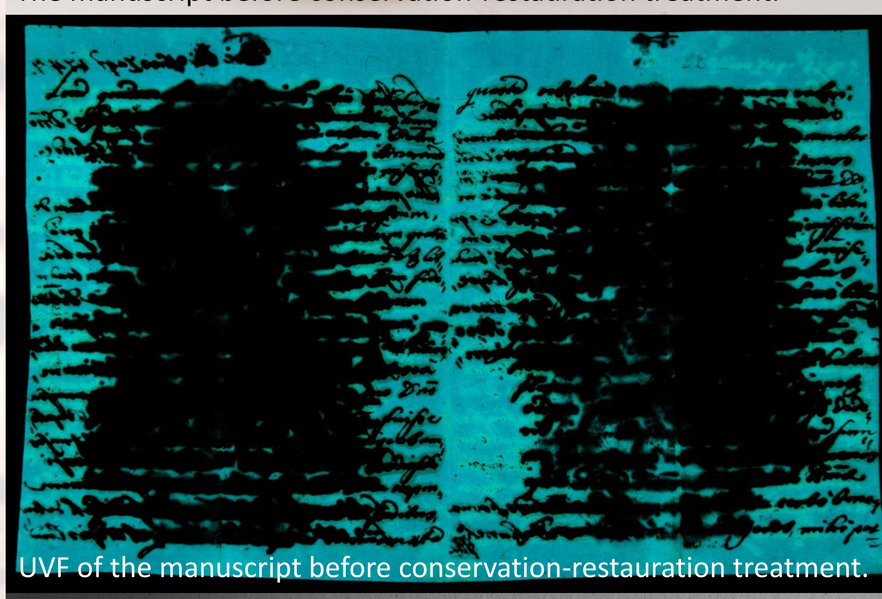


XRF results for yellow sediments.

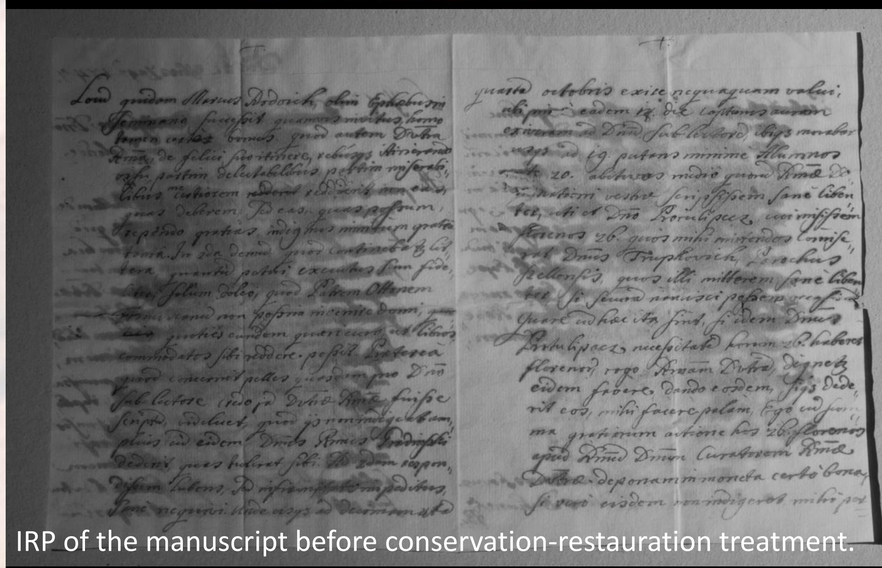
CONCLUSION

The source of the crystals on the surface of the ink is presumably twofold. It is not possible that they formed only from ink components due to inadequate storage conditions. At least partly they must have originated from an outside source, probably a form of blotting sand. It is possible that under certain conditions ink components crystalized on the surface of the ink using blotting sand as a form of nucleus to crystalize around it. Presence of ink impurities allows for such presumptions. Further research is needed to completely explain this mechanism.
With conducted conservation-restauration treatment, it was possible to slow down the deterioration processes by eliminating reactive metal ions (visible as reduced UV fluorescence on UVF after treatment) and the source of reoccurring sediments contained within the ink.

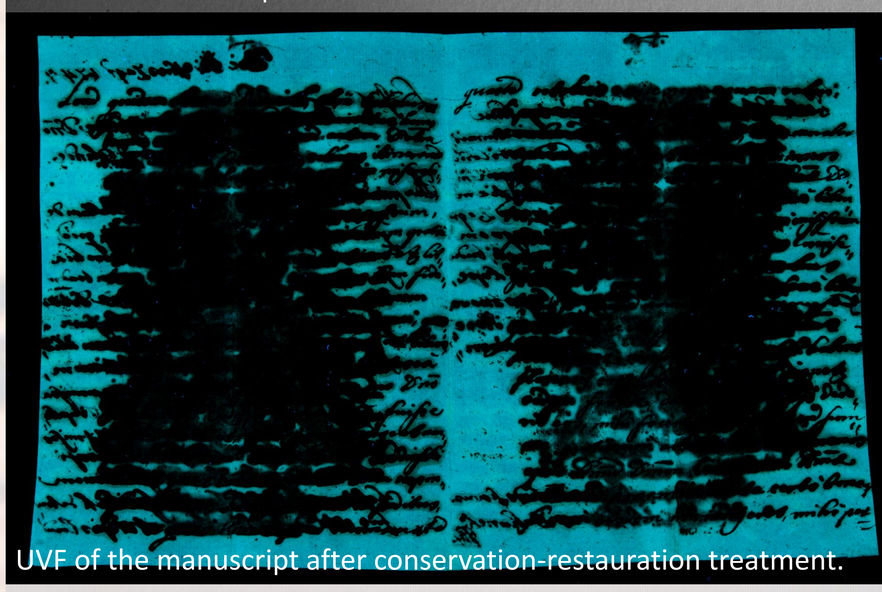
The manuscript before conservation-restauration treatment.



UVF of the manuscript before conservation-restauration treatment.



IRP of the manuscript before conservation-restauration treatment.



UVF of the manuscript after conservation-restauration treatment.

The manuscript after conservation-restauration treatment.

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