

## ELECTROCHEMICAL DETERMINATION OF SELECTED PESTICIDES IN ENVIRONMENTAL WATER SAMPLES

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### ABSTRACT

Electrochemical detection of various contaminants has been widely used as a powerful tool in quality control of food and analysis of environmental samples. In this work, electrochemical procedures for determination of pesticides imidacloprid, metribuzin and metamitron are presented. Thin film layer electrode is used as a working electrode, while chronopotentiometry is applied as an electroanalytical technique. For all analysed pesticides, several solution conditions and instrumental parameters influencing the electroanalytical response of the analytes are examined and optimised in respect to the height of the analytical signals. The obtained analytical signals for the investigated pesticides are the result of irreversible reduction of the analyte on the working electrode surface, and for each analyte one reduction wave is obtained. Under the optimal experimental conditions, proposed chronopotentiometric methods are validated with the respect to linearity, limit of detection, limit of quantification, precision, selectivity, recovery and accuracy. Validated chronopotentiometric methods are applied for analysis of selected pesticides in spiked tap and river water samples. In the analysis of real samples, proposed methods showed to be sensitive and reproducible, fast (1-5 s analysis time), and simple since no complicated sample preparation is needed, and therefore are suitable for routine analysis of pesticides in water samples.

**Keywords:** *imidacloprid, metribuzin, metamitron, electroanalysis, water*

### INTRODUCTION

In recent years, pesticides have been widely used in agriculture to eliminate or control a variety of agricultural pests that can damage crops and reduce farm productivity. As a result of increased and uncontrolled usage of pesticides, they have been found frequently remaining in fruit, vegetables and crops (Ballesteros & Parrado, 2004; Cheng et al., 2011; Shi et al., 2014). Pesticides and their degradation products may also spread through the environment and contaminate water resources, consequently causing environmental problems (Herrero-Hernández et al., 2013; De Gerónimo et al., 2014). In intensive agricultural areas contamination of surface and ground waters is more likely to occur. Exposure of the general population to pesticides occurs mainly through eating food and drinking water contaminated with pesticides (Damalas & Eleftherohorinos, 2011). Generally, pesticides have been developed with target function against the certain pest, but not to be toxic for other species in ecosystem and hazard for human beings. However, there are a lot of published data about harmful effects of pesticides on animals and humans (Damalas & Eleftherohorinos, 2011). Hence, the monitoring of the pesticide residue levels in food and environmental water samples is of special concern to human health and environmental safety.

In water samples, pesticides are mainly determined by sophisticated techniques such as gas chromatography and high-performance liquid chromatography (Berijani et al., 2006; Polati et al., 2006; Tran et al., 2007). Those techniques require complicated sample preparation procedures, usually involving liquid-liquid extraction, solid-phase extraction and dispersive liquid-liquid microextraction. These procedures are time-consuming and expensive, and often, especially in case of liquid-liquid extraction, require usage of high volumes of toxic organic solvents. On the other hand, electroanalytical techniques represent an attractive alternative for pesticide analysis, since they imply low cost and relatively simple instrumentation, and possibility of on-situ testing of untreated samples with satisfactory



precision and accurate results (Đurović et al., 2018). They also offer practically unlimited possibilities for new sensor platform designs and miniaturization of sensing elements.

In his work, simple chronopotentiometric methods using a thin film mercury electrode (TFME) are described for determination of pesticides imidacloprid, metribuzin and metamitron. Imidacloprid is the first discovered neonicotinoid insecticide with widespread use, while metribuzin and metamitron are selective pre- and post-emergence herbicides commonly used for weed control. The developed methods are based on the reduction of the pesticides in the Britton–Robinson (BR) buffer. After the optimization of experimental parameters and validation of procedures, developed methods are applied for analyses of selected pesticides in spiked tap and river water samples.

## MATERIAL AND METHODS

Stock solutions of imidacloprid, metribuzin and metamitron are prepared weekly and stored in refrigerator in the dark. Working standard solutions are prepared daily by dilution of stock solutions with the supporting electrolyte. The BR buffer (0.04 mol/L) is prepared by dissolving the appropriate amount of boric, acetic and orthophosphoric acids (Lach-Ner, Neratovice, Czech Republic) in doubly distilled water. The desirable pH of the buffer is adjusted with sodium hydroxide (0.2 mol/L) (Lach-Ner, Neratovice, Czech Republic). All chemicals used are of analytical reagent grade. Doubly distilled water is used throughout the experiments.

All electrochemical measurements are performed using a M1 analyzer of domestic construction. Standard three-electrode electrochemical cell is used. Ag/AgCl (3.5 mol/L KCl) and platinum wire are used as a reference and counter electrode, respectively. Reported values of the potentials are shown versus Ag/AgCl (3.5 mol/L KCl) reference electrode. TFME is used as a working electrode. Deposition of a thin mercury film is performed potentiostatically from a solution containing 0.11 g/L of  $\text{Hg}^{2+}$  and 0.02 mol/L of HCl, at the potential of 0.4 V for 240 s. As an inert support for thin film of mercury, previously polished glassy carbon disc electrode is used (total surface area of 7.07 mm<sup>2</sup>). Prior to deposition of mercury film the surface of the glassy carbon is cleaned with filter paper wetted firstly with acetone, and then with doubly distilled water. After approximately 50 analyses the film is mechanically removed by the filter paper, and deposition is repeated as described.

Tap and river water samples collected from different locations on the territory of Vojvodina are used for preparation of BR buffer, by dissolving of the appropriate acids in the samples, and by adjusting the appropriate pH value. For performing the chronopotentiometric analysis 20 mL of the solution is transferred into the electrochemical cell and analyzed.

## RESULTS AND DISCUSSION

Selection of the appropriate supporting electrolyte is the crucial step in development of electroanalytical method. Thus, firstly influence of the supporting electrolyte is evaluated in a solution containing 2.5 and 10 mg/L of each pesticide in various electrolytes including acetate, citrate, phosphate and BR buffers, and 0.025 mol/L of sulphuric acid. Applied reduction current was around -6  $\mu\text{A}$ , while chronopotentiometric measurements are performed in the potential range from 0 to  $\sim -1.3$  V. Since the highest and the sharpest analytical signals are obtained in BR buffer, it is accepted as optimal and used in all further experiments. Effect of pH value of the BR buffer on the analytical signal of each analyzed pesticide (2 mg/L) is studied over the pH range of 2.0-12.0. Results are shown on Figure 1. Due to the highest analytical signal obtained with a good reproducibility and shape of chronopotentiogram, BR buffer (0.04 mol/L) at pH levels 9.0, 5.0 and 7.0 were chosen as the most appropriate supporting electrolytes for imidacloprid, metribuzin and metamitron, respectively. Mean reduction potentials were -1.023 V, -0.805 V and -0.830 V for imidacloprid, metribuzin and metamitron, respectively.



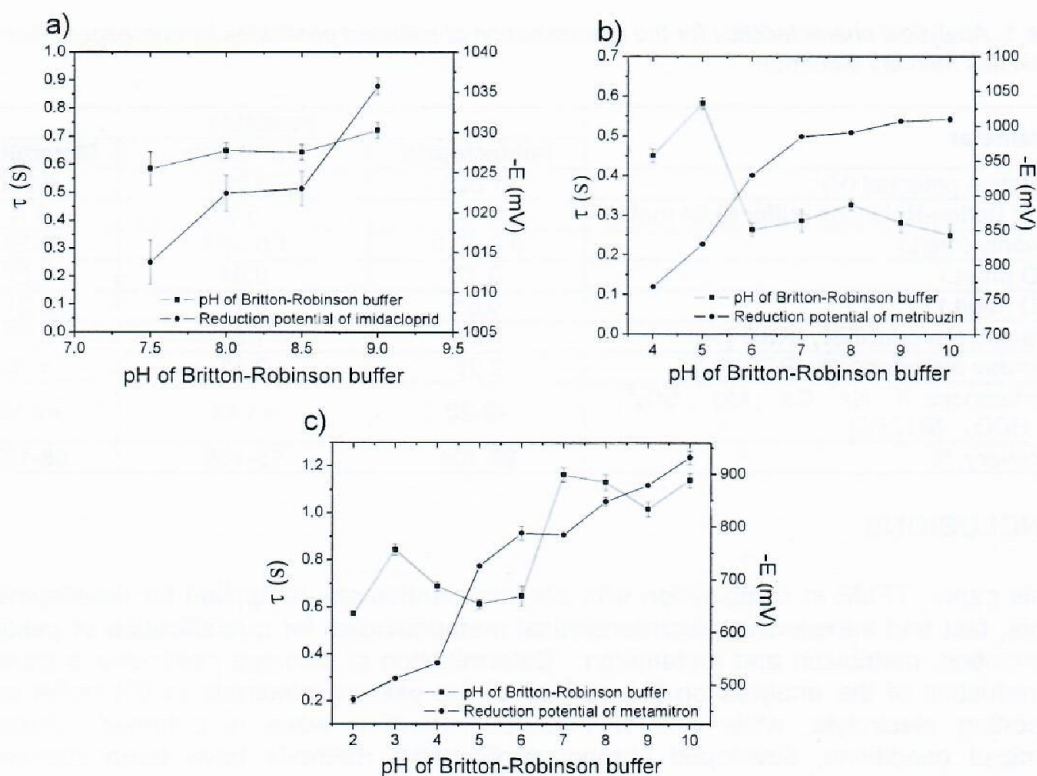


Figure 1. Effect of pH on analytical signal of a) imidacloprid, b) metribuzin and c) metamitron (2 mg/L) in 0.04 mol/L Britton-Robinson buffer

Influence of the initial potential on the height of the analytical signal is examined in the range from  $\sim 0$  V to  $-0.9$  V, in the solutions containing 2.0 mg/L of each pesticide in the supporting electrolyte. Reduction current was  $\sim 5$   $\mu$ A. With more negative initial potential the transition time of all pesticides decreased significantly. An initial potential value of  $-0.18$  V is chosen as suitable for all analysed pesticides, considering the heights of the pesticides transition times and their reproducibility (RSD < 2.59%).

In chronopotentiometry, the choice of the optimal value of the reduction current depends on the concentration of the analyte. Generally, for higher concentrations higher values of the reduction current should be applied, and vice versa. Influence of the reduction current on the analytical signal is studied for two concentrations of each pesticide (1 mg/l and 5 mg/L of imidacloprid, and 2 mg/L and 10 mg/L of metribuzin and metamitron). In all three cases, reduction times exponentially decreased with reduction current increase. Optimal current values were in range from  $-3.8$   $\mu$ A to  $-27.6$   $\mu$ A for imidacloprid, from  $-6.6$   $\mu$ A to  $-21.6$   $\mu$ A for metribuzin and from  $-2.3$   $\mu$ A to  $-9.5$   $\mu$ A for metamitron. With respect to the required sensitivity, a particular value of the cathodic current should be chosen from the given ranges. After the optimization of experimental parameters, an analytical procedures for quantitation of analysed pesticides by chronopotentiometry are validated with respect to linearity, limit of detection (LOD), limit of quantification (LOQ), precision, selectivity and recovery, according to ICH guidelines (ICH, 1996). Results are presented in Table 1. As can be seen, linearity is obtained for wide concentration range, accompanied with quite good sensitivity for all pesticides. Influence of potentially present interferences was minimal (relative error less than 4.50%), confirming good selectivity of developed methods. By analyzing spiked tap and river water samples, recovery was in range from 95% to 104%, indicating good accuracy of proposed methods and that they can be applied in analysis of real drinking and environmental water samples.



Table 1. Analytical characteristics for the determination of selected pesticides by chronopotentiometry on thin film mercury electrode

Parameter	Pesticide		
	Imidacloprid	Metribuzin	Metamitron
Detection potential (V)	-1.023	-0.805	-0.830
pH of Britton-Robinson buffer (0.04 mol/L)	9.0	5.0	7.0
Linearity (mg/L)	0.8-30.0	1.0-30.0	0.8-30.0
LOD (mg/L)	0.17	0.04	0.07
LOQ (mg/L)	0.51	0.13	0.21
Intra-day reproducibility, RSD (%)	1.27	1.56	0.88
Inter-day reproducibility, RSD (%)	2.28	2.13	1.75
Interferences: K <sup>+</sup> , Na <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , HCO <sub>3</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> (%)	<2.20	<4.48	<4.50
Recovery, %	99-104	95-100	98-100

## CONCLUSIONS

In this paper, TFME in combination with chronopotentiometry is applied for development of simple, fast and inexpensive electroanalytical methodologies for quantification of pesticides imidacloprid, metribuzin and metamitron. Determination of selected pesticides is based on the reduction of the analytes on the surface of the working electrode in BR buffer as the supporting electrolyte, while one well-defined reduction wave is obtained. Under the optimized conditions, developed chronopotentiometric methods have been successfully applied for determination of selected pesticides in spiked tap and river water samples, without any sample preparation steps which are fundamental in a number of other analytical procedures. Due to high simplicity, sensitivity, short analysis time and suitability for field measurements, developed methods can be a useful alternative to chromatographic methods for determination of selected pesticides in real drinking and environmental water samples.

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