

Voltammetric Determination of Insecticide Thiamethoxam on Silver Solid Amalgam Electrode



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ABSTRACT

This work demonstrates the applicability of differential pulse voltammetry (DPV) for the determination of the insecticide thiamethoxam at a non-toxic mercury meniscus modified silver solid amalgam electrode (m-AgSAE). The optimum supporting electrolyte was found to be Britton-Robinson (BR) buffer, pH 10. The target compound was quantified directly in spiked drinking and river water samples in the range from 100 $\mu\text{mol L}^{-1}$ to limits of determination (LOQs) 0.36 and 0.46 $\mu\text{mol L}^{-1}$, respectively. After preliminary separation and preconcentration by solid phase extraction (SPE) using Lichrolut EN cartridges, quantification in spiked river and drinking water samples was possible in the range from 100 nmol L^{-1} to LOQs 1.3 and 1.1 nmol L^{-1} , respectively. m-AgSAE is practically non-toxic, possesses good mechanical stability and is easy to handle and activate and thus represents a suitable alternative to the hanging mercury drop electrode (HMDE).

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1. Introduction

Over the last years, the use of pesticides in agriculture has been instrumental in the increase in the agricultural production. Although the presence of pesticides is currently not only necessary but rather unavoidable, there are rising concerns about their excessive use and the potential side effects to human health, caused by the consumption of food with pesticides' residues.

Neonicotinoids are registered globally in more than 120 countries, representing nearly 25% of the global pesticide market, and they are among the most effective insecticides for control of sucking insect pests. Thiamethoxam, (3-[(2-chloro-5-thiazolyl)methyl] tetrahydro-5-methyl-N-nitro-4H-1,3,5-oxadiazin-4-imine, see Fig. 1) belongs to this group, and acts selectively on the central nervous system of insects with minimal effects on beneficial insects and with low toxicity toward mammals without causing teratogenic or mutagenic effects [1–6]. Marked as Actara for foliar treatment and as Cruiser for seed treatment, to date thiamethoxam is registered for 116 types of crops in at least 64 countries [1,5,7,8].

Although thiamethoxam does not possess any toxicity for mammals, it has to be considered toxic to bees. In January 2013, the European Food Safety Authority presented its conclusions on the risk assessment for bees for three of the neonicotinoids which are clothianidin, thiamethoxam and imidacloprid. According to this investigation, on May 2013 the European Union voted for a two-year restriction on neonicotinoid insecticides [9,10].

Consequently, the development of techniques for their determination is increasingly necessary. Several analytical methods have been proposed for the determination of neonicotinoid insecticides in foods, agricultural and environmental samples based on gas chromatography (with prior derivatization) [11] and high performance liquid chromatography (HPLC) with UV [12], diode array [12–14], and mass spectrometric detection [11,15–18] or flow determination with amperometric (reductive pulsed mode) detection on nanoparticles modified glassy carbon electrode [19].

Different voltammetric methods have been developed for the determination of thiamethoxam using several types of working electrodes, summarized in Table 1 [1,5,6,8,19,20]. Relying on previous polarographic investigations, the detection of thiamethoxam was based on the irreversible reduction of its nitro group. The shape of the cathodic voltammograms depends on the pH of the medium, which can be explained by the significant role played by protons in the reduction mechanism [7,20,21].

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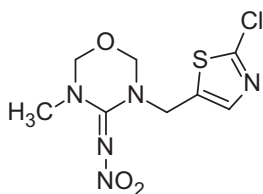


Fig. 1. Structural formula of thiamethoxam.

Mercury electrodes are unique because of their high sensitivity, reproducibility, and wide cathodic potential window. However, because of the fears of mercury toxicity, its use is currently either regulated and/or even banned. As a consequence, non-toxic electrode materials have appeared that are suitable for cathodic determinations. Two groups, working independently, presented various amalgam electrodes as viable alternatives to classical mercury electrodes. The Trondheim group introduced the dental amalgam electrodes [27] while Prague research group developed electrodes based on metal amalgamated powders [22,23]. Several practical applications of these electrodes have been reported [22,24–42]. The main advantages of the amalgam electrodes are their wide range of working potentials, simple regeneration of the electrode surface, rapid pretreatment procedure, long-term activity without significant changes in their sensitivity, mechanical stability, simple preparation in different sizes and shapes and low toxicity, enabling their use in mobile laboratories and for measurements in flowing systems (HPLC, FIA etc.). The preparation of the mercury meniscus modified silver solid amalgam electrode (m-AgSAE) is described in [25].

The aim of this work was to elaborate a sensitive and inexpensive voltammetric method using m-AgSAE and to verify its applicability to the direct determination of thiamethoxam in real water samples. The attempt to achieve nanomolar concentration levels has prompted the use of solid phase extraction (SPE) for preliminary separation and preconcentration of this insecticide.

2. Experimental

2.1. Chemicals and Reagents

The analytical standard of thiamethoxam (Sigma-Aldrich, Germany) was of purity 99.7%. A 1.0×10^{-3} mol·L⁻¹ stock solution of the substance was prepared in double deionized water. Britton-Robinson (BR) buffers were prepared by mixing a solution of 0.04 mol L⁻¹ in phosphoric acid, 0.04 mol L⁻¹ in acetic acid and 0.04 mol L⁻¹ in boric acid with the appropriate amount of 0.2 mol L⁻¹ sodium hydroxide solution. Potassium chloride and ethyl acetate were supplied by Lachner, Neratovice, Czech Republic, sodium hydroxide was from Penta (Czech Republic) and methanol was provided by Merck (Germany). Deionized water was produced by a Milli-Q plus system (Millipore, Billerica, MA, USA). All the chemicals were used without further purification and all the

solutions were stored in glass vessels in the dark at laboratory temperature.

LiChrolut EN SPE cartridges (200 mg) were purchased from Merck (Germany). They are filled with highly cross-linked ethylvinylbenzene-divinylbenzene copolymer, an outstanding sorbent with a specific surface area of approximately 1200 m²g⁻¹, that shows hydrophilic properties without any surface modification. Due to its micro-porous structure (particles of 10–120 μm), it exhibits a high adsorptive capacity, about 10 times higher than C-18 phase [18].

2.2. Water Samples

The drinking water sample was collected from the tap of Department of Analytical Chemistry of Charles University in Prague, Hlavova 2030/8, CZ 12843 Prague 2 and the river water sample was collected from Vltava river, at Cihelná street, Praha-Malá Strana, Czech Republic. For measurements with SPE preconcentration, river water samples were filtered through filter paper of pore size 14 μm (Filtrak, Grade 388, Germany).

2.3. Apparatus

Voltammetric measurements were carried out using a computer controlled Eco-Tribo-Polarograph with Polar Pro software version 5.1 (both from Polaro-Sensors, Prague, Czech Republic) with a three-electrode system in a 10 mL glass vessel. The three-electrode system comprised platinum auxiliary electrode PPE (Monocrystals Turnov, Czech Republic), silver/silver chloride (Ag|AgCl (3 M KCl), Type 10-20+, Electrochemical Detectors, Turnov, Czech Republic) reference electrode and m-AgSAE (2-0907, 0.5 mm diameter, J. Heyrovský Institute of Physical Chemistry of the AS CR, v.v.i., Prague, Czech Republic) working electrode. The software worked under the operational system Microsoft Windows XP Professional (Microsoft Corporation). The pretreatment of the m-AgSAE consisted of three steps: amalgamation, electrochemical activation and electrochemical regeneration. These procedures are described in previous work [25].

Scan rate of 20 mV s⁻¹, pulse amplitude of -50 mV and a pulse width of 100 ms were used in DPV; for direct current voltammetry (DCV), the same scan rate was used. Oxygen was removed by passing nitrogen (purity 99.99%, Linde Praha, Prague, Czech Republic) through the solution for 5 min. All experiments were conducted at laboratory temperature.

Spectrophotometric measurements were performed with an Agilent 8453 UV-Vis spectrophotometer driven by the UV-Visible ChemStation 9.01 software (both Agilent Technologies, Santa Clara, CA, USA) in absorption quartz cuvettes with an optical path length of 10 mm (Hellma, Müllheim, Germany). The wavelength of the measurements in methanol (MeOH) was 254 nm, in ethyl acetate (ETA) 258 nm and in the mixture MeOH/ETA (50:50) was 256 nm. pH values of the prepared BR buffers were measured by a digital

Table 1
Comparison of LOQs for the voltammetric determinations of thiamethoxam on various electrodes.

Method	Electrode	LOQ (μmol L ⁻¹)	Ref.
Cyclic voltammetry	Glassy carbon electrode (GCE)	95.0	[1]
DPV	Bismuth film electrode	4.3	[20]
DPV	Mercury film electrode	2.6	[20]
Differential pulse polarography	Dropping mercury electrode	0.1	[5]
DPV	Tricresyl phosphate-based carbon paste electrode	1.3	[6]
Square-wave voltammetry	Hanging mercury drop electrode	3.1	[8]
Square-wave voltammetry	Silver amalgam film electrode	2.4	[8]
Cyclic voltammetry	Nanosilver/surfactant modified GCE	15.9	[19]
DPV	Nanosilver/surfactant modified GCE	0.4	[19]

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