

X-ray fluorescence spectrometry (XRF) is a commonly used analytical technique in the elemental analysis of a wide variety of solid samples. Nevertheless, direct analysis of liquid samples is still associated with technical difficulties, which contribute to significant errors in the obtained results. Moreover, the typical detection limits at the level of mg L^{-1} are unsatisfactory for environmental and industrial requirements. Therefore, most of the research related to the analysis of liquid samples using the XRF technique requires preconcentration procedures prior to analysis. Considering that solid samples are favorable in XRF analysis, it is preferable to use preconcentration methods leading to thin solid samples (e.g., membranes). For the thin layer, the matrix effects, which are one of the significant sources of error in XRF analysis, can be neglected, and the low detection limits at the level of ng L^{-1} can be achieved due to the high signal to background ratio.

The aim of the PhD thesis was to develop the new analytical procedures based on the metal ion adsorption on the surface of cellulose-silica membranes and their direct detection by energy dispersive X-Ray fluorescence spectrometry (EDXRF). New adsorbents such as cellulose/SiO₂/SH, cellulose/SiO₂/1N, cellulose/SiO₂/2N, and cellulose/SiO₂/3N were prepared by covering the fibers of the cellulose filter with silica via the hydrolysis of tetraethoxysilane in an alkaline solution. Next, the surface of the membranes was modified using organosilanes containing thiol and amino groups. The structure and chemical composition of obtained membranes were characterized by scanning electron microscopy with energy-dispersive X-ray spectroscopy, X-ray diffraction, and X-ray fluorescence spectrometry. Moreover, the pH value of the zero point of the membranes was determined by the potentiometric titration method. In the next step, adsorptive properties of obtained membranes toward selected ions of metals, i.e., Cu^{2+} , Ni^{2+} , Co^{2+} , Pb^{2+} , Cr^{3+} , CrO_4^{2-} , AsO_3^{3-} , AsO_4^{3-} , SeO_3^{2-} and SeO_4^{2-} were investigated. For this purpose, the influence of pH, sample volume, and adsorption time were investigated. Then, the adsorption capacity of the obtained membranes for selected ions of metals was determined, and the influence of foreign ions on adsorption was verified. The studies showed that the thiol-modified membranes selectively adsorb As(III) ions, while the amino-modified membranes groups adsorb Cr(VI) ions. In the next part of the work, analytical methods for the concentration and determination of trace amounts of As(III) and Cr(VI) ions were developed using miniaturized membranes with 5 mm diameter and an EDXRF spectrometer equipped with an X-ray tube of 9W power. Detection limits were obtained at the level of $0,045 \mu\text{g L}^{-1}$ and $0,16 \mu\text{g L}^{-1}$ for As(III) and Cr(VI), respectively. Obtaining such low detection limits, lower by 3-4 orders of magnitude compared with direct XRF analysis of liquid samples, was possible due to the low background and high enrichment factors of 972 and 650, respectively. The developed analytical procedures were successfully applied to the analysis of drinking, tap, sea, ground-water, and sewage samples.