Title:

Thin-film method in X-ray fluorescence analysis of selected materials of the non-ferrous metals industry

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Abstract:

In this PhD thesis, three analytical procedures for the quantitative determination of major and trace elements in selected materials from the non-ferrous metals industry, using X-ray fluorescence spectrometry (XRF), were developed. The samples were prepared as a thin layer to minimize matrix effects, a major source of error in XRF analysis.

In the theoretical section of the thesis, the basics of XRF spectrometry, including the interaction of X-rays with matter, matrix effects, and the influence of sample thickness on fluorescence radiation intensity, are discussed. In the literature section, the papers on the determination of major and trace elements in thin-layer samples are reviewed.

In the experimental section:

- The methods for the determination of the major elements in CuMnNi alloys, phosphorus copper CuP, and phosphorus copper with silver CuPAg, were developed. The digested samples were deposited on a properly selected sample carrier, which, after drying, were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF). Calibration has been performed using reference materials (CuMnNi alloys) and synthetic samples (CuPAg alloys).
- A method for the determination of trace elements in high-purity copper was developed. The copper matrix was electrolytically removed, and the remaining elements were preconcentrated and deposited on a Mylar foil. The resulting thin-film samples were analyzed by energy-dispersive X-ray fluorescence spectrometry (EDXRF). The synthetic samples were used for calibration.

The research showed an inhomogeneous distribution of elements on the sample carrier surface, which had a negative impact on the precision and accuracy of the obtained results. The use of an internal standard significantly corrected the effect of sample inhomogeneity and lead to obtaining results that meet the requirements of the non-ferrous metals industry.

The use of the thin-film method led to reducing the spectral background and improving the signal-to-background ratio. In addition, the preparation of thin samples resulted in the minimization of matrix effects, which are one of the main sources of error in XRF analysis. As a consequence, a linear relationship between the signal and the concentration of the analyte (or its mass per unit area) was obtained, and the application of matrix correction methods (fundamental parameters or influence coefficients algorithms) was not necessary.

Theoretical calculations (Rhodes criterion) showed that the samples meet the criterion of thin samples, except for the determination of phosphorus in CuP and CuPAg alloys, which emits low-energy radiation. The emission-transmission method indicated a certain absorption of characteristic radiation in the sample carrier. However, its composition is constant, therefore the attenuation of radiation is constant in all samples and can be neglected if the reference and analyzed samples are prepared using the same sample carrier.

The developed methods were validated and the accuracy was checked using real and reference materials. The obtained results meet the requirements of analysis of materials from the non-ferrous metals industry. The developed methods of sample preparation are an alternative to materials that cause difficulties in direct XRF analysis.