

The presented Thesis describes development of new electroanalytical methods for the determination of toxic nitro and amino derivatives of fluoranthene. These compounds are drawing attention as highly hazardous substances. Fluoranthene and other PAH are emitted to the environment as a result of incomplete combustion of organic materials, during industrial processes, and other human activities and may undergo further photochemical atmospheric reactions when a number of other more polar products are formed. Among them, NPAH represent a considerable health risk to humans due to their genotoxicity and/or carcinogenicity. Nitrofluoranthenes are ones of the most prevalent nitro derivatives of PAH in polluted urban air. Amino derivatives of PAH are other extensively studied compounds. They are mainly of anthropogenic origin because of their widespread use as intermediates in chemical industry. Moreover, they are metabolites of NPAH and thus are used as biomarkers of exposure.

Taking these facts into account, large scale monitoring of environmental pollutants has become more and more important together with the studies of their biological impact on humans and other organisms. This requires development of independent, sensitive and selective detection techniques.

This Thesis represents a contribution to the search on new analytical methods applicable on environmental and biological samples. The current state-of-art concerning the formation, occurrence, and biological activity of 3-nitrofluoranthene and 3-aminofluoranthene was summarized in Chapter 2. Further experimental work was focused on assessment of new approaches in the detection of the studied compounds. Attention was paid mainly to the different electrode materials used for the determination of studied compounds by electroanalytical methods.

It has been shown in Chapter 3 that mercury electrodes in combination with modern polarographic and voltammetric techniques are suitable sensors for the determination of submicromolar and nanomolar concentrations of 3-nitrofluoranthene. New electrochemical methods were developed applying DC fast polarography and DPP at DME in methanol – BR buffer pH 3 (9:1) medium, resulting pH 5.1, and in methanol – BR buffer pH 12 (9:1) medium, resulting pH 11.7, achieved determination limits were 3×10^{-6} mol L⁻¹ for DCTP and 1×10^{-7} mol L⁻¹ for DPP. Moreover the determination of 3-nitrofluoranthene by DPV at HMDE in both above mentioned solutions as well as in methanol – 0.01M NaOH (9:1) medium were developed with the determination limits of 3×10^{-8} mol L⁻¹. The most sensitive method was

AdSV, using optimized conditions methanol – 0.01M NaOH (1:9) medium with the limit of determination of 5×10^{-9} mol L⁻¹.

Careful and sensitive monitoring of the presence of NPAH as the pollutants in the environment is a matter of great interest due to their toxicity even in very low concentrations. The need on sensitive methods for determination of 3-nitrofluoranthene in water is given by its proved occurrence in that matrix. Hence, the electroanalytical methods suitable for the determination of 3-nitrofluoranthene in model deionized, drinking, and river water samples were developed. The preliminary separation and preconcentration of 3-nitrofluoranthene was necessary to reached satisfactory L_Q . First, liquid-liquid extraction with hexane was applied but the reached L_Q for the determination of 3-nitrofluoranthene in river water samples was only 3×10^{-8} mol L⁻¹. Moreover, DP voltammetric determination after solid phase extraction using LiChrolut[®] RP-18e columns for the analyte preconcentration was reliable method for the determination of 3-nitrofluoranthene, characterized by sufficient recovery (72 %) and repeatability (RSD ~ 4 %). Subnanomolar L_Q of 4×10^{-10} mol L⁻¹ for SPE from 500 mL of drinking water samples and 2×10^{-9} mol L⁻¹ from 500 mL of river water samples were achieved.

The reduction mechanism studied by cyclic voltammetry in acidic medium corresponded to the well known mechanism of nitro group containing aromatics at mercury electrodes with the main signal corresponding to the four-electron reduction of the nitro to the hydroxylamino group followed by two electron reduction of the hydroxylamine to the amine. The same reduction mechanism was observed in alkaline medium as well.

In Chapter 4, the electrochemical reduction process of 3-nitrofluoranthene was studied on recently developed silver solid amalgam electrode, which is a promising nontoxic material fully compatible with the concept of green analytical chemistry. The reduction mechanism in acidic as well as in alkaline medium was similar to one observed at mercury electrodes with the main signal corresponding to the four-electron reduction of the nitro to the hydroxylamino group. The reduction of 3-nitrofluoranthene was shifted ~ 80 mV to more negative potentials in comparison with the reduction at HMDE. The meniscus modified silver solid amalgam electrode proved satisfactory for the determination of submicromolar concentrations of 3-nitrofluoranthene ($L_Q \sim 4 \times 10^{-7}$ mol L⁻¹) using DPV in methanol – 0.01 mol L⁻¹ NaOH (9:1) medium.

In Chapter 5, the voltammetric determination of 3-nitrofluoranthene at a boron doped diamond thin-film electrode along with the determination at a traditional glassy carbon

electrode was demonstrated. The electrochemical process of 3-nitrofluoranthene at BDDE was similar as one observed at HMDE with two cathodic peaks. However, the reduction of 3-NF at GCE involved the only peak of four-electron reduction of the nitro group to the hydroxylamino group, which was about 90 mV shifted to more negative potentials compared to BDDE. Reached L_Q for voltammetric determinations of 3-NF in methanol – BR buffer pH 12 (1:1) medium, resulting pH 12.2, were similar: $3 \times 10^{-8} \text{ mol L}^{-1}$ (for BDDE) and $4 \times 10^{-8} \text{ mol L}^{-1}$ (for GCE). On the other hand, to get reproducible results GCE had to be polished with a wet filter paper and a wet piece of velvet after each measurement, whereas only 60 s of stirring was applied between two measurements with BDDE. Both L_Q were comparable with one achieved for determination of 3-NF at HMDE. Moreover, observed potential window at GCE was shorter, and background was higher in comparison with BDDE (for CV).

In Chapter 6, the electrochemical oxidation process of 3-aminofluoranthene was compared at boron doped diamond thin-film electrode, glassy carbon electrode, and carbon paste electrode. Oxidation process was rather complicated and it was believed to form of an amine polymer. The easiest oxidation of 3-AF was at CPE followed by BDDE and by GCE. The oxidation process of 3-AF, which gave one main anodic irreversible peak at BDDE and at GCE, was similar. However, the situation was quite different at CPE, where two main peaks were observed, one reversible and one irreversible. L_Q of $2 \times 10^{-7} \text{ mol L}^{-1}$ was reached for DPV determination of 3-AF at BDDE as well as at CPE in methanol – BR buffer pH 4 (1:1) medium, resulting pH 4.8. But the achieved L_Q at GCE was about one order of magnitude higher. On the other hand, lower limit of determination was achieved used AdSV at GCE ($4 \times 10^{-7} \text{ mol L}^{-1}$) and at CPE ($2 \times 10^{-8} \text{ mol L}^{-1}$) both in methanol – BR buffer pH 4 (1:99) medium.

Last part of the Thesis was devoted to use of a thin-layer amperometric detector with working boron doped diamond thin-film electrode for HPLC determination of 3-aminofluoranthene. Reached limit of detection ($5 \times 10^{-8} \text{ mol L}^{-1}$) was in the same concentration range as one for spectrophotometric detector ($2 \times 10^{-8} \text{ mol L}^{-1}$). The repeatability of the electrochemical detector at higher concentrations was similar to spectrophotometric detector but a little worse at lower concentrations. Thus, tested electrochemical detector represents a cheap alternative to UV-VIS detector, and can be satisfactorily used for the determination of 3-aminofluoranthene.