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Study and determination of the pesticide Imidacloprid by square wave adsorptive stripping voltammetry

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Abstract

An electroanalytical method has been developed for the detection and determination of the pesticide 1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2ylidineamine (Imidacloprid) by square wave adsorptive stripping voltammetry on a hanging mercury drop electrode (HMDE) in aqueous solution with Britton–Robinson buffer as supporting electrolyte. The best adsorption conditions were found to be pH 7.2, an accumulation potential of -1050 mV (HMDE vs. Ag/AgCl–KCl 3M) and an accumulation time of 50 s. Effects of square wave frequency, step potential and pulse amplitude were examined for the optimization of instrumental conditions. Calibration curve is linear in the range 2×10^{-8}–5×10^{-7} M with a detection limit of 1.6×10^{-8} M (Clayton et al. method). The method is applied to the direct determination of the pesticide in river water samples. For a concentration of 4.1×10^{-8} M a recovery value of $104 \pm 3\%$ is obtained. In order to determine lower concentrations, previous preconcentration and cleaning steps (liquid–liquid extraction into CH_2Cl_2 and solid-phase extraction with Sep-Pak C_{18} cartridges) are carried out. The recovery values obtained in spiked river water are $89 \pm 4\%$ for 2×10^{-8} M and $90 \pm 6\%$ for 8×10^{-9} M.

Keywords: Adsorptive stripping voltammetry; Square wave; Imidacloprid; River water

1. Introduction

Insecticides are used in agriculture and they have an important roll, but the prevention of their negative effects requires a systematic control of their content remaining in agricultural products, food, soil and water.

1-(6-Chloro-3-pyridylmethyl) × -*N*-nitroimidazolidin-2ylidineamine (Imidacloprid) (Fig. 1) is a new type of insecticide [1]. It has good contact properties and powerful systemic action.

Some analytical procedures for the quantitative determination of this pesticide have been proposed. It has been determined in different kinds of samples such as soils [2], liver samples of birds [3], agrochemicals [4,5] and water samples [6,7]. High-performance liquid chromatography and gas chromatography (where a derivatization is re-

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quired) [8–11] are commonly used. In HPLC, UV (at 270 nm) [2,7,12–14] or amperometric [15] (reductive pulsed mode) detection are employed. In the amperometric detection a hanging mercury drop electrode (HMDE) at −1300 mV (vs. Ag/AgCl reference electrode) was used; and by applying a cleaning and conditioning potentials of −500 and −1150 mV to overcome fouling problems. There is also a fluorimetric method [6] described. In relation of polarographic techniques, Navalón et al. [4] reports the behaviour of this pesticide by differential pulse polarography and applies the proposed method to its determination in commercial formulations.

In these procedures some preconcentration steps are employed like extraction with CH_2Cl_2 [7], with a mixture of acetonitrile–methanol–water [15] or by using cartridges of Extract-Clean and elution with methanol [2].

The aim of this paper is to develop a square wave adsorptive stripping voltammetry method for the determination of Imidacloprid at trace levels and to determine this pesticide in river water samples.

2. Experimental

2.1. Apparatus

The studies carried out were performed with an Autolab computer-controlled potentiostat (Eco Chemie, Holland) PSTAT 10 equipped with a Metrohm (Herisau, Switzerland) 663 VA stand. This system was connected with a PC 486 equipped with the General Purpose Electrochemical System (GPES 3) version 3.2 software package (Eco Chemie, Holland). The stand includes a three-electrode system, an Ag/AgCl–3 M KCl reference electrode, a platinum wire auxiliary electrode and a mercury drop electrode as working electrode.

2.2. Reagents

Imidacloprid (content > 98%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany) and used without further purification. Stock solutions in water (3.9×10^{-4} M) were prepared and were stored in the dark at 4°C.

Britton–Robinson buffer solutions (prepared from a stock solution 0.04 M in phosphoric (Panreac), boric (Merck) and acetic (Romil) acids; and by adding sodium hydroxide (Merck) 0.2 M up to the pH value required) were also prepared and used as supporting electrolytes. HPLC-grade water was obtained from a Water Pro™ PS (Labconco) system. All chemicals were of analytical reagent grade.

2.3. General procedure

The solution containing the Britton-Robinson buffer of pH 7.2 (5 ml of this in 25 ml volumetric flask) and Imidacloprid at an appropriate concentration was placed into the polarographic cell, through which a nitrogen stream was passed for 600 s before recording the voltammogram. The selected accumulation potential ($E_{acc} = -1050$ mV) was applied during the accumulation period ($t_{ac} = 50$ s) while the solution was kept under stirring. After the accumulation time had elapsed, stirring was stopped and the selected accumulation potential was kept on the mercury drop for a rest time ($t_r = 15$ s), after which a potential scan was performed between −1050 and −1600 mV by using square wave voltammetry (Osteryoung version). In square wave voltammetry the selected conditions were: frequency ($f = 100$ Hz), step potential ($\Delta E_s = 5$ mV) and pulse amplitude ($\Delta E = -40$ mV).

2.4. Procedure for the determination in river water samples

River water samples (50 ml) of pH 3 were extracted twice with 10 ml of CH_2Cl_2; the combined extracts were dried under N_2; the residue was dissolved in 25 ml of HPLC grade water and

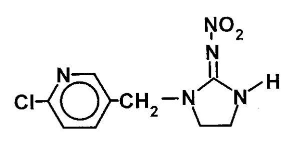

Fig. 1. Structure of Imidacloprid.

it was passed by a Sep-Pak C_{18} cartridge (previously conditioned with 7 ml of methanol and 7 ml of HPLC grade water). A cleaning step was done with 3 ml of 25% (v/v) methanol/water, and the elution was done by using 1.5 ml of 50% (v/v) methanol/water. After that, the general procedure is applied, using in this case 10 ml volumetric flask.

3. Results and discussion

The influence of pH on the polarographic behaviour of Imidacloprid has been studied by Navalón et al. [4], using sampled DC and DPP; the compound shows two reduction signals. Two peaks were observed in the pH range of 2.5–11.0 by applying square wave voltammetry. The E_p of the first peak changes when increasing the pH up to pH 6 ($E_p = 0.110$; pH 0.278). At higher pH values the peak potential is independent of pH. The second peak shifts with pH towards more negative potentials according to $E_p = -0.072$ pH -0.847. A third peak (maybe due to an adsorptive process) (Fig. 2a), appears just between pH 4 and 5 and has a more negative peak potential ($E_p = -1270$ mV) and a low peak intensity. The first and second peaks show a maximum intensity in the range pH 8–10 for the first peak, and pH 7–9 for the second; and the values of peak intensities are higher for the first peak. These two signals coincide with those described in the literature [4,15,16] for nitrocompounds. The first correspond to a four-electron transfer to give the hydroxylamine derivative and the second correspond to a two electron-transfer (being this signal the half that the first signal as is expected taking into account the number of electron transferred). This can be assigned to the reduction of the hydroxylamine group to give the corresponding amine [4] or well to the reduction of the azomethinic group present in this compound [15].

The two main reduction waves of Imidacloprid, obtained by staircase DC sampled technique (scan rate of 10 mV s^{-1}) present a maximum (Fig. 2b) in the pH range 6 and 10 which can indicate the participation of adsorptive processes as it is pointed out by Ruiz et al. [15]. It is confirmed by

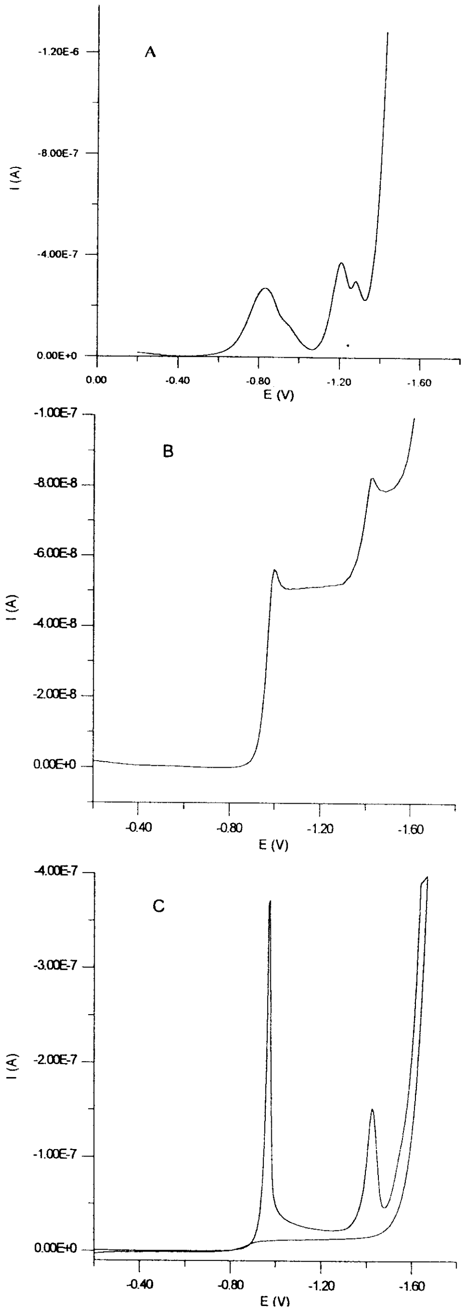

Fig. 2. (A) Imidacloprid, 1.25×10^{-5} M, pH 5.05 with Britton–Robinson buffer. SWV, $f = 50$ Hz, $\Delta E_s = 5$ mV, $\Delta E = -50$ mV. (B) Imidacloprid, 1.25×10^{-5} M, pH 8.08 with Britton–Robinson buffer. DC Sampled, scan rate = 10 mV s^{-1}. (C) Imidacloprid, 1.25×10^{-5} M, pH 8.08 with Britton–Robinson buffer. CV, scan rate = 50 mV s^{-1}.

the study of the influence of the scan rate in cyclic voltammetry, where a linear relationship between peak current (I_p) and scan rate is found. The cyclic voltammetric curves indicate the non-reversibility of the electrode processes, as is shown in Fig. 2c.

On the other hand, the influence of pH on the polarographic behaviour of 6-chloronicotinic acid was also studied, which is the major metabolite of Imidacloprid. The 6-chloronicotinic acid has polarographic response only in acidic media, up to pH 6, showing two signals at potential values of -850 and -1150 mV at pH 2.9.

3.1. Optimization of conditions for the stripping analysis

The voltammetric determination of analytes at trace levels normally involves very small current response. For that reason it is important to optimize all those parameters which may have an influence on the measured current.

The effect of the pH (by using Britton–Robinson buffer solutions) and of the accumulation potential (E_{acc}) it was studied at a fixed accumulation time of 60 s (Fig. 3). Differential pulse (DPV) and square wave (SWV) voltammetric techniques were used, with and without stirring. For this study several solutions of the 5×10^{-7} M concentration level were prepared with different pH values. The voltammograms of them were obtained after applying different accumulation potentials during the mentioned time of 60 s Fig. 3. The behaviour of the two signals is the same by DPV and SWV. In general, at any pH value, the peak current of the first peak increases up to an accumulation potential of -500 mV, and after that it decreases. In the case of the second peak there is a similar behaviour but its maximum peak current was found to be using -1100 mV as accumulation potential. The highest intensities were found at a pH value of 7.2. The second peak has the highest peak current (Fig. 4), then it was chosen as the analytical signal. Comparing the peak height obtained in DPV and SWV, SWV gives peaks around ten times higher than by DPV (even by using $\Delta E = 100$ mV). Then SWV technique with stirring, at a pH value of 7.2 and by using the second peak is selected.

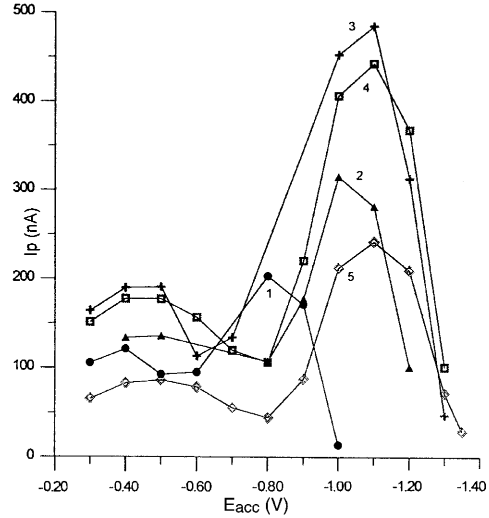

Fig. 3. Influence of accumulation potential (E_{acc}) and pH on I_p (peak II, square wave). Imidacloprid 5×10^{-7} M. pH values: (1) 3.7; (2) 6.2; (3) 7.2; (4) 7.7; (5) 8.1. $t_{ac} = 60$ s with stirring, $t_r = 15$ s, $f = 50$ Hz, $\Delta E_s = 5$ mV, $\Delta E = -50$ mV.

A more detailed study of the influence of the accumulation potential (E_{acc}) was done in the selected conditions (SWV with stirring and pH

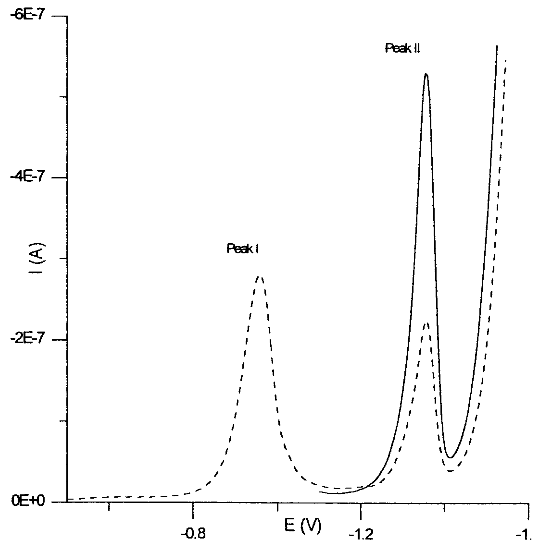

Fig. 4. Imidacloprid, 5×10^{-7} M, pH 7.2. Square wave voltammogram with stirring. —, $E_{acc} = -1100$ mV;---, $E_{acc} = -500$ mV; $t_{ac} = 60$ s, $t_r = 15$ s, $f = 50$ Hz, $\Delta E_s = 5$ mV, $\Delta E = -50$ mV.

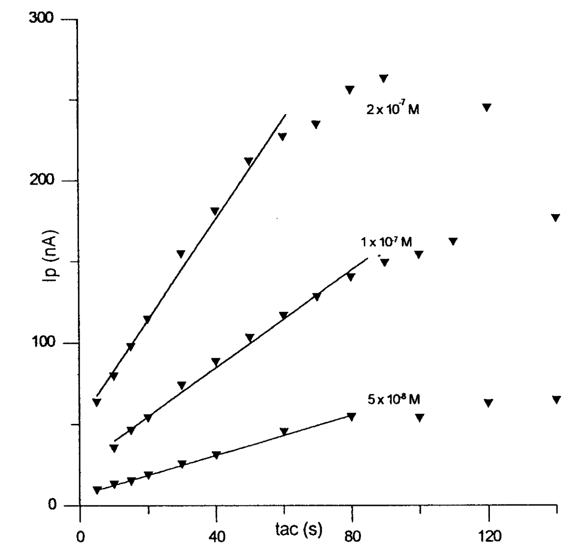

Fig. 5. Influence of t_{ac} on I_p, at different concentration values of Imidacloprid. $E_{acc} = -1050$ mV, $t_r = 15$ s, $f = 100$ Hz, $\Delta E_s = 5$ mV, $\Delta E = -40$ mV.

7.2) showing a maximum value of peak current around -1050 mV. Then this value was chosen for the subsequent studies as the accumulation potential. At this E_{acc} there is an accumulation on the drop mercury of the hydroxylamine derivative.

For the optimization of instrumental conditions, the square wave frequency (f), the step potential (ΔE_s) and the pulse amplitude (ΔE) were examined, varying one of them and maintaining constant the others. The variable ranges were: 2–10 mV for the step potential; 20–350 Hz for the frequency and 10–100 mV for the pulse amplitude. The peak current increase by increasing all of these instrumental parameters. At higher step potential values the peak width increase; at higher frequency values the current background and the peak potential increase. Finally, the conditions selected were: $\Delta E_s = 5$ mV, $f = 100$ Hz and $\Delta E = -40$ mV.

The dependence of peak current on accumulation time at different concentrations of Imidacloprid was studied (Fig. 5). The concentration values were 2×10^{-7}, 1×10^{-7} and 5×10^{-8} M, and the accumulation times were between 15 and 140 s. The useful range of accumulation time is from 0 to 60 s. Within this range the peak current rises linearly with increasing accumulation time. Finally a value of 50 s was selected.

3.2. Polarographic determination of Imidacloprid and analytical characteristics of the method

Using the selected conditions already mentioned, a study was made of the relationship between peak current and concentration. There is a linear relationship in the concentration range 2×10^{-8} and 5×10^{-7} M. Twelve different standards were prepared in triplicate and the following regression parameters were found:

$r = 0.9989$

Slope (A.I. mol 1)	1.01	S.D. of slope	8.99×10^{-3}
Intercept (A)	-4.10×10^{-9}	S.D. of intercept	1.97×10^{-9}

The analytical sensitivity has been calculated as the ratio between the standard deviation of the regression of Y to X (signal to concentration) and the slope of the straight line [17] being 7.35×10^{-9} mol l^{-1}. The relative standard deviations (RSD) of the analytical signals at several concentration values were calculated by using the calibration data, being between 13% for 2×10^{-8} M and 1% for 4×10^{-7} M. The detection limit has been obtained by the Clayton et al. method [18], selecting a false positive and a false negative probabilities of 0.05, being 1.6×10^{-8} M.

The possible interference of the 6-chloronicotinic acid (the major metabolite of Imidacloprid) in the determination of Imidacloprid was studied and no interference up to a molar relation 1:1 was found.

3.3. Determination of Imidacloprid in river water samples

The proposed method was applied to the analysis of the pesticide Imidacloprid in river water samples, spiked with it at different concentration levels. For this purpose the standard addition

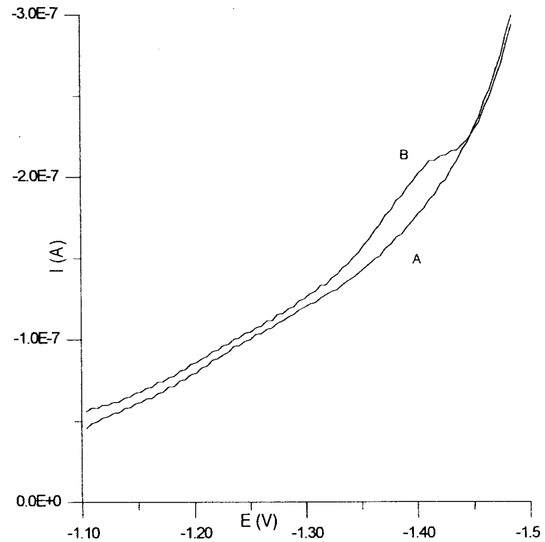

Fig. 6. Square wave adsorptive voltammogram (conditions as explained in the text). (A) Blank (river water sample); (B) as (A) spiked with 4.1×10^{-8} M of Imidacloprid.

method was used in order to eliminate the matrix effects.

For concentrations of 4.1×10^{-8} M or greater, it is possible the direct analysis (without any other preconcentration step than this included in the stripping technique), by adding Britton–Robinson buffer solution according to the general procedure, and recording the voltammogram. Recovery of $104 \pm 3\%$ was obtained for 4.1×10^{-8} M. One voltammogram of Imidacloprid at 4.1×10^{-8} M in river water sample is shown in Fig. 6.

In order to determine lower concentrations, previous preconcentration and cleaning steps (liquid–liquid extraction into CH_2Cl_2 and solid-phase extraction with Sep-Pak C_{18} cartridges) were carried out. The samples were treated and analyzed as described in Section 2.

The results were good with regard to both recovery and repeatability, and they are $89 \pm 4\%$ for 2×10^{-8} M and $90 \pm 6\%$ for 8×10^{-9} M.

4. Conclusions

An easy square wave adsorptive stripping voltammetric method to determine the pesticide Imidacloprid on hanging mercury drop electrode is developed. Its second reduction peak was used for the quantitative measurement. As it is an accumulation method the detection limit of the Imidacloprid determination is low (LD $= 1.6 \times 10^{-8}$ M). The results indicate that SWV is more suitable than DPV as a redissolution technique for the determination of this insecticide. The detection limit of the proposed method is comparable to those obtained using chromatographic techniques. The 6-chloronicotinic acid does not interfere in the determination of Imidacloprid. The method proposed for the Imidacloprid determination has been applied to determine this insecticide in river water samples directly or by using cleaning and preconcentration steps, with good results.

Acknowledgements

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