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Short communication

SHORT COMMUNICATION

Voltammetric determination of the neonicotinoid insecticide thiamethoxam using a tricresyl phosphate-based carbon paste electrode

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Abstract: The objective of the work was to investigate the possibility of using a tricresyl phosphate-based carbon paste electrode for the direct voltammetric determination of the neonicotinoid insecticide thiamethoxam. The analyte was determined by differential pulse voltammetry in Britton–Robinson buffer pH 7.0 in the concentration range of 3.72–41.5 μg mL^{-1}. The reproducibility of the analytical signal at the 7.29 μg mL^{-1} level was characterized by a relative standard deviation of 1.3 %. The applicability of the developed method was evaluated by determining thiamethoxam in a river water sample and a commercial formulation Actara 25 WG.

Keywords: pesticide; thiamethoxam; differential pulse voltammetry; carbon paste electrode; tricresyl phosphate.

INTRODUCTION

Neonicotinoids are among the most effective insecticides for the control of sucking insect pests, such as aphids, whiteflies, leaf- and plant-hoppers, thrips, some micro lepidoptera and a number of coleopteran pests. Their broad spectrum of efficacy, together with their systemic and translaminar action, pronounced residual activity and unique mode of action make neonicotinoids the most rapidly expanding class of insecticidals.[1,2]

Launched in 1998 by Syngenta, thiamethoxam ((*EZ*)-3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro)amine) is marketed

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as Actara for foliar and as Cruiser for seed-treatment uses. To date, thiamethoxam holds registration for 115 crop uses in at least 64 countries on a wide range of crops, such as vegetables, potatoes, rice, cotton, fruit, tobacco and cereals. It is the second biggest neonicotinoid in terms of sales.[1,2]

Due to its wide and constantly expanding areas of application, there is a growing need for new analytical methods for the determination of thiamethoxam, both in commercial formulations and real environmental samples, using simple and cost-effective instrumental techniques.

Analytical techniques that are employed most frequently for the determination of thiamethoxam include high-performance liquid chromatography (HPLC) with a diode array detector (DAD),[3,4] mass spectrometric,[5–7] thermal lens spectrometric[8] and electrochemical detection.[9] Ultra-sensitive automated flow fluorescent immunoassay[10] has also been employed for the rapid, selective and sensitive analysis of different samples containing thiamethoxam. Several electroanalytical methods, such as cyclic voltammetry (CV),[11] differential-pulse polarography (DPP)[12] and differential-pulse voltammetry (DPV),[13–15] have also been employed for the determination of thiamethoxam in model solutions and some real samples.

Over the last five decades, carbon paste, a mixture of carbon powder and pasting liquid, has become one of the widely used electrode materials for the preparation of various electrodes, sensors, and detectors. In 2008, the 50th anniversary of the introduction of carbon paste electrode (CPE) was celebrated and corresponding reviews appeared.[16,17] On the other hand, to the best of our knowledge, there is only one publication dealing with the application of a CPE in the analysis of neonicotinoids. Namely, imidacloprid was determined by DPV in different samples using a tricresyl phosphate-based CPE (TCP–CPE).[18]

In this work, a voltammetric investigation of thiamethoxam was performed at a TCP–CPE and an electroanalytical method was developed for its DPV determination in an aqueous Britton–Robinson buffer solution (pH 7.0) as the supporting electrolyte. The developed voltammetric procedure was tested by determining thiamethoxam in a river water sample and the commercial formulation Actara 25 WG. The results of the developed electroanalytical method were compared with those obtained by HPLC/DAD.

EXPERIMENTAL

Chemicals and solutions

All employed chemicals were of analytical reagent grade and the solutions were prepared in doubly distilled water. The analytical standard of thiamethoxam (Sigma-Aldrich Laborchemikalien GmbH, Germany) was of 99.7 % purity. The concentration of the thiamethoxam stock solution was 186.9 μg mL^{-1}, which was further diluted as required. Britton–Robinson buffer solutions for voltammetric characterization and determination were prepared from a stock solution 0.040 M phosphoric (Merck, Germany), boric (Merck) and acetic (Merck) acid, by

adding 0.20 M sodium hydroxide (Merck) to obtain the required pH value. For the preparation of the mobile phase in the HPLC experiments, acetonitrile (J. T. Baker, The Netherlands, purity 99.8 %) and 0.20 % phosphoric acid (made by diluting phosphoric acid (Centrohem, Serbia)) were used. The commercial formulation of thiamethoxam was Actara 25 WG (Syngenta Crop Protection AG, Switzerland). The river water sample was collected from the Danube River (Novi Sad, Serbia) and stored in the dark at 4 °C for one week before analysis.

Apparatus

Voltammetric experiments were performed on an Autolab (PGSTAT12, Ecochemie, The Netherlands) electrochemical analyzer operated *via* GPES 4.9 software (Ecochemie). The cell stand included a three-electrode system with a CPE as working, a saturated calomel electrode (SCE) (Amel, Italy) as the reference, and a platinum (Amel) auxiliary electrode. All potentials are quoted *vs*. SCE as reference.

Comparative HPLC measurements were performed using an Agilent 1100 liquid chromatograph (Agilent Technologies Inc., USA), Zorbax Eclipse XDB-C18 (4.6 mm×250 mm, 3.5 μm) column, equipped with a DAD.

Procedures

Preparation of the CPE. Carbon paste was made by intimate hand-mixing of CR 5 graphite powder (Maziva Týn, the Czech Republic) with tricresyl phosphate (mixture of isomers, Sigma-Aldrich Chemie GmbH, Switzerland) as the pasting liquid. The detailed procedure of the electrode preparation was described earlier.[18]

Voltammetry on CPEs. In the model systems and real samples, thiamethoxam was measured in 5.00 mL of solution of different concentrations, to which 5.00 mL of Britton–Robinson buffer solution was added. The scan rate in the cyclic voltammetry (CV) was 50 mV s^{-1}. The DPV measurement parameters were as follows: pulse amplitude 50 mV, pulse width 50 ms, scan rate 25 mV s^{-1}.[13-15] The deaerated solutions (nitrogen stream, 10 min) were measured at ambient temperature without filtering.

Chromatography. For the HPLC/DAD analysis, all aliquots were filtered through Millex 0.22 μm syringe filters. The mobile phase was a mixture of water (0.20 % phosphoric acid) and acetonitrile (70:30, v/v).[4,12] The separation was performed isocratically at a flow rate of 1.0 mL min^{-1}. The column temperature was held at 25 °C. Thiamethoxam was detected at a working wavelength of 252 nm and a retention time of 2.5 min. The concentration of the investigated compound was determined from the area of the corresponding peak.

Sample preparation. The commercial formulation Actara 25 WG was powdered and homogenized in a porcelain mortar and then dissolved in doubly distilled water. This solution was diluted stepwise to the required concentration. Aliquots of the river water sample were spiked with the standard solution of thiamethoxam and kept in the dark at 4 °C for 1 h before analysis, without any sample pretreatment. Filtering was performed only for HPLC measurements.

RESULTS AND DISCUSSION

Voltammetric investigation of thiamethoxam at CPE

Relying on previous polarographic investigations,[12] the detection of thiamethoxam was based on the irreversible reduction of its nitro group. Before applying TCP–CPE for quantitative determinations, it was necessary to perform characterization of the compound. The CV (Fig. 1) and DPV (Fig. 2) curves were

recorded in the pH range from 2.0 to 8.0 to study the pH dependence of the peak potentials, which shifted to more negative values with increasing pH. The sharpest, most symmetrical and intense peaks were obtained in the neutral and slightly alkaline solutions (pH 7.0 and 8.0), which is in good agreement with previous voltammetric investigations of neonicotinoids with a nitro-group.[11–15,18–21] Based on these results and with the aim of avoiding possible hydrolysis of the TCP binder in alkaline media, pH 7.0 was chosen for the determinations. Studies of the reproducibility of the TCP–CPE signals were also performed, first to check the signal stability and possible changes in its shape during the measurement. Voltammograms obtained for a 7.29 μg mL^{-1} solution of thiamethoxam showed good reproducibility of the analytical signal during approximately 30 min.

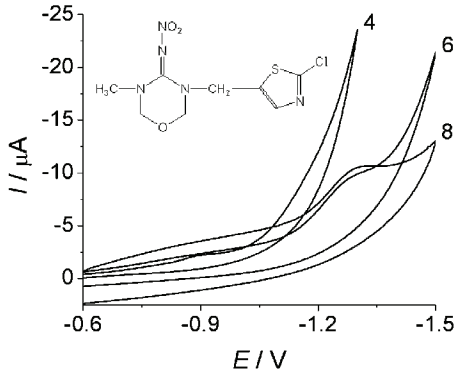

Fig. 1. Influence of pH on the CV signals of thiamethoxam (the pH values of the solutions are indicated at the curves). The inset shows the structural formula of thiamethoxam. Measurement parameters: v = 50 mV s^{-1}, c = 31.6 μg mL^{-1}.

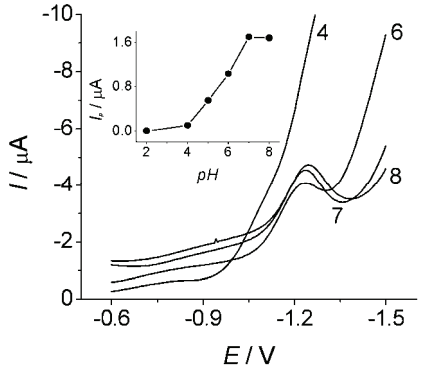

Fig. 2. Influence of pH on DPV signals of thiamethoxam (the pH values of the solutions are indicated at the curves). The inset shows the dependence of the peak current on pH. Measurement parameters: v = 25 mV s^{-1}, pulse amplitude: 50 mV, pulse width: 50 ms, c = 31.6 μg mL^{-1}.

Purging the solutions with nitrogen (10 min) led to a lower background current and better reproducibility of determination in this fairly negative potential region. It was shown earlier that the use of membrane plasticizers (*e.g.*, TCP, dioctyl phthalate) in CPEs as the pasting liquids instead of the usual binders, such as Nujol or silicone oil, can significantly reduce the amount of oxygen absorbed in the graphite.[22] Hence, no special attention was paid to the oxygen in the paste. The electrochemical properties of the TCP–CPE were improved and stabilized by potential cycling. In the study, all electrodes were subjected to electrochemical activation by potential cycling in the range from –0.60 to –1.50 V (10 cycles) prior to the measurements. Increasing the number of potential cycles lead neither to a further widening of the potential window nor a lowering of the background current or signal stabilization.

Determination of thiamethoxam in model systems and selected real samples

The quantitative DPV determination of thiamethoxam at a TCP-CPE in model systems (Fig. 3) is based on the linear relationship between the peak current intensity ($|I_p|$) and the thiamethoxam concentration (c). For the tested range of 3.72–41.5 μg mL^{-1}, the following equation was obtained:

$$|I_p| = 0.07516c - 0.04634, \; r = 0.999$$

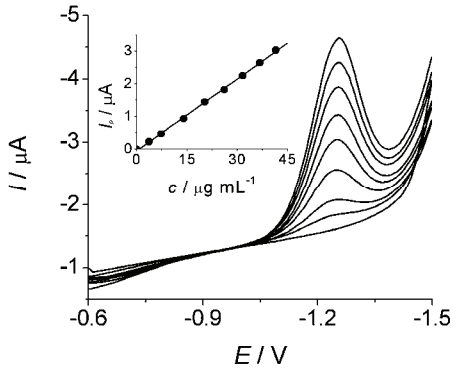

Fig. 3. Differential pulse voltammograms recorded at the TCP–CPE for different concentrations of thiamethoxam (3.72, 7.29, 14.0, 20.3, 26.2, 31.6, 36.7 and 41.5 μg mL^{-1}) in Britton–Robinson buffer solution. The inset shows the corresponding calibration plot.

The reproducibility of the analytical response was assessed by comparing peak the heights of six replicate recordings at a thiamethoxam concentration level of 7.29 μg mL^{-1}. The obtained *RSD* value of 1.3 % indicates a relatively good precision of the developed method.

The applicability of the elaborated voltammetric procedure was tested by determining the thiamethoxam concentration in several real samples. As can be seen from Fig. 4, the matrix from the river water sample (the Danube) and the

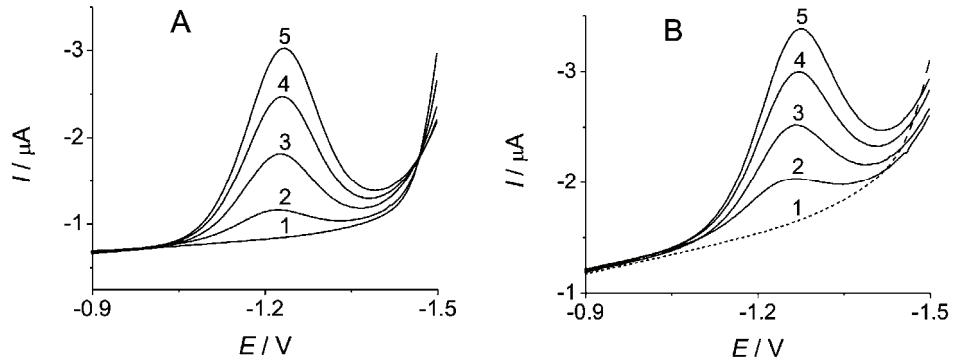

Fig. 4. Determination of thiamethoxam in real samples. River water (A): sample (1), spiked sample (2), successive standard additions (8.82, 16.9 and 24.2 μg mL^{-1}; 3–5), and the commercial formulation Actara 25 WG (B): baseline (1), sample (2), and successive standard additions (7.15, 13.8 and 20.0 μg mL^{-1}; 3–5).

commercial formulation Actara 25 WG did not block the electrode surface and did not show voltammetric interferences, which are favorable facts for the determination. The standard addition method was applied for the determination of the active compound in real samples. The good correlation between the determined and declared/added amounts, as well as the low *RSD* values reflects the high accuracy and precision of the proposed method (Table I). On the other hand, the somewhat lower precision observed for the commercial formulation in comparison with that for model solutions and river water probably arises from the incomplete homogenization of the solid sample. Furthermore, the insecticide concentrations determined by DPV agreed well with the results of the comparative HPLC/ /DAD analysis (Table I). The determination of lower concentrations of the target compound, especially in the case of river water samples, can be achieved, *e.g.*, by applying different preconcentration or extraction methods before the analysis.

TABLE I. Assay of thiamethoxam in real samples (n = 5)

Analyte	Method of determination			
	DPV		HPLC/DAD	
	Found	*RSD* / %	Found	*RSD* / %
Danube water[a]	7.90 μg mL^{-1}	3.0	8.06 μg mL^{-1}	0.53
Actara 25 WG[b]	23.6 %	4.9	23.4 %	1.0

[a]The added value: 8.12 μg mL^{-1}; [b]nominal value: 25±6 %

CONCLUSIONS

This study confirmed the applicability of a TCP–CPE for the direct cathodic voltammetric determination of the insecticide thiamethoxam. DPV in Britton–Robinson buffer solution of pH 7.0 was found to be suitable for the determination of thiamethoxam with a linear response in the concentration range of 3.72–41.5 μg mL^{-1}. The developed procedure might be applied for the determination of thiamethoxam in selected real samples. The voltammetric results were validated by comparative HPLC/DAD measurements. Voltammetry using a TCP–CPE can be a fast and inexpensive tool for obtaining information about insecticide concentrations, especially in commercial formulations in which the analyte concentration is higher.

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ИЗВОД

ВОЛТАМЕТРИЈСКО ОДЕЂИВАЊЕ НЕОНИКОТИНОИДНОГ ИНСЕКТИЦИДА ТИАМЕТОКСАМА ПРИМЕНОМ ЕЛЕКТРОДЕ ОД УГЉЕНИЧНЕ ПАСТЕ НА БАЗИ ТРИКРЕЗИЛ-ФОСФАТА

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Циљ рада је био да се испита могућност примене електроде од угљеничне пасте на бази трикрезил-фосфата за директно волтаметријско одређивње неоникотиноидног инсектицида тиаметоксама. Аналит је одређиван диференцијалном пулсном волтаметријом у Британ–Робинсон пуферу, pH 7,0, у концентрационом опсегу 3,72−41,50 μg mL^{-1}. Репродуктивност аналитичког сигнала карактерише релативна стандардна девијација (на нивоу од 7,29 μg mL^{-1}) од 1,3 %. Применљивост развијене методе је проверена одређивањем тиаметоксама у речној води и комерцијалној формулацији инсектицида Actara 25 WG.

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