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Antimony film electrodes for voltammetric determination of pesticide trifluralin

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ABSTRACT

Antimony film electrodes (SbFEs) were prepared *ex situ* on various substrate electrodes (namely copper, gold, silver, polished silver solid amalgam, and glassy carbon electrode) and their performance was compared with bare substrate electrodes. The antimony film glassy carbon electrode (SbFGCE) provided the best results. Additionally, parameters of antimony film preparation and other experimental parameters for the determination of pesticide trifluralin were optimised. SbFGCE exhibited good electroanalytical performance for the determination of trifluralin in highly acidic methanolic medium in the concentration range from 1×10^{-6} to 1×10^{-4} mol L^{-1} with a limit of quantification 1.2×10^{-6} mol L^{-1}. Furthermore, SbFGCE was used for the determination of trifluralin in model river samples with similar characteristics. Solid phase extraction (SPE) used for preliminary separation and preconcentration in model river water samples enabled to decrease the limit of quantification to 1.3×10^{-8} mol L^{-1}.

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1. Introduction

The search for of new electrode materials and surfaces for sensors is systematically pursued in modern electroanalytical chemistry. For decades mercury electrodes had been providing the best characteristics for application in electrochemical analysis of metals and some reducible organic compounds. In recent years the use of mercury-based electrodes has been decreasing because of the fear of their toxicity and handling problems. Search for new electrode materials or modifications of currently used materials possibly replacing mercury electrodes and applicable for metallic and organic analytes resulted in the introduction of antimony film electrodes (SbFEs) [1].

The development of film electrodes started with mercury film electrodes which were introduced to eliminate some of disadvantages of the dropping mercury electrode and the hanging mercury drop electrode, such as instability of a mercury drop in flow systems and high consumption of mercury [2]. In the year 2000 bismuth film electrodes were introduced [3] and they have been accepted and used in electroanalytical laboratories for determination of heavy metals and some organic compounds providing performance comparable to mercury film electrodes [4]. In 2007, the antimony film electrode (SbFE) was introduced in a study of trace heavy metals. The SbFE was reported to be superior to bismuth and mercury film electrodes in very acidic media giving lower detection limit and better reproducibility [1].

Generally, film electrodes are prepared by depositing metals (*e.g.* mercury, bismuth or antimony) on the substrate electrode. This is usually an electrochemical process, where the film is deposited on the substrate electrode either from a solution of a metal compound (*ex situ*) or the metal compound is directly added to the solution with determined analytes (*in situ*). The *in situ* method is preferred when studying heavy metals. The most frequently used substrate electrodes are glassy carbon electrodes (GCE). Another commonly used substrate electrodes are made from gold, platinum or silver [2,4]. Concerning the SbFE, glassy carbon [5–7], carbon paste [8], boron doped diamond [9], and silica chip [10] were so far used as substrates for the preparation of the SbFE.

Since the introduction of the SbFE, there have been numerous studies devoted mainly to the determination of heavy metals by anodic stripping voltammetry [5,8,11]. On the contrary, only few organic compounds have been studied exclusively on antimony film carbon-based electrodes, *i.e.* drugs sulfasalazine [12] and pantoprazole [13] and food dyes allura red with tartrazine [14]. Therefore, further investigation of SbFEs formed at different substrate electrodes and its application for the determination of organic compounds using pesticide trifluralin as a model compound was performed in this paper.

Trifluralin is one of the most used pesticides in the USA [15], but it is currently banned in the EU [16] because of its high toxicity to water organisms in concentrations as low as 0.2 μmol L^{-1} (LC$_{50}$, rainbow trout) [17]. Trifluralin belongs to the class of so called dinitroaniline herbicides [18] and as the name suggests, it contains two nitro groups on benzene moiety (see Fig. 1). Both these groups are electrochemically reducible *via* simultaneous 8-electron reduction to hydroxylamine groups in

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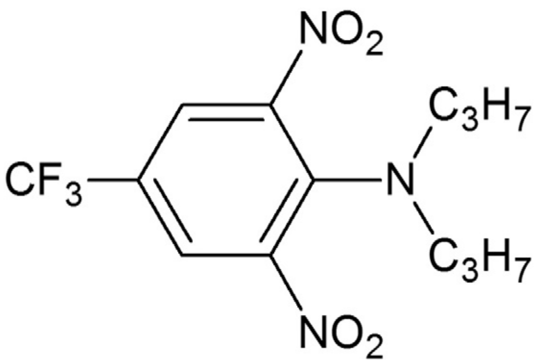

Fig. 1. Chemical structure of trifluralin.

acidic medium [19,20]. This substance was previously studied by voltammetric methods on amalgam electrode [21] or glassy carbon electrode [22]. Moreover, various chromatographic methods have been used for its determination [23,24]. Solid phase extraction (SPE) was applied to improve limits of detection [25,26], which was the inspiration for extraction carried out in this work.

This study has been focused on the characterization and the comparison of different substrate electrode materials used for the preparation of antimony film electrodes. Differential pulse voltammetry (DPV) has been used to demonstrate the applicability of prepared antimony film electrodes for the determination of low concentrations of trifluralin. Practical applicability of this method has been verified by the determination of submicromolar concentrations of trifluralin in model river water samples after SPE.

2. Experimental

2.1. Chemicals and reagents

A stock solution of trifluralin (0.01 mol L^{-1}, CAS name: 2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)-benzenamine, CAS number: 1582-09-8, 99.2% from Sigma Aldrich, Germany) was prepared by dissolving 33.53 mg of the substance in 10 mL of methanol (p.a. Penta, Czech Republic). More diluted solutions were prepared by exact dilution of the stock solution with methanol. A plating solution was prepared by dissolving antimony chloride in 2.5 mol L^{-1} hydrochloric acid (both p.a. Lach-ner, Czech Republic) with concentration 1 g L^{-1} of Sb(III) ions. Britton–Robinson buffers were prepared by mixing 0.04 mol L^{-1} phosphoric, acetic, and boric acid with 0.02 mol L^{-1} sodium hydroxide (all p.a., Lach-ner). All prepared solutions were stored in glass vessels in dark at the laboratory temperature. Deionised water was produced by Millipore Milli-Q system (Millipore, USA).

2.2. Apparatus

All voltammetric measurements were carried out on Eco-Tribo Polarograph controlled by Polar Pro 5.1 software (both Polaro-Sensors, Czech Republic). Voltammetric measurements were carried out in a three-electrode system with Ag|AgCl|3 mol L^{-1} KCl (Elektrochemicke detektory, Turnov, Czech Republic) reference electrode and a platinum wire auxiliary electrode (Eco-Trend Plus, Czech Republic). Five working disk electrodes were used: silver (Elektrochemicke detektory), gold (Metrohm, Switzerland), copper (labmade), glassy carbon (Metrohm), and polished silver solid amalgam electrode (Eco-Trend Plus) with diameters summarized in Table 1. pH measurements were conducted with pH-meter Jenway 3510 (Bibby Scientific Ltd., United Kingdom) with Jenway combined glass electrode (924 005).

2.3. Procedures

All solutions for voltammetric measurements were prepared by measuring 5.0 mL of 0.1 mol L^{-1} HCl (or Britton–Robinson buffer of appropriate pH) into a 10.0 mL volumetric flask. Afterwards, appropriate amount of the stock solution of trifluralin in methanol was added and the flask was filled with methanol to the mark and thus obtained solution was transferred to a voltammetric cell. The solution was then purged with nitrogen for 5 min and corresponding voltammogram was recorded. The purging was repeated for 30 s before every single measurement. All voltammetric curves were measured at least 5 times at the laboratory temperature. Scan rate 20 mV s^{-1} was used in direct current (DC) and DP voltammetry, pulse width of 100 ms and pulse amplitude −50 mV were used in DPV. Cyclic voltammetric (CV) measurements were carried out at scan rate of 100 mV s^{-1}.

The DPV peak height was evaluated from the line connecting minima before and after the peak. All calculated parameters were evaluated with Origin software (OriginLab Corp., USA). Limits of quantification were calculated as a concentration corresponding to tenfold of a standard deviation of ten subsequent measurements at the lowest measurable concentration.

2.4. Preparation of SbFE

All tested substrate electrodes used were polished before the deposition of the film with aqueous slurry of an alumina powder (1.1 μm) on a polishing pad for 5 min and then rinsed with deionised water. The electrode was transferred into the plating solution with 20 mg L^{-1} Sb(III) in 0.1 mol L^{-1} HCl. An electrode-specific potential (summarized in Table 1) was then applied to the electrode for 60 s in stirred solution. Applied potentials were determined from cyclic voltammograms of the plating solution on the given substrate electrode from which a potential of Sb(III) reduction was obtained. For DPV determination of trifluralin on the SbFGCE deposition parameters were optimised to 40 mg L^{-1} Sb(III) concentration in the plating solution with the applied potential of −800 mV for 90 s in the stirred solution.

2.5. Voltammetric determination of trifluralin in model samples of river water

River water samples from Vltava River in Prague (Czech Republic) were used. Volume of 4.5 mL of the river water sample spiked with stock trifluralin solution was transferred into a 10.0 mL volumetric flask and 0.5 mL of 1 mol L^{-1} HCl was added. Afterwards, the flask was filled with methanol to the mark, the solution was transferred to the voltammetric cell and after 5 min bubbling with nitrogen corresponding voltammogram was recorded.

2.6. Solid phase extraction

SPE cartridges (Li-Chrolut RP-18 E, 200 mg, Merck, Germany) were used to process deionised water samples, SPE cartridges (Li-Chrolut RP-18 E, 1000 mg) were used to process river water samples. Cartridges with 200 or 1000 mg of stationary phase were prewashed by 3 or 6 mL of methanol three times and rinsed with 3 or 6 mL of deionised water three times. River water samples were prefiltered through filtration paper (GF-3, Macherey-Nagel, Germany). 500 mL of deionised water or filtered river water was spiked with trifluralin stock solution and passed through the cartridge under vacuum at 4 mL min^{-1} (200 mg cartridge) or 10 mL min^{-1} (1000 mg cartridge), the cartridge was then dried by pulling air for 10 min. Trifluralin was eluted by 2.0 mL of methanol, diluted with 0.1 mol L^{-1} HCl to 4.0 mL and then transferred to the voltammetric cell for the measurement.

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