

Abstract

The proposed dissertation thesis deals with the development and investigation of electrochemical flow systems using both conventional and unconventional electrode materials.

In the first part of this thesis, the problem of porous flow-through large area electrodes is addressed. As a working electrode material, a free-standing porous boron-doped diamond (fs-pBDD) was used. This was used for the first time in the construction of an electrochemical cell designed for amperometric detection in flow methods. Testing of this electrode was performed using amperometric detection combined with flow injection analysis of a ruthenium complex solution. The detection limits achieved on this material were in the submicromolar range and the linear dynamic range of the concentration dependence spanned over three orders of magnitude. In addition to amperometry, fs-pBDD was also subjected to testing by cyclic voltammetry. The main reason for using this method was to determine the electrochemically active area, which contributed to the overall physicochemical characterization of this promising material. However, it was this step that brought into question the accuracy and precision of the calculation used. For this reason, the search for new ways to calculate the electrochemically active area of the working electrode is also included in this part of the work. The calculation methods presented here are based both on the classical Randles-Ševčík equation and the adapted peak-charge method using cyclic voltammetry, and on the electrolysis equation using data obtained from chronoamperometry.

The second part of the thesis focuses on the steps towards the miniaturization of electrochemical detectors using flow-through working electrodes. The first step in this part was to find a suitable material from which a stable simple reference electrode could be constructed. The materials tested were palladium, antimony, bismuth and platinum, whose potential depends on the pH of the solution, and silver, whose potential is defined by the concentration of chloride ions. Based on tests using potentiometric, voltammetric and amperometric techniques, an antimony-based reference electrode was selected as the most suitable. This electrode was subsequently used in the design of a compact electrochemical cell using two auxiliary, two reference and one large area flow-through working electrode. The design of the flow cell presented here was chosen to minimise the effect of the ohmic drop on the behaviour of the porous working electrodes. This theory was verified using a carbon felt working electrode, whose electrochemical behaviour has already been characterized, and a newly prepared multitubular boron-doped diamond electrode.

The third part proposes a procedure for semi-automated stop-flow injection analysis with a

voltammetric endpoint for nucleic acid detection. The aim of this part was to transfer, until now only a batch, method based on selective desorption of nucleotides from the reaction mixture after amplification of the oligonucleotide chain and its subsequent voltammetric detection. The proposed procedure consists of (i) dosing and adsorption of a complex sample onto the surface of a working electrode made of pyrolytic graphite, (ii) selective desorption using a sodium dodecyl sulfate solution zone, (iii) washing off the desorption reagent, and (iv) detection of the adsorbed oligonucleotide with evaluation of the relative abundance of each base. The limits of detection achieved by the method proposed herein reach almost to nanomolar values.