COMPARATIVE ELEMENTAL ANALYSIS OF EIGHTEENTH-CENTURY INKS IN HISTORICAL HANDWRITTEN DOCUMENTS BY X-RAY FLUORESCENCE SPECTROMETRY

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Iron-gall ink, prepared from tannin extracts, iron salts, and gum arabic, was widely used in Europe from antiquity until the 20th century. Variations in recipes, raw material sources, and salt impurities result in significant differences in elemental composition, which may be used to distinguish between inks. Hahn's fingerprinting approach, based on non-destructive X-ray fluorescence spectrometry (XRF), uses elemental ratios such as Cu/Fe, Zn/Fe, and Mn/Fe to differentiate between iron-gall inks [1].

This study examined three handwritten copies of the Constitution of 3 May 1791 preserved in the Central Archives of Historical Records (AGAD, Warsaw). Visual inspection suggested the presence of iron-gall ink in the main text, corrections, and deputies' signatures. The aim was to assess elemental variability across different written sections and to investigate possible relationships between the chemical composition of the main text, annotations, and signatures. Due to the exceptional historical value of the manuscripts, only non-destructive methods could be applied [2].

Measurement conditions were optimized by testing acquisition times from 30 to 300 s and several radiation shields (Rh, Pd, Si, Al, Au, acrylic, graphite) to minimize signal contribution from underlying pages. An acquisition time of 210 s and a rhodium shield were selected as optimal. Detection and quantification limits for selected elements were established using a model ink solution and its serial dilutions. The manuscripts were analyzed in situ at AGAD using a portable Bruker ELIO XRF spectrometer.

The results were evaluated to determine the elemental composition of inks in all measured areas. In addition, machine-learning-based dimensionality reduction methods were applied to compare chemical signatures of different writings. The approach enabled discrimination between iron-gall and plant-based inks and indicated that some corrections may be chemically associated with deputies' signatures.

[1] O. Hahn, W. Malzer *et al*: Characterization of iron-gall inks in historical manuscripts and music compositions using x-ray fluorescence spectrometry. *X-Ray Spectrom*., 33: 234-239 (2004).
[2] J. Wouters: Reflections on the Position of Science in Multidisciplinary Approaches. Chemistry International 30, 1: 4-7 (2008).

Acknowledgements: Research supported by the National Science Centre, Poland, under the project "Spectral Analysis of Legacy Inks using machiNe leArning: ALiNA" (No. UMO-2021/41/B/ST4/02860).