

Studies on Novel Flow-Based Electrochemical Methods for Trace and Ultratrace Analysis of Some Harmful Substances

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This work describes the development of novel flow-based electrochemical methods and their application to the determination of some harmful substances: antibiotics (lincomycin, chloramphenicol), antibacterial agents (sulfonamides), and heavy metals (lead, cadmium and zinc), in pharmaceuticals, foods, and drinking water.

The electroanalysis of lincomycin was investigated using boron-doped diamond thin film (BDD) electrodes. First, the electrochemistry of lincomycin was studied by cyclic voltammetry as a function of pH of the solution, scan rate and the concentration of lincomycin. Comparison experiments were carried out using glassy carbon electrode. Boron-doped diamond thin film electrode provided well-resolved oxidation irreversible cyclic voltammogram. It was found that the peak position was 1.2 V (vs. Ag/AgCl reference electrode). Second, the amperometric detection with BDD electrode was coupled with the flow injection analysis for the determination of lincomycin. The linear range of 0.25 to 125 μ M and the detection limit of 0.02 μ M were obtained. This proposed method was also applied to a drug formulation sample. It was found that the results (293 mg mL⁻¹) were comparable to those labeled (300 mg mL⁻¹). The percent recovery was shown in a range of 96.32 to 103.1.

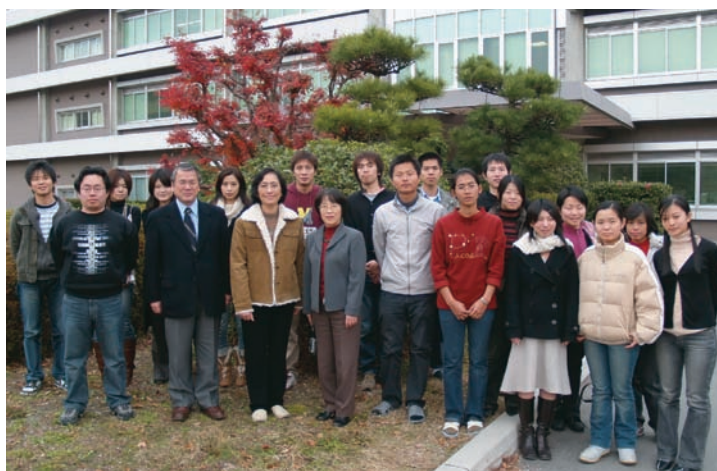
Sulfonamides (SAs) were electrochemically investigated using cyclic voltammetry at a boron-doped diamond (BDD) electrode. Comparison experiments were carried out using a glassy carbon electrode. The BDD electrode provided well-resolved oxidation, irreversible cyclic voltammograms and higher current signals when compared to the glassy carbon electrode. Results obtained by using the BDD electrode in a flow injection system coupled with amperometric detection were illustrated. The optimum potential from a hydrodynamic voltammogram was found to be 1,100 mV vs. Ag/AgCl, which was chosen for the HPLC-amperometric system. Excellent results of linear range and detection limit were obtained. This method was also used for determination of sulfonamides in egg samples. The standard solutions of 5, 10, and 15 ppm were spiked in a real sample, and recoveries were found to be between 90.0 and 107.7%.

The electrochemical properties of chloramphenicol at a boron-doped

diamond thin-film (BDD) electrode were studied using cyclic voltammetry. The highest current response of chloramphenicol was obtained with phosphate buffer, pH 6 (0.1 M) in 1% ethanol. The relationship between the concentration of chloramphenicol and the current response was linear over the range of 0.1 – 10 mM ($R^2 = 0.9990$). The amount of chloramphenicol was analyzed by flow-injection analysis. A thin-layer flow cell equipped with a BDD electrode was used as an amperometric detector, and experiments were carried out at -0.7 V (*vs.* Ag/AgCl). The linear relationship between the current response and the concentration of chloramphenicol in the range of 0.1 – 50 μ M ($R^2 = 0.9948$) and the limit of detection of 0.03 μ M ($S/N = 3$) were obtained. This method has been successfully applied to the determination of chloramphenicol in sterile eye drops and milk sample by the standard addition method. The average recoveries of chloramphenicol in eye drops were 98.0%, and the average recoveries of chloramphenicol from spiked milk were 93.9 – 103%.

A sequential injection – square wave anodic stripping voltammetry (SIA-SWASV) is proposed for the simultaneous determination of Pb (II), Cd (II) and Zn (II) employing *in situ* plated bismuth film screen-printed carbon electrode (Bi-SPCE) as a working electrode and hydrochloric acid as a supporting electrolyte. Bi (III) and analyte metal ions were on-line deposited on a SPCE at -1.4 V *vs.* Ag/AgCl for 180 s. At a stopped flow, the square-wave voltammogram was recorded from -1.3 to 0 V *vs.* Ag/AgCl. The experimental conditions were optimized. Under the optimum conditions, linear ranges were 0 – 70 μ g L⁻¹ for Pb (II) and Cd (II), and 75 – 200 μ g L⁻¹ for Zn (II). The limits of detection ($S/N = 3$) were obtained at the concentrations as low as 0.89 μ g L⁻¹ for Pb (II) and 0.69 μ g L⁻¹ for Cd (II) at 180-s deposition time. The proposed method was applied to the determination of Pb (II), Cd (II) and Zn (II) in water samples with satisfactory results.

An automated on-line preconcentration method was developed for simultaneous determination of Pb (II), Cd (II) and Zn (II) by square-wave anodic stripping voltammetry (SWASV) using bismuth film screen-printed carbon electrode (Bi-SPCE). The preconcentration of metal ions was performed with a mini-column of a chelating resin, which was installed on a switching valve in the automated system consisted



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of a syringe pump, an 8-port selection valve and a switching valve. The laboratory-assembled automated on-line pretreatment system (Auto-Pret ASV system) was controlled by the Visual Basic program written by the authors. The metal ions collected on the resin were eluted with 1 M hydrochloric acid, subsequently transported into the flow cell for on-line deposition of analytes on Bi-SPCE at $-1.4\text{ V vs. Ag/AgCl}$; then the flow of the solution was stopped and the voltammogram was recorded from -1.2 to 0.2 V vs. Ag/AgCl by scanning a potential in the square-wave waveform. Experimental conditions, such as pH of sample, a sample flow rate, an eluent volume and its flow rate were optimized. Under the optimum conditions, the analytical characteristics were studied. In addition, the proposed method was applied to the analysis of water samples.



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