

Streszczenie w języku angielskim

The following doctoral dissertation is devoted to the preparation, characterization and application of screen-printed carbon electrodes modified with bismuth or lead film prepared with or without the use of mediator in trace analysis of metal ions (Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI)) in environmental water samples.

The research carried out within this study included optimization of the procedure of surface modification of screen-printed carbon electrodes with bismuth or lead film, i.e. selection of the type and concentration of modifier ions, potential and time of film plating, concentration of the mediator, potential and the time of its removal from the electrode surface. Modification of screen-printed carbon electrodes surfaces with bismuth or lead film contributed to significant enhancement of analytical signals of the determined ions Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI). Additional amplification of Cd(II) and Pb(II) signals was obtained by using a reversibly deposited mediator at the stage of bismuth film plating. The morphology of unmodified electrodes surface and electrodes modified with the metal film was examined with the use of optical microscopy and profilometry, atomic force microscopy, scanning and transmission electron microscopy. The surface composition of unmodified and modified electrodes was studied using X-ray photoelectron spectroscopy and X-ray energy-dispersive spectroscopy. The obtained results confirmed, among others, significant differences in the structure, morphology and surface composition of unmodified and modified electrodes, and the dependence of microscopic surface structure on the parameters of the metal film plating procedure. In order to obtain additional characteristics of working electrode surface in the research on Mo(VI) determination, the size of the unmodified electrode's active surface in relation to that of the electrode modified with lead film, and the rate of electron kinetics were calculated and compared. On the basis of the conducted calculations, it was found that the modification of the electrode surface only slightly increased the active surface area but contributed to the increase the speed of electron transfer kinetics.

In the course of the research for this dissertation, optimization of voltammetric procedures for determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) ions, i.e. the type of electrolyte, its concentration and pH, as well as the type and concentration of the complexing agent (in case of adsorptive stripping voltammetry) was performed. In addition, the potential and time of the analyte deposition on the electrode surface were optimized. The technique of

voltammograms registration and its parameters, such as amplitude, frequency, scan rate, were also selected.

Voltammetric procedures for determination of selected metal ions described in this dissertation are characterized by one of the lowest (in the case of Cd(II) and Pb(II)) or the lowest (in the case of Tl(I), U(VI), Mo(VI)) detection limits among the works available in the literature in which screen-printed electrodes were used for the determination of these ions. The additional advantage of these electrodes is a simple and fast surface modification process.

Within the framework of the research covered by this PhD dissertation, experiments were also conducted to examine the influence of the matrix of environmental waters samples (metal ions and surface active substances) on the signal of the determined ions. In the case of the occurrence of interferences, procedures for their minimization have been proposed and optimised. This stage enabled the application of the developed procedures for the analysis of selected metal ions in water samples without the need of their mineralization. Negative effects of Cd(II) and Pb(II) ions on the Tl(I) signal were minimized by using a solution of ethylenediaminetetraacetic acid disodium salt (EDTA) as an agent complexing the disturbing ions. The effect of suppression of the analytical signal Tl(I), U(VI) and Mo(VI) by surface active substances was minimized by the use of adsorptive resin (Amberlite XAD-7 or Amberlite XAD-16). This method is more advantageous than laboratory mineralization of the sample due to the shorter time of removing the organic matrix from water samples and the possibility to perform this stage in field conditions. The EDTA concentration, the mass of the resin and the time of shaking with the sample were properly selected based on the experimental tests carried out.

Confirmation of the applicability of the proposed screen-printed electrodes in the determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) ions concentrations was achieved by analysis of certified reference materials: TMRAIN-04 (rainwater), SRM 1640a (natural water) and SPS SW2 (surface water). In the case of simultaneous Cd(II) and Pb(II) determination method, measurements were also performed for samples of the waters from the Krzna River and the Baltic Sea, while the U(VI) procedure was used for the analysis of samples collected from the Bystrzyca River. The recovery values close to 100% confirm the small influence of analyzed water samples matrix on the analytical signal of the determined metal ions.

On the basis of the obtained results it was found that the developed voltammetric procedures for the determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) using screen-printed carbon electrodes modified with bismuth or lead film can be used in the analysis of environmental waters samples. The procedures developed with the use of screen-printed

carbon electrodes modified with bismuth or lead film can be used not only in laboratory conditions but also in portable electrochemical analyzers, enabling the field analysis.