Mikrochim. Acta 130, 261–265 (1999)

Mikrochimica Acta

Differential-Pulse Polarographic Determination of the Insecticide Imidacloprid in Commercial Formulations

Alberto Navalón, Rachid EI-Khattabi, Antonio González-Casado, and **José Luis Vilchez***

Department of Analytical Chemistry, University of Granada, E-18071 Granada, Spain

Abstract. The reduction reaction of imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] at a mercury electrode shows two well-defined waves in the range of pH 2.0–11.0. The characteristics of the electrode processes were examined. The analyte captures four electrons in the first step and two in the second to give the hydroxylamine and amine derivatives, respectively. A differential-pulse polarographic method for the determination of imidacloprid based on the first reduction peak of this compound is presented. Britton-Robinson buffer was used as a supporting electrolyte and optimum pH value was found to be pH 8.0. The applicable concentration range was from 10 to 200 ng/ml, with a relative standard deviation of 1.5% (for a level of 80 ng/ml) and a detection limit of 3 ng/ml. The method has been satisfactorily applied to the determination of imidacloprid in commercial formulations.

Key words: imidacloprid, differential-pulse polarography, pesticides.

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine] (Fig. 1) belongs to a new group of active ingredients, the chlornicotinyl insecticides. It has a new mode of action, low toxicity to warm-blooded animals, good systemic properties and a lasting action.

This insecticide, introduced by Bayer AG, is used for the control of mites present in vegetable crops [1]. Its development, activities, mode of action and effectiveness have been described by Leicht [1] and its physical, chemical and toxicological properties have been summarized in pesticide manuals [2].

Some high-performance liquid chromatography (HPLC) methods for the detection and determination of imidacloprid have been proposed. Thus, Placke and Weber [3] measured residual levels of imidacloprid in different fruits and vegetables by HPLC-UV. Sample extraction is followed by multi-step clean-up involving three evaporations followed by either partition or an elution through a clean-up solid-phase cartridge.

Fernández-Alba et al. [4] proposed a HPLC-diode array detection method for the determination of imidacloprid residues extracted from vegetables involving acetone and C_{18} reverse-phase cartridges.

Since imidacloprid has low volatility, gas chromatography (GC) seems to be ruled out. However, gas chromatographic-mass spectrometric (GC-MS) methods for the determination of imidacloprid in water and soil samples [5] and vegetable samples [6] have been proposed, whereby the pesticide is previously transformed into an adequate volatile compound by hydrolysis in basic medium followed by a liquid-liquid extraction with chloroform for the extraction and preconcentration of the hydrolysis product.

Recently, a HPLC method with pulsed reductive amperometric detection for the determination of imidacloprid in soils (with a detection limit of 100 ng/ml) has been proposed [7]. Electrochemical data of this compound are not reported.

In this paper a polarographic method, using the differential-pulse technique, for the determination of imidacloprid in commercial formulations is reported. It is simple, quite sensitive and it could be used for the

* To whom correspondence should be addressed

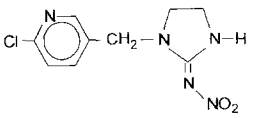

Fig. 1. Structure of imidacloprid

routine control of commercial products containing imidacloprid.

Experimental

Reagents

All the experiments were performed with analytical-reagent grade chemicals and pure solvents. Reverse osmosis-type quality water was used throughout.

Imidacloprid stock solution, 100 μg/ml. Prepared by exact weighing of the reagent (Bayer AG) and dissolution in deionised water. The solution was stable for at least two weeks if stored in the dark at 4°C. Working solutions were obtained by appropriate dilution with deionised water.

The supporting electrolyte was Britton-Robinson buffer prepared in the usual way, *i.e.*, by adding to a solution 0.04 *M* in orthophosphoric acid (Merck), 0.04 *M* in acetic acid (Merck) and 0.04 *M* in boric acid (Merck) with the appropriate amount of 0.2 *M* sodium hydroxide (Merck) solution.

Apparatus and Software

Cyclic voltammetric curves and *i versus E* curves were recorded using an Amel 471 multipurpose and an Amel 460 stand. The polarographic measurements were carried out using a thermostatically controlled Amel 494 cell.

The working electrode was a mercury capillary under the following conditions: rate of mercury flow, $m = 0.80$ mg/s; drop time, $t = 3.0$ s; open circuit; buffered solution at pH 8.0; and height of the mercury column, $h = 41$ cm.

The three-electrode system was completed using a platinum wire as the auxiliary electrode and a saturated calomel reference electrode. All potentials are given relative to this saturated calomel electrode.

For cyclic voltammetry, the working electrode was a Metrohm E 410 mercury hanging drop electrode.

All pH measurements were made with an Ingold combined glass-calomel saturated electrode using a previously calibrated Crison 501 digital pH-meter.

Statgraphics software package [8] was used for regression analysis (linear model).

Basic Procedure

To a 50-ml calibrated flask containing between 10 and 200 ng/ml of imidacloprid, 5 ml of Britton-Robinson buffer solution (pH = 8.0) were added, and the mixture was diluted with deionized water to the mark. The solution obtained was transferred to the electrochemical cell, deaerated by passing a nitrogen stream through it for 5 min and the polarogram was registered at 20.0±0.5°C under an inert atmosphere in the cell.

The differential-pulse mode was used with a pulse amplitude of 50 mV, a drop time of 3 s and a scan rate of 5 mV/s unless stated otherwise.

A blank solution was prepared and treated in a similar way.

The calibration graph was constructed in the same way using imidacloprid solutions of known concentrations.

Procedure for Commercial Formulations

Confidor (Bayer AG) and *Gaucho* (Bayer AG): 1.0 ml of the commercial formulation was diluted to 1–1 with deionized water and 2.0 ml of this solution was diluted to 1–1 with deionised water. A suitable aliquot of the solution was transferred into a 50-ml calibrated flask and 5 ml of Britton-Robinson buffer solution (pH = 8.0) were added. The mixture was diluted with deionised water to the mark. The measurement was carried out using the *Basic Procedure*.

Results and Discussion

D.c. Polarography

Imidacloprid contains a nitro group that can be reduced at the dropping-mercury electrode (DME) giving two polarographic waves in aqueous solution. Both waves were observed over the complete pH range studied (pH 2.0–11.0). Fig. 2 shows a representative polarogram at pH 8.0, $(E_{1/2})_1 = -1.035$ V and $(E_{1/2})_2 = -1.530$ V.

The nature of such waves was investigated through the dependence of the limiting current on the height of the mercury column and on the temperature. Thus, the diffusive nature of both waves was confirmed [9].

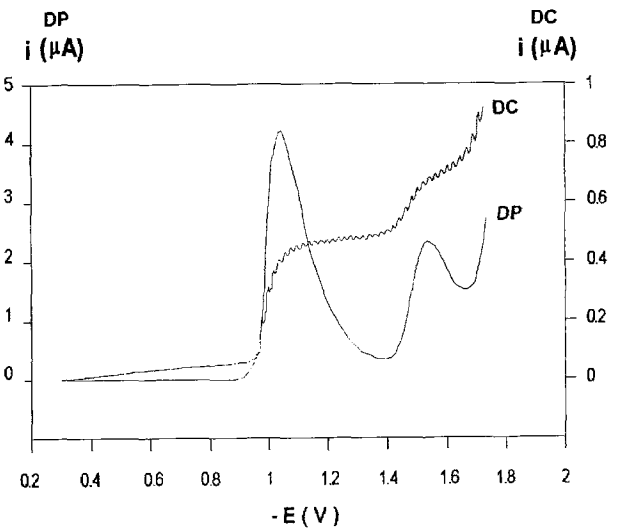

Fig. 2. Typical differential-pulse peaks and d.c. waves polarograms of imidacloprid at pH = 8.0 (Britton-Robinson buffer solution)

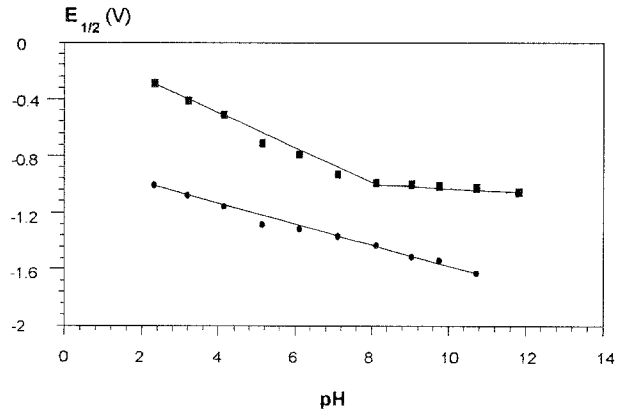

Fig. 3. Influence of pH on $E_{1/2}$. (▪) first wave. (•) second wave

The diffusion current constant (I) and the diffusion coefficient (D) were determined from the slopes of the i_L *vs.* concentration plots. The values obtained were: $I = 7.92$ and $D = 1.06 \times 10^{-5}$ cm^2/s for the first wave and $I = 4.43$ and $D = 1.34 \times 10^{-5}$ cm^2/s for the second wave. The half-wave potential remains constant with an increase in concentration for both waves. The transfer coefficient determined from Tafel's slope was $\alpha = 0.300$ and $\alpha = 0.580$ for the first and second wave, respectively.

Effect of pH

The dependence of $E_{1/2}$ on pH in current-sampled d.c. polarography was also studied in order to determine how many hydrogen ions are involved in the reduction. Both waves strongly depend on pH, shifting cathodically with increasing pH. Fig. 3 shows the graph of $E_{1/2}$ *vs.* pH for both waves. For the first wave, there are two straight lines with a break at pH 8.1, the slopes being −125 mV and −23 mV, respectively. For the second wave, there is only one straight line (slope −70 mV). Therefore, the number of hydrogen ions (p) involved in the reduction must be $p = 4$ for the first wave for pH < 8.1 and $p = 2$ for the second wave throughout the pH range studied.

Cyclic Voltammetry

The cyclic voltammetric curves for the reagent at different scan rates and concentration were recorded, invariably presenting two cathodic waves. No anodic waves were found over the potential range scanned, which indicates the non-reversibility of the electrode processes as known for the nitro group reduction [10].

The values of the transfer coefficients (α) calculated from cyclic voltammetry agree with those calculated polarographically.

Coulometry

The number of electrons involved in the reduction processes was determined by controlled-potential coulometry using a mercury pool cathode. The concentration of the sample before and after electrolysis was measured polarographically to ensure that the reduction reached completion. It appears that the reduction of imidacloprid involves four electrons in the first step and two electrons in the second step.

Mechanism of Polarographic Reduction

The above results show that the electrochemical reduction of imidacloprid takes place in two waves by a mechanism commonly proposed for the nitro-compounds [10–12]. For the first wave, the nitro group of the imidacloprid molecule takes four electrons to give the corresponding hydroxylamine derivative [12] and then in the second reduction step this compound takes two electrons in order to be transformed in the corresponding amine derivative.

Accordingly, a global reduction mechanism for each one of two reduction waves of imidacloprid can be proposed (Fig. 4).

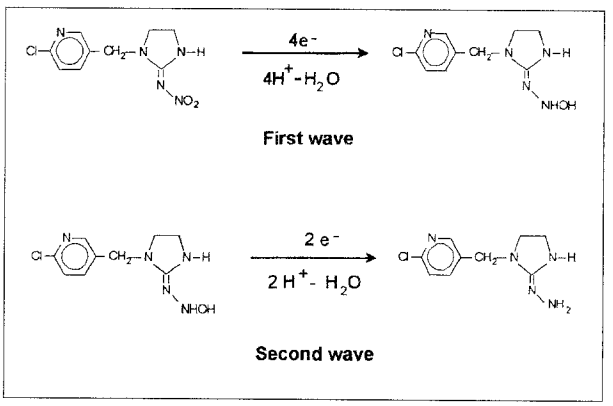

Fig. 4. Reduction mechanism of imidacloprid at a mercury electrode (pH < 8.1)

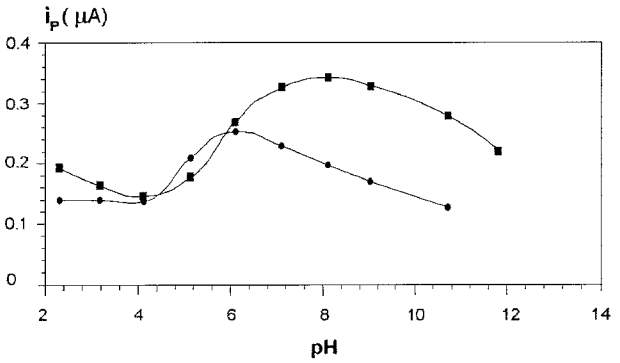

Fig. 5. Influence of pH on i_p in differential-pulse polarography. (■) first peak. (●) second peak

Polarographic Determination of Imidacloprid

Figure 2 shows a differential-pulse polarogram of imidacloprid. Two cathodic peaks were observed between −0.2 and −2.0 V.

The influence of pH on peak current (i_p) for both peaks was studied. As shown in Fig. 5, i_p is maximum in the range of pH 7.0–9.0 for the first peak and pH 5.5–6.5 for the second peak. Consequently, the values of i_p are high for the first peak, which was chosen as the analytical signal and the working pH value was 8.0. The buffer solution used was a Britton-Robinson solution prepared as indicated in the Experimental section.

The effects of pulse amplitude, drop time and scan rate on i_p were evaluated and the highest sensitivity was obtained with a pulse amplitude of 50 mV, a drop time of 3 s and a scan rate of 5 mV/s.

Analytical Parameters

Under the recommended conditions, there is a linear relationship between the analytical signal (height of the first peak) and imidacloprid concentration over the range 10–200 ng/ml. The lack-of-fit test [13] was used to check the linearity using two replicates for each one of ten standards prepared to obtain the calibration graph.

The repeatability of the proposed method was checked with two series of ten samples with an imidacloprid concentration of 40 ng/ml and 80 ng/ml, respectively. The relative standard deviations (RSD) were 3.2 and 1.5%, respectively. The IUPAC detection limit ($k=3$) [14] was 3 ng/ml and the quantification limit ($k=10$) [15] 10 ng/ml.

Table 1. Analytical parameters

Intercept (*a*) (μA)	0.00008
Slope (*b*) (μA · ml · ng^{-1})	0.00050
Correlation coefficient	0.999
Lack-of-fit test (*P*-value)	0.45
Linear dynamic range (ng/ml)	10–200
Linearity [1-RSD (*b*)] % [16]	98.69
Detection limit (ng/ml)	3
Quantification limit (ng/ml)	10

Table 2. Determination of imidacloprid in commercial formulations

Proprietary name	Composition* (% w/v)		Found** (% w/v)	Recovery (%)
Confidor (*Bayer AG*)	Imidacloprid	20	20.3±0.3	101.5
Gaucho (*Bayer AG*)	Imidacloprid	35	34.8±0.5	99.4
	Saccharin	0.2		

* As indicated by the supplier, referred to the original formulations.

** Mean ± standard deviation for six determinations.

The analytical parameters are summarised in Table 1.

Application of the Method

The proposed method was applied to commercial formulations containing imidacloprid as an active ingredient. Samples were treated and analysed as described under the Experimental section. The results obtained, summarised in Table 2, show good agreement with the composition values indicated by the supplier, Bayer AG.

Acknowledgements. This research was supported by the Spanish Interministerial Comission of Science and Technology (CICYT) (Project No. PB-96-1404).

References

[1] W. Leicht, *Plfanzenschutz Nachr. Bayer*, **1993**, *4*, 17.
[2] C. Tomlin, *The Pesticide Manual: A World compendium, 10th ed.*, British Crop Protection Council, Croydon, 1994.
[3] F. J. Placke, E. Weber, *Plfanzenschutz Nachr. Bayer*, **1993**, *46*, 109.
[4] A. R. Fernández-Alba, A. Valverde, A. Agüera, M. Contreras, S. Chiron, *J. Chromatogr. A* **1996**, *725*, 93.
[5] J. L. Vilchez, R. El-Khattabi, J. Fernández, A. González-Casado, A. Navalón, *J. Chromatogr. A* **1996**, *746*, 289.
[6] A. Navalón, A. González-Casado, R. El-Khattabi, J. L. Vilchez, A. R. Fernández-Alba, *Analyst* **1997**, *122*, 579.
[7] N. Ruiz de Erenchun, Z. Gómez de Balugera, M. A. Goicolea, R. J. Barrio, *Anal. Chim. Acta* **1997**, *349*, 199.

[8] Statgraphics version 6.0, Manugistics Inc. and Statistical Graphics Corporation, 1992.
[9] P. Zuman, *The Elucidation of Organic Electrode Processes*, Academic Press, New York, 1969.
[10] G. Pezzatini, R. Guidelli, *J. Electroanal. Chem.* **1979**, *102*, 205.
[11] J. A. Squella, Y. Borges, C. Celedon, P. Peredo, L. J. Núñez-Vergara, *Electroanalysis* **1991**, *3*, 221.
[12] A. F. Alvarez-Lueje, M. Bastías, S. Bollo, L. J. Núñez-Vergara, J. A. Squella, *J. Assoc. Off. Anal. Chem.* **1995**, *78*, 637.
[13] Analytical Methods Committee, *Analyst* **1994**, *119*, 2363.
[14] IUPAC, "Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis-II", *Spectrochim. Acta B* **1978**, *33B*, 242.
[15] "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry", *Anal. Chem.* **1980**, *52*, 2242.
[16] L. Cuadros-Rodríguez, A. M. García Campaña, C. Jiménez-Linares, M. Román-Ceba, *Anal. Lett.* **1993**, *26*, 1243.

Received January 27, 1998. Revision September 10, 1998.