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Flow microsensors in analysis of heavy metal ions

R. Kizek (1,2), L. Trnkova (1), J. Sileny (3), V. Adam (1,2), J. Hubalek (3)

(1) Department Chemistry, Faculty of Science, Masaryk University, Kamenice 5, CZ-625 00 Brno, Czech Republic

(2) Department of Chemistry and Biochemistry, Faculty of Agronomy, Mendel University of Agriculture and Forestry, Zemedelska 1, CZ-613 00 Brno, Czech Republic

(3) Department of Microelectronics, Faculty of Electrical Engineering and Communication, Brno University of Technology, Udolni 53, CZ-602 00 Brno, Czech Republic

Heavy metal ions are natural components of Earths crust. The content of them in soil is varying from very low (femtograms) to high (milligrams). Due to anthropogenic activities their content can be elevated in the site of the action. It is a common knowledge that toxic heavy metal ions (lead, cadmium and mercury) are able to enter to organisms and interfere several important metabolic processes. At plants the presence of the toxic ions damage homeostasis, transpiration etc. Plants are capable to survive this abiotic stress due to number of protective mechanisms. The result is that the plant lives and develops in the pollute environment and, moreover, accumulates the heavy metal ions in the tissues. If such plants are harvested, the foodstuffs from them pose a threat to animal and human health. Due to this developing and proposing of simple analytical instruments, methods and procedures with low detection limits are needed. Among the very sensitive analytical methods for detection of heavy metal ions belong the electrochemical ones. The classic instruments are consisted of potentiostat/galvanostat with electrochemical cell including three electrodes (working, referent and auxiliary). However the trend of the analytical techniques is to be miniaturized the whole instrument. The aim of this work was to utilize electrochemical instruments, both classical and miniaturized, for easy and sensitive determination of heavy metal ions. Further the instruments were employed to analyse real samples.

Differential pulse anodic stripping voltammetry belongs to the most sensitive ana-

lytical techniques used for heavy metal ions detection. However from a technological point of a view, the insolid electrodes have lower miniaturization potential as solid electrodes, like silver, gold, carbon or platinum. The printing of electrodes is a promising technology for further miniaturization. The screen-printing is an undemanding non-vacuum method for spreading of thixotropic materials. The single layers are created by pressing the paste on the susbtrate through the screen. The advantage of this technique is its simplicity, high mechanic and electric properties, easy connection to other circuits and particularly low-cost. In the present work we utilized the screen-printed electrodes connected to Biostat instrument for detection of heavy metal ions (cadmium and lead) and compared the results with the standard electrochemical instrument Autolab with hanging mercury drop electrode as working one. The procedure of using of the electrodes was optimized. We used acetate buffer pH = 5 as suitable supporting electrolyte for analysis of heavy metal ions based on the previously published results. For base lane establishing 10 μl of the supporting electrolyte was introduced on the electrodes surface, then 2 μl of the sample was added and the changes of the electrical current were determined. The electrode surface was mechanically polished with redistilled water and filter paper prior to further analysis. We determined hydrodynamic voltammogram and found the best detection potential. Moreover we measured the calibration curves. The curves were linear (R^2 (Cd) = 0.99; R^2 (Pb) = 0.99). To compare the results obtained we used Autolab instrument. The resulted calibration curves were also linear (R^2 (Cd) = 0.99; R^2 (Pb) = 0.99) with detection limits for cadmium ions 6 pM (LOD, 3S/N) and for lead ions 20 pM. By using of both instruments we determined the heavy metal ions in soil samples. We added 0, 10, 50, 100 and 500 μM of Cd(II) and Pb(II) to the soil samples. The samples were shaken for 30 min. and analysed. At low concentrations added the ions of the heavy metals were accumulated to the soil compared to liquid in 40-60 %. At concentrations 100 μM the content of accumulated heavy metal lowered to 5-30 %.

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