PROCEEDINGS OF THE

23rd International Symposium on Analytical and Environmental Problems

October 9-10, 2017

University of Szeged, Department of Inorganic and Analytical Chemistry

**Szeged
Hungary**

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Publisher:
University of Szeged, Department of Inorganic and Analytical
Chemistry, H-6720 Szeged, Dóm tér 7, Hungary

2017.
Szeged, Hungary

The 23rd International Symposium on Analytical and Environmental Problems

Organized by:

SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi Munkabizottsága

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ANTIMONY FILM ELECTRODE FOR CHRONOPOTENTIOMETRIC DETERMINATION OF INSECTICIDE IMIDACLOPRID

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Abstract
The most important experimental parameters were investigated for chronopotentiometric determination of imidacloprid using thin film antimony electrode as a working electrode. The film of antimony was *ex-situ* plated on the glassy carbon electrode. Britton-Robinson buffer pH 10 was used as an optimal supporting electrolyte, where imidacloprid provided a well define and reproductive reduction signal at the potential of -1100 mV (*vs.* Ag/AgCl, 3.5 mol/dm^3 KCl). Based on the height and reproducibility of the analytical signal, initial potential of -0.51 V was accepted as optimal, while selected optimal ranges of reduction current were from -5 µA to -14.4 µA, and from -4.6 µA to -18.2 µA, for concentrations of 2 mg/dm^3 and 10 mg/dm^3, respectively. It was determined that analytical signal of imidacloprid decreased exponentially with more negative values of reduction current. Before application of this method to environmental samples, additional experiments related to method validation are necessary.

Introduction
Agricultural production is an important sector of the worldwide economy. As the human population is growing every day, in order to increase food production, the use of pesticides is inevitable. An estimation is that millions tons of these chemicals are applied in agriculture annually worldwide, but less than 1% of the total applied pesticides reaches the target pests, while the rest remains in the environment, where they can be toxic to humans and other non-target animals [1]. The persistence and mobility of the pesticides in the environment is influenced and controlled by many processes and numerous biological, physical and chemical reactions [2]. Furthermore, the physical and chemical properties of the molecule determine its soil and water mobility and volatility.

Imidacloprid (IM) is the most frequently used neonicotinoid group of insecticide. According to the mode of action, IM is acting as a systematic neurotoxin. It interferes with the synaptic transmission of stimuli in the central nervous system, that is more abundant in insects than in mammals [3]. Despite much lower toxicity of this insecticide to mammals than to vertebrates, many studies shown that IM causes hazards to other non-target organisms such as beneficial insects [4], birds [5], and many aquatic species [6, 7]. Owing to its chemical properties: high water solubility and long half-life in soil and water, IM exhibits a high runoff and releasing potential to surface and groundwater [6]. The highest reported concentration of this insecticides were reported in Netherland 0,32 mg/l [8]. Therefore, development a simple, sensitive and fast analytical method for IM determination in environmental water samples is necessary in analytical chemistry. Principally, IM is analysed by chromatographic techniques that are expensive and time-consuming. On the other hand, electrochemical methods can serve

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as an alternative technique for determination of this insecticide, owing to their simplicity, high sensitivity, and simple instrumentation.

For the long time mercury-based electrodes have been extensively used in electrochemistry for determination of many different compounds, due to their reproducibility and wide cathodic potential window [9], but the toxicity of mercury triggered the search for other environment friendly electrode materials. Antimony film electrodes (SbFEs) were introduced in 2007, and revealed interesting characteristics: wide potential window, and favourable performance in very acid media [10]. In most cases the antimony film is plated on a carbon substrate via *in-situ* or *ex-situ* procedure, and the most frequently used substrate electrodes are glassy carbon electrodes [11]. Since the introduction, SbFEs, combined with *in-situ* procedure, were mostly used for determination of heavy metals. On the other hand, a small number of studies describing the use of these electrodes for determination of organic substances: drugs [12], food dyes [13] and pesticides [11].

The main objective of the present study was to investigate the optimal experimental: chemical and instrumental parameters for determination of IM. Chronopotentiometry was used as an electrochemical technique to demonstrate applicability of *ex-situ* prepared SbFE. Developed method can be used as a fast and economical method for quantification of IM in different environmental samples.

Experimental

Chemicals and instrumentation

Standard stock solution of IM (0.4 g/dm^3) was prepared by dissolution of solid standard (Dr. Ehrenstorfer, Augsburg, Germany) in double distilled water. Britton-Robinson (BR) buffer was prepared from equimolar 0.04 mol/dm^3 stock solutions of orthophosphoric, boric, and acetic acids (Lach-Ner, Brno, Czech Republic). Required pH value of the BR buffer was adjusted by addition of 0.20 mol/dm^3 sodium hydroxide solution (Lach-Ner, Brno, Czech Republic). Saturated solution of sodium sulphite (Centrohem, Stara Pazova, Serbia) was prepared by dissolution of the appropriate amount of the substance in double distilled water. Double distilled water was used throughout the experiments.

Chronopotentiometric measurements were carried out using an automatic stripping analyser, of domestic construction. A three-electrode configuration was used with the working SbFE, Ag/AgCl (3.5 mol/dm^3 KCl) reference electrode and a platinum wire as counter electrode. A glassy carbon disc electrode of a total surface area of 7.07 mm^2 was used as an inert support for the SbFE. All values of the potential were shown versus Ag/AgCl, 3.5 mol/dm^3 KCl, reference electrode.

Before the deposition of the antimony film, glassy carbon electrode was polished with aqueous slurry of an aluminium oxide (0.5 μm, Merck, Darmstadt, Germany) on a polishing pad until a mirror-like surface was obtained, and then rinsed with doubly distilled water. The electrode was transferred into the plating solution with 40 mg/dm^3 Sb^{3+} in 0.005 mol/dm^3 HCl. A specific potential of -0.8 V was then applied to the electrode for 240 s in stirred solution. Thin film of antimony was mechanically removed with filter paper wetted with acetone, and then with double distilled water.

For performing chronopotentiometric measurements, SbFE was placed in the electrochemical cell filled with 20 cm^3 of the analysed solution. Dissolved oxygen was removed from the solution by adding 1 cm^3 of the saturated solution of sodium sulphite, and stirring the solution for 30 s. After a 10-s quiescence time, chronopotentiogram was recorded by applying a

negative potential scan from -0.51 V to -1.2 V. All experiments were performed using three replicates at the ambient temperature(23–25°C).

Results and discussion

Preliminary experiments performed in this study were performed by recording chronopotentiograms of IM standard solution (2 mg/dm^3) in potential range from: -0.70 V to -1.2 V, with applied reduction current of -5.8 μA. The performed experiments included the choice of the optimal chemical (supporting electrolyte and its pH value), and instrumental parameters (initial potential and reduction current) of the chronopotentiometric analysis of IM. Experiments included different supporting electrolytes: 0.04 mol/dm^3 BR buffer, 0.1 mol/dm^3 acetate, citrate, phosphate buffer, and 4.5 g/dm^3 sodium sulphite. In BR buffer and 4.5 g/dm^3 sodium sulphite solution IM provided a single well-defined reduction wave. In reversible potential scan no corresponding signal was recorded indicating that the electrode process can be regarded as electrochemically irreversible. Since BR buffer showed better performances in terms of sensitivity, reproducibility and sharpness of the analytical signal, this buffer was accepted as optimal in further experiments.
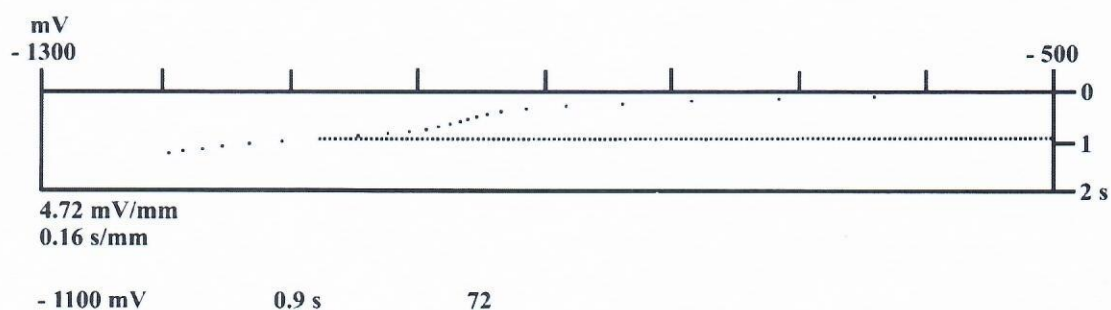
In order to choose optimal pH value of the BR buffer, chronopotentiograms of fixed concentrations of imidacloprid (2 mg/dm^3), with varying pH value of the buffer in the range from 2 to 12, were recorded, while other parameters of the analysis were kept constant. The signal of the insecticide was obtained in pH range from 9 to 12 (Table 1), while in acid and neutral media the peak totally disappeared. It was also noticed that peaks shifted to more negative potentials by increasing the pH, from -950 mV to -1150 mV. The highest peak intensities were recorded at pH 10 (Table 1), and this value was consequently selected for further analytical studies (Figure 1).

Table 1 Influence of pH of Britton-Robinson buffer on the analytical signal of imidacloprid concentration of 2 mg/dm^3

pH of Britton-Robinson buffer	Reduction time (s) ± SD[*]	RSD (%)
9	0.93 ± 0.03	3.33
10	1.05 ± 0.02	2.10
11	0.89 ± 0.03	5.31
12	0.96 ± 0.03	2.63

[*]X_{mean} ± SD, n = 3.

Figure 1. Chronopotentiogram of imidacloprid on antimony film electrode in Britton-Robinson buffer pH 10, C_{im} = 2 mg/dm^3, $E_{initial}$ = -0.51 V, I = -5.8 μA.

mV
- 1300   - 500
                                                                              0

                                                                              1

                                                                              2 s

4.72 mV/mm
0.16 s/mm

- 1100 mV   0.9 s   72

Influence of the initial potential on the reduction time of IM was investigated in the range from +0.20 V to -0.75 V, in solution containing 2 mg/dm^3 IM. Applied reduction current was -5.8 µA, and the value of the final potential was -1.2 V. It was observed that initial potentials higher than -0.416 V produced a protracted chronopotentiograms, while at values lower than -0.695 V the response of IM was not observed. Considering the height and reproducibility of IM signal (τ_{red} = 0.85 s, RSD = 1.67%, Table 2), initial potential of -0.51 V was chosen as a suitable.

Table 2 Influence of the initial potential on the analytical signal of imidacloprid concentration of 2 mg/dm^3

Initial potential (V)	Reduction time (s) ± SD[*]	RSD (%)
-0.695	0.84 ± 0.04	4.45
-0.649	0.87 ± 0.04	4.33
-0.602	0.83 ± 0.03	3.43
-0.556	0.84 ± 0.04	5.04
-0.510	0.85 ± 0.01	1.67
-0.464	0.84 ± 0.02	2.94
-0.416	0.84 ± 0.03	3.36

[*]X_{mean} ± SD, n = 3.

Reduction current represents one of the most important experimental parameters in chronopotentiometric analysis, due to its significant influence on height and sharpness of the analytical signal. Influence of the reduction current on IM analytical signal was investigated in model solutions containing 2 mg/dm^3 and 10 mg/dm^3 of IM. Investigated ranges of the reduction current were from -5 µA to -14.4 µA for solution containing 2 mg/dm^3 of IM, and from -4.6 µA to -18.2 µA for solution containing 10 mg/dm^3 of IM. IM reduction time exponentially decreased with more negative value of the reduction current, for both lower (τ_{red} = 2.6238 e$^{0.1891\,I}$, r = 0.9943) and higher (τ_{red} = 11.228 e$^{0.215\,I}$, r = 0.9969) concentrations of IM.

Conclusion

In this study optimization of basic experimental and instrumental parameters was performed using SbFE as a working electrode, and insecticide IM as the tested compound. Thin film of antimony was *ex-situ* plated on the glassy carbon electrode. By using chronopotentiometry, BR buffer of pH 10 was selected as an optimal supporting electrolyte. Optimal instrumental parameters of chronopotentiometric analysis, included the choice of the optimal value of the initial potential, and the ranges of reduction current. Chronopotentiometry in combination with SbFE can be used as a simple and fast method for determination of IM in different environmental samples, still before application further experiments are necessary.

Acknowledgements

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