X-ray fluorescence spectrometry in comparative studies of the chemical composition of handwritten historical notes: the case of the *Constitution Act* of 3rd May 1791

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Iron-gall ink, made by mixing tannin extracts with iron salts and gum arabic, was commonly used in Europe since antiquity until the 20th century. Due to salt impurities and the use of various recipes and ingredients from different sources, iron-gall ink can exhibit significant variations in its elemental composition, which allows for distinguishing between ink-written documents. Hahn proposed a method called *fingerprinting*, which is based on results obtained from a non-destructive technique – X-ray fluorescence spectrometry (XRF) [1]. It uses ratios of minor elements such as Cu, Zn, Mn to iron to distinguish between different inks.

The objects of this study were three handwritten copies of the *Constitution Act* of 3rd May 1791, which are currently held by the Central Archives of Historical Records (Archiwum Główne Akt Dawnych, AGAD) in Warsaw. Visual inspection indicated the use of iron-gall ink in the text, annotated amendments, and deputies' signatures. The objective of the thesis was to assess the elemental variability of various sections of the documents, and to attempt to correlate the chemical composition of the main text and the inscriptions. The necessity of non-destructive techniques was dictated by the objects' historical value [2].

Measurement parameters were optimized by testing different acquisition times (30-300 s) and radiation shields (Rh, Pd, Si, Al, Au, acrylic, graphite), the purpose of their use being to prevent X-rays from exciting atoms on the pages beneath the one being measured. The optimal acquisition time was set (t = 210 s), and a rhodium plate was selected as the optimum radiation shield. The limits of detection and quantification of the selected elements were determined by preparing a model ink solution, which was then diluted at varying rates and measured consecutively. The measurements of the historical documents were carried out *in situ* in AGAD using a portable XRF device ELIO (Bruker) without the necessity of transporting the objects to the laboratory. The results were evaluated individually to see what is the main elemental composition of the ink in all measured areas. Additionally, machine learning-based data reduction techniques were used to compare chemical signatures of different writings. It allowed the iron-gall ink to be distinguished from plant-based ink, and some amendments could be matched to the signatures of the deputies.

Bibliography:
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