

Square wave adsorptive stripping voltammetric determination of diazinon in its insecticidal formulations

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Received: 24 June 2011 / Accepted: 2 November 2011 / Published online: 15 November 2011
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Abstract The pesticide diazinon was determined in its insecticidal formulations by square wave adsorptive stripping voltammetry. The method of its determination is based on the irreversible reduction reaction at the hanging mercury drop electrode. The optimal signal was detected at -1.05 V vs. Ag/AgCl in Britton–Robinson buffer at pH 4.4. Various parameters such as pH, buffer concentration, frequency, amplitude, step potential, accumulation time, and potential were investigated to enhance the sensitivity of the determination. The highest response was recorded at an accumulation potential -0.4 V, accumulation time 60 s, amplitude 75 mV, frequency 100 Hz, and step potential 5 mV. The pesticide electrochemical behavior was considered under experimental conditions. The electroanalytical procedure enabled diazinon determination in the concentration range 4.0×10^{-8} – 3.9×10^{-7} mol L $^{-1}$ in supporting electrolyte. The detection and quantification limit were found to be 1.1×10^{-8} and 3.7×10^{-8} mol L $^{-1}$, respectively. The method was applied successfully in the determination of the active ingredients in the insecticidal formulations Diazinon 10GR and Beaphor 275.

Keywords Diazinon · Square wave adsorptive stripping voltammetry (SWAdSV) · Determination · Insecticidal formulations

Introduction

Environmental pollution is one of the serious predicaments of the modern world (Hela et al. 2005). Organophosphorus pesticides are ubiquitously applied compounds worldwide. Diazinon (*O,O*-diethyl-*O*-2-isopropyl-6-methyl-4-pyrimidinylphosphorothioate) belongs to this group and is used to control harmful insects on livestock, domestic animals, crops, and in buildings. The extensive use of pesticides in public health and agriculture has caused significant environmental pollution and potential health risk and therefore is cause of concern. The diazinon mode of action—similar to other organophosphates—is based on the inhibition of acetylcholinesterase activity through covalent binding to its serine residues, so this is not a specific way of action (Abu-Quare and Abou-Donia 2001). It is mostly used in control of insects and its larvae, like cockroaches, aphids, saprophytes, ants, fleas, ticks, and flies.

Diazinon is moderately toxic to small land animals (LD $_{50}$ (mice) 120 mg kg $^{-1}$) and highly toxic to insects (LD $_{50}$ (fly) 0.12 μ g/insect), fish (rainbow trout LC $_{50}$ (96 h) 16 mg L $^{-1}$), and water organisms; therefore, its

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use should be carefully controlled near water reservoirs (California Environmental Protection Agency 1997). This pesticide through its possible bioaccumulation and extreme persistence in ground water (185 days at pH 7.4; California Environmental Protection Agency 1997) can cause particular population extinction.

There are many types of techniques used in pesticide screening. Among them, voltammetry-based methods are also often employed (Sreedhar et al. 2010; Thriveni et al. 2007, 2009; Guzsvany et al. 2006, 2011; Papp et al. 2010; Fischer et al. 2011). Recently, we have also checked voltammetric applicability in determination of several pesticides (Mirceski et al. 2010; Guziejewski et al. 2011a, b) and drugs (Skrzypek 2010; Skrzypek et al. 2007). Various electrochemical methods for determination of diazinon were employed, including biosensors (Somerset et al. 2006, 2007; Brun et al., 2004), Nafion-coated glassy carbon electrode (Erdogdu 2003), or DNA-composed carbon nanotube electrode (Ly 2008). The use of direct current and differential pulse polarography has been performed in the work of Carabias Martinez et al. (1990). In this paper, some preliminary studies with the use of differential pulse adsorptive stripping voltammetry have been also reported. In the current study, we are presenting the usage of the square wave adsorptive stripping voltammetry (SWAdSV). The electroanalytical technique is not only fast but also the most sensitive one among the other voltammetric techniques (Skrzypek et al. 2005). It combines advantages of the pulse voltammetric techniques capable to discriminate against the capacitive current and the cyclic voltammetry that provides an insight into the mechanism of the electrode reaction (Mirceski et al. 2005; Nosal-Wiercinska 2010). Generalizing, effectiveness, speed, easy to use, and cheapness are the most important characteristics in the current voltammetric methods. In our study, we have applied a hanging mercury drop electrode (HMDE) for the voltammetric assay of diazinon in its insecticidal formulations.

Materials and methods

Apparatus

All experiments were performed at microAutolab/General Purpose Electrochemical System (Version

4.9, Eco Chemie, the Netherlands) computer-controlled electrochemical system. A controlled growth mercury drop electrode (MTM Anko Instruments, Poland) was used as working electrode (electrode area 0.0102 cm²). All potentials were referred to the Ag/AgCl (3 mol L⁻¹ KCl) reference electrode, whereas the counter electrode was a platinum wire. A pH meter (type CP-315, Elmetron, Poland) with a conjugated glass membrane electrode was used.

Reagents

Diazinon (99.5%) and other pesticides (acibenzolar *S*-methyl, acephate, aldicarb, clothianidin, cyromazine, dodine, metam sodium, methamidophos, methidathion, and thiophanate methyl) were purchased from Dr. Ehrenstorfer (Germany) or Sigma-Aldrich. Citrate buffers (0.1 mol L⁻¹, pH 4.4–5), acetate buffers (0.2 mol L⁻¹, pH 4–5), and Britton–Robinson (BR) buffers (0.04 mol L⁻¹, pH 2–6) were used as supporting electrolyte. All other chemicals were of analytical grade (POCh Gliwice, Poland; Merck or Sigma-Aldrich). Triply distilled and deionized water was used throughout the experiments.

Voltammetric procedure

The general procedure used to obtain square wave adsorptive stripping voltammograms was as follows: 10.0 mL of the supporting electrolyte (5.0 mL of the buffer mixed with 5.0 mL of the water) was placed in the voltammetric cell, and the solution was purged with argon for 10 min with stirring. Next, the accumulation step at a constant potential was applied. At the end of the accumulation period, the stirring was stopped and the solution was equilibrated for 5 s. Following the equilibrium step, a negative ongoing potential scan was applied. If some reagents were subsequently added, the test solution was purged with argon for further 30 s. The reported signals were measured after subtracting of the blank solution. In the present study, the highest precision was obtained in BR buffer at pH 4.4 with an accumulation potential -0.4 V, accumulation time 60 s, amplitude 75 mV, frequency 100 Hz, and step potential 5 mV. All measurements were performed at room temperature.

Preparation of solutions and sample treatment

Fresh stock solution of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ diazinon was prepared daily by dissolving 13.7 μL of the compound in 5.0 mL water and used for further dilutions. Insecticidal formulations were used as test samples. No additional operations were performed except proper dilution. All diazinon solutions were prepared in the mixture of ethanol and water (1:1, v/v).

Diazinon 10GR

The diazinon declared content in formulation package (200 g) was 10%. Sample of formulation (0.01067 g) was weighed and transferred to a 50-mL calibrated flask. Twenty microliters of the solution was introduced by means of a micropipette into the voltammetric cell where assumed diazinon (according to the producer label) concentration was $1.3 \times 10^{-7} \text{ mol L}^{-1}$.

Beaphar 275

The formulation was packed into 0.37 mL vials. In each one, the declared diazinon concentration was equal to 275 mg mL^{-1} . A sample of 150 μL was transferred to 50 mL calibrated flask. The received solution was further diluted in order to obtain $5.4 \times 10^{-6} \text{ mol L}^{-1}$ concentration. Next the sample of 160 μL was finally transferred to the voltammetric cell containing supporting electrolyte. The final

diazinon concentration was assumed to be $8.0 \times 10^{-8} \text{ mol L}^{-1}$.

Voltammograms of insecticidal formulation samples were recorded at the same parameters as for model solution with supporting electrolyte only. The recovery of the pesticide was calculated in six runs. Quantifications were performed by means of the calibration line method.

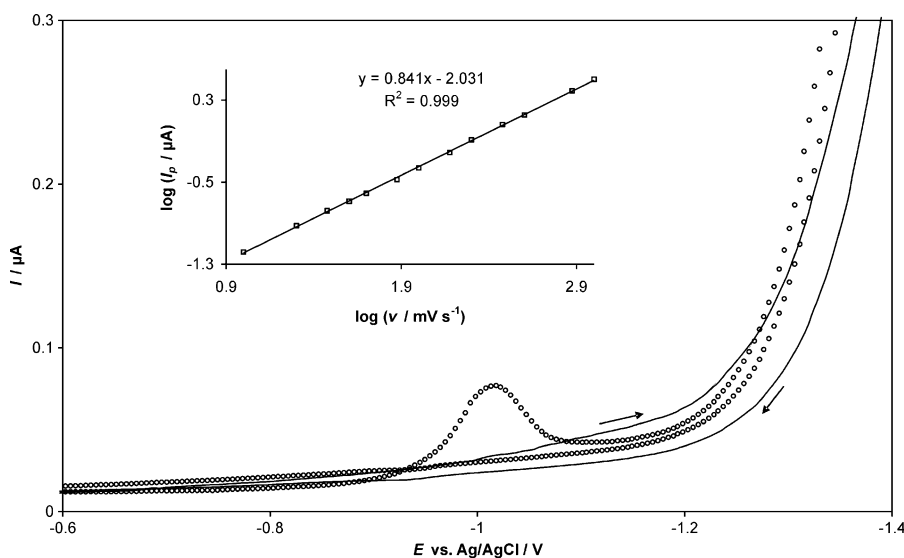
Results and discussion

Cyclic voltammetric studies

The cyclic voltammetric behavior of diazinon yielded one well-defined and sharp peak in acidic media such as Britton–Robinson (Fig. 1), acetate, and citrate buffers. The cyclic voltammetric measurements showed an irreversible nature of the reduction process. The scanning started at -0.4 V in the negative direction, and the only one cathodic reduction peak (at pH 4.4) occurred at about -1.05 V . On repetitive cyclic voltammograms, the second and successive scans showed a substantially smaller peak, indicating passivation of the electrode surface. By reversing potential scanning at -1.5 V , no oxidation peak was observed on the anodic branch.

Scan rate studies were carried out in order to understand whether the process was diffusion or adsorption controlled. The peak potential shifted about 190 mV to more negative potentials in BR

Fig. 1 CV voltammograms of $2 \times 10^{-6} \text{ mol L}^{-1}$ diazinon (circles) recorded in BR buffer solution (line) at pH 4.4, accumulation for 60 s at -0.4 V . The parameters of the potential modulation were scan rate $\nu = 100 \text{ mV s}^{-1}$ and step potential $\Delta E = 5 \text{ mV}$. Inset: the logarithmic dependence of the peak current I_p of cyclic voltammograms on the scan rate ν recorded over the potential interval from -0.4 to -1.5 V



buffer at pH 4.4, when the scan rate increased. When the scan rate was varied from 10 to 1,000 mV s^{-1} in $2.0 \times 10^{-6} \text{ mol L}^{-1}$ diazinon solution, a linear dependence ($r=0.998$) of the peak intensity I_p (microamperes) upon the scan rate (millivolts per second) was found, demonstrating an adsorptional behavior (Laviron et al. 1980). The mathematical relation was expressed with the following equation: $I_p=0.0031\nu+0.1077$ ($n=13$).

A logarithmic plot of peak current versus logarithm of scan rate gave a straight line (inset in Fig. 1) with a slope of 0.841 close to the theoretical value of 1.0, which is expressed for an ideal reaction of the adsorption-controlled electrode process (Laviron et al. 1980; Uslu et al. 2005). The equation obtained is as follows: $\log I_p (\mu\text{A})=0.841 \log \nu (\text{mV s}^{-1})-2.031$ ($r=0.999$, $n=13$).

The plot of the peak potential versus logarithm of scan rate was linear with a correlation coefficient of 0.995, and this was consistent with the EC nature of the mechanism in which the electrode reaction is coupled with an irreversible follow-up chemical step (Brown and Large 1971).

SWAdSV studies

In order to achieve optimum analytical voltammetric conditions for diazinon determination using HMDE, we selected the square wave voltammetry technique as one of the most sensitive. Its superior characteristics in combination with stripping analysis are already well-known and recognized (Lovric 2010; Mirceski et al. 2007).

Effect of pH

The SWAdSV current of diazinon ($2.0 \times 10^{-6} \text{ mol L}^{-1}$) has been recorded in Britton–Robinson buffers (pH from 2.0 to 6.0), acetate buffers (pH 4.0–5.0), and citrate buffers (pH 4.4–5.0). In BR buffers, the peak current was increasing as pH approached the value 4.4. Further increase of the pH caused marked decrease of the response. No response was visible for $\text{pH}>6$. In the other buffer solutions, the maximum response was also achieved in the range 4.0–5.0. Position of the peak moved linearly toward more negative potentials as pH increased in all investigated buffers with a slope -0.0571 and $r=0.997$ (in BR buffer). Such results suggest equal number of protons

and electrons involved in the electrode process (Erdogdu 2003; Kul et al. 2010). For further studies, BR buffer pH 4.4 was chosen in regard to the shape and sensitivity as in a such medium the optimal ratio between peak current and its half peak width was received (Fig. 2).

Effect of accumulation

The dependence of the SWAdSV peak current on the accumulation potential was examined over the potential range from 0.3 to -0.8 V (curve 1 in Fig. 3). The maximum response for diazinon occurred at the potential -0.4 V . Therefore, this value was chosen as the optimal accumulation potential for further analytical measurements.

The dependence of the peak current on the accumulation time was studied in the range between 0 and 200 s at the concentration level of $2.0 \times 10^{-6} \text{ mol L}^{-1}$ for diazinon (curve 2 in Fig. 3). Maximum peak current was obtained at 60 s. Further analytical studies were performed at an accumulation time of 60 s at HMDE.

Effect of potential modulation parameters

The influence of amplitude was studied in the range from 10 to 200 mV. The diazinon peak current reached the maximum as the amplitude value approached 75 mV and remained almost constant up to 200 mV.

The influence of a scan rate in square wave technique is investigated by alteration both frequency

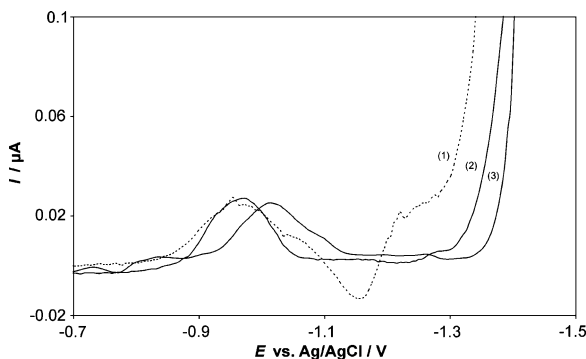


Fig. 2 SW voltammograms of $4 \times 10^{-6} \text{ mol L}^{-1}$ diazinon recorded at pH 4.4 in buffers: 1 acetic, 2 BR, and 3 citrate. The parameters of the SWV potential modulation are frequency $f=25 \text{ Hz}$, amplitude $E_{\text{sw}}=20 \text{ mV}$, and step potential $\Delta E=5 \text{ mV}$. Accumulation time and potential 30 s and 0.2 V, respectively

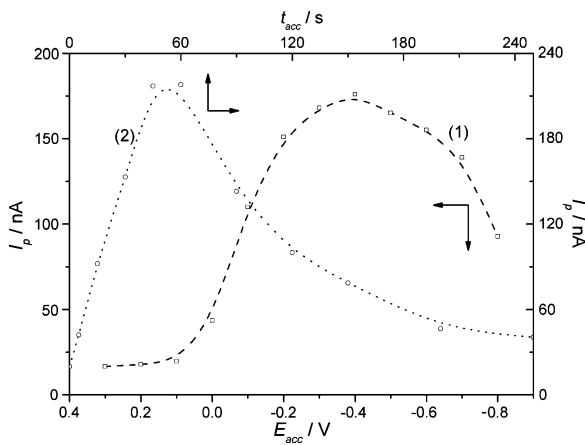


Fig. 3 Dependence of the 2×10^{-6} mol L⁻¹ diazinon SWV net peak current I_p on the accumulation potential E_{acc} (curve 1, left and bottom ordinate). Effect of the accumulation time t_{acc} on the 2×10^{-6} mol L⁻¹ diazinon SWV net peak current I_p (curve 2, right and upper ordinate). The supporting electrolyte is BR buffer pH 4.4; the parameters of the SWV potential modulation are the same as in Fig. 2

and step potential. The highest and best-shaped response was observed with step potential 5 mV. Frequency 100 Hz was chosen for further analytical studies as with this value the best response was recorded. In all the investigated range (8–1,800 Hz), the peak potential of the pesticide reduction shifted toward more negative value (from -1.00 to -1.28 V) with increasing the frequency. A scan rate of 500 mV s⁻¹ was established for further SWAdSV studies.

Effect of interferences

We have examined several other commonly used pesticides. The presence of these compounds (in BR buffer pH 4.4 and under optimal potential modulation parameters) was investigated with respect to the peak current and potential of the diazinon reduction. The diazinon concentration was fixed during the experiments and was equal to 2.0×10^{-7} mol L⁻¹. Other pesticides in the ranges from 1.0×10^{-8} to 1.0×10^{-5} mol L⁻¹ were added to the voltammetric cell. This corresponds to the pesticide/diazinon ratios: 0.05, 0.5, 2.5, 5, and 50. The presence of acephate, aldicarb, clothianidin, cyromazine, and methamidophos did not interfere with respect to the diazinon peak current and potential. The presence of metam had minor effect on the recorded peak current; only 50-fold concentration caused decrease (of about 15%)

in the peak current. Dodine and methidathion had no effect at the concentration ratio up to 2.5. Their 5- and 50-fold excess in the investigated solution caused significant decrease in the recorded diazinon peak current. Nevertheless, no additional signals appeared in the scanned potential region. Obviously these compounds are likely to adsorb at the mercury electrode surface, hence hinder the possibility of diazinon adsorption and its subsequent reduction. The presence of thiophanate methyl and acibenzolar S-methyl caused significant systematic decrease in the recorded diazinon peak current. In the meantime, the presence of additional peaks was noticed. Thiophanate methyl gave signal at the potential more negative (~-1.2 V) and acibenzolar at more positive (~-0.55 V) potential with respect to the recorded diazinon peak potential.

The influence of common heavy metal salts was also investigated. Their concentration was of the same level as in the case of pesticides. The presence of lead and copper had no effect on the recorded diazinon peak current and potential. Cadmium and zinc (only at 5- and 50-fold concentration) caused minor decrease in the diazinon peak current of about 15% and 25%. None of the investigated heavy metals gave signal in the chosen voltammetric conditions.

Quantitative analysis

SWAdSV as the analytical method for diazinon determination was tested using previously described conditions. The tested concentration interval was from 2.0×10^{-8} to 7.0×10^{-7} mol L⁻¹. Correlation between the peak current and diazinon concentration was obtained over the range 4.0×10^{-8} – 3.9×10^{-7} mol L⁻¹ (Fig. 4a). The mathematical relation between analytical signal (microamperes) and the concentration of the diazinon c (micromoles per liter) is $I_p = 4.27c + 0.04$, for a confidence interval 95%. The linear response was evaluated by the coefficient of determination 0.998. Relative standard deviations (RSD; in percent) for the lowest and highest diazinon concentration were 9.5 and 2.4, respectively. The lowest detectable concentration (LOD) and the lowest quantitative concentration (LOQ) of the pesticide (1.1×10^{-8} and 3.7×10^{-8} mol L⁻¹, respectively) were estimated based on the following equations: $LOD = 3 s/m$ and $LOQ = 10 s/m$. Abbreviation s represents the standard deviation of the peak current (six runs),

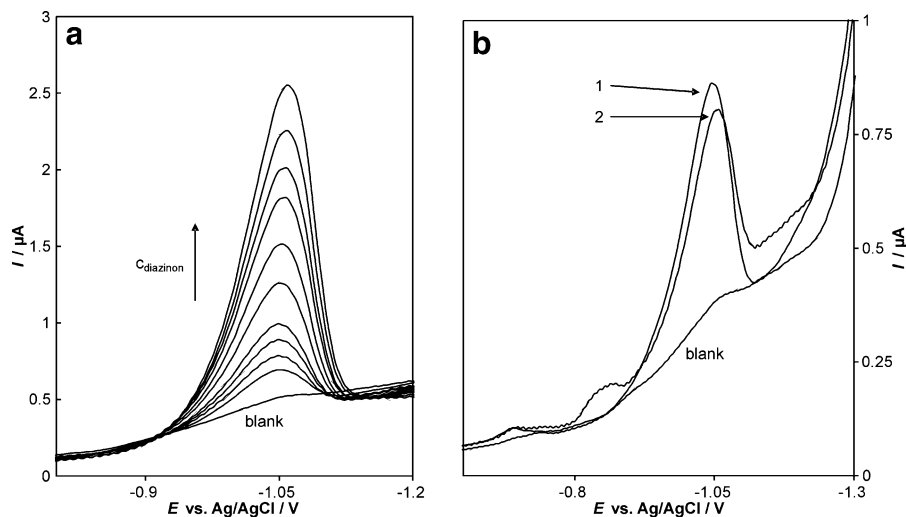


Fig. 4 **a** SW voltammograms of diazinon recorded in BR buffer solution at pH 4.4. Increasing concentration of the pesticide from the bottom c (diazinon $\times 10^{-7}$): 0, 0.40, 0.60, 0.79, 1.00, 1.5, 2.0, 2.4, 2.9, 3.4, and 3.9 mol L⁻¹. **b** SW voltammograms of diazinon recorded in its formulations: 1 Diazinon 10GR and 2

Beaphar 275. The conditions of the potential modulation were frequency $f=100$ Hz, amplitude $E_{sw}=75$ mV, and step potential $\Delta E=5$ mV; accumulation for 60 s at -0.4 V, supporting electrolyte BR buffer pH 4.4

and m stands for the slope of the related calibration curve (Gumustas and Ozkan 2011). The repeatability (during 1 day) of the voltammetric procedure was assessed on the basis of six repetitive measurements at a single diazinon concentration. In the investigated linear concentration range, the RSD of the peak current changed from 7.6% to 2.3%. The summarized

statistical analysis is presented in Table 1 (Riley and Rosanske 1996; Swartz and Krull 1997). Statistical parameters show a satisfactory performance in the presented method of diazinon determination. Based on the International Conference on Harmonization (ICH), these values were satisfactory for analytical procedures, for which recovery efficiencies from 70%

Table 1 Accuracy and precision of diazinon determination with the proposed method

Added ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$) ^a	Precision [RSD (%)]	Accuracy (%) ^b
Supporting electrolyte			
0.040	0.04±0.004	9.5	98.4
0.060	0.06±0.002	3.9	95.6
0.079	0.08±0.002	2.9	96.7
0.10	0.10±0.002	1.9	99.3
0.15	0.15±0.004	2.8	101.8
0.20	0.20±0.003	1.3	104.0
0.24	0.25±0.01	2.0	103.1
0.29	0.30±0.01	2.7	102.8
0.34	0.34±0.01	1.9	100.7
0.39	0.38±0.01	2.4	98.1
Insecticidal formulations			
Diazinon 10GR			
0.13	0.12±0.004	2.1	90.1
Beaphar 275			
0.08	0.079±0.0002	2.0	92.7

^a t ($S/n^{1/2}$), $p=95\%$

^bAccuracy= $[(\text{Found}-\text{Added})/\text{Added}]\times 100\%$

to 130% are accepted as an indication of suitability (Dantas et al. 2010; ICH-Q2Bn 1996).

Determination of diazinon in insecticidal formulations

The optimized voltammetric procedure was successfully applied for diazinon determination in its insecticidal formulations. No extraction steps have been undertaken prior to the voltammetric analysis. Due to the high concentration of the pesticide (Diazinon 10GR contained 10% of the active ingredient and Beaphar 275–275 mg mL⁻¹), appropriate dilution as described in the “Materials and methods” was required in order to achieve diazinon concentration fitted to the voltammetric linear concentration response (Fig. 4b). The recovery results of diazinon in formulations are given in Table 1. The method is sufficiently acceptable in order to be applied to the determination of pesticide in its insecticidal formulations.

Conclusions

This study showed the effectiveness of a hanging mercury drop electrode for the analysis of diazinon in insecticidal formulations using square wave adsorptive stripping voltammetry method. Cyclic voltammetric experiments have shown that the electrode mechanism is an irreversible reduction controlled by adsorption of the diazinon. The presence of other commonly used pesticide like acephate, aldicarb, clothianidin, cyromazine, and methamidophos did not influenced on the possible diazinon determination. Also metal ions like lead and copper did not interfere. The elaborated SWAdSV method was applied for diazinon determination in its insecticidal formulations. The proposed voltammetric method is simpler, faster, and less expensive than the other reported in the literature non-electrochemical procedures for the analysis of diazinon.

Acknowledgments This work was supported by grant no. 505/708 from the University of Lodz, Poland.

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