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Journal of Hazardous Materials 141 (2007) 700–706

Journal of Hazardous Materials

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Determination of insecticide pymetrozine by differential pulse polarography/application to lake water and orange juice☆

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Received 13 May 2006; received in revised form 14 July 2006; accepted 17 July 2006
Available online 21 July 2006

Abstract

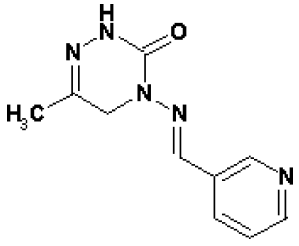
A simple, fast and sensitive differential pulse polarographic method (DPP) for the determination of pymetrozine insecticide in pure form, agrochemical formulation, natural water and orange juice samples is proposed. The polarographic behavior of pymetrozine exhibited a double well-defined polarographic peaks at −580 and 950 mV (versus SCE), respectively. The peak potentials were strongly pH-dependent in that they shifted to more negative values with increasing pH. The polarographic reduction corresponding to the first peak at pH 2.0 (B–R buffer solution) showed quantitative increments with the additions of standard pymetrozine solution under the optimal conditions and the corresponding peak current was linearly proportional to pymetrozine concentration in the range of 4.97×10^{-7} to 7.35×10^{-5} mol L^{-1}. The limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.48×10^{-7} and 4.93×10^{-7} mol L^{-1}, respectively. The mean recoveries of the 5.0×10^{-6} mol L^{-1} pymetrozine spiked to lake water and orange juice were $(4.89 \pm 0.23) \times 10^{-6}$ and $(4.97 \pm 0.19) \times 10^{-6}$ mol L^{-1} at 95% confidence level, respectively. The method was extended to the determination of pymetrozine in agrochemical insecticide formulation Plenum® and accuracy was in agreement with that obtained by HPLC comparison method. Influences of some interfering ions and some other pesticides were also investigated. The mechanistic study was not pursued.

Keywords: Insecticide active compound; Pymetrozine; Polarography; Determination; Water and orange juice

1. Introduction

Insecticides are important environmental pollutants. The continuous increase in agricultural production promotes an equivalent increase in the level of insecticide residues in water, soil land foodstuff. Prevention of the negative effects of the insecticides requires a systematic control of the content of their remains in agricultural products, food, fodder, soil, and water. Therefore, reliable analytical methods are needed for their correct determinations.

Pymetrozine, a pyridine azomethine compound, is a novel insecticide with selective activity against homopteran insects like the cotton aphid and the tobacco white flies in cotton [1,2]. It acts in a unique way interfering in the nervous regulation of feeding behavior, which consequently results in death due to starvation after a few days [2]. Pymetrozine, 4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one (IUPAC), is a selective insecticide developed by Novartis Crop Protection, Inc. [3], whose general structure is



As the expected concentration of the insecticides in agricultural and environmental samples is rather low, sensitive analytical methods are needed for their correct determination. So far, chromatographic techniques have been the most widely used for the determination of various insecticides [4–6], but electroanalytical techniques have also been used for the determination and studying several insecticides in different matrices like water, soils, plants and food [7–9]. So, the voltammetric

☆ Contact grant sponsor: Gazi University Research Fund; contact grant number: 05/2006-26.
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doi:10.1016/j.jhazmat.2006.07.029

methods are increasingly used for the determination of biologically active substances, including pesticides; these methods offer sufficiently low detection limits, broad intervals of contents determined, and selectivity.

The polarographic technique presents some advantages in relation to many other analytical techniques. Progress obtained with pulse techniques has increased the range of practical applications of voltammetry by enabling determinations of electroactive species at lower concentrations. When compared to chromatography, the polarographic procedures have several advantages such as their low cost and short time required for analysis [10–12]. On the other hand, electroanalytical methods offer useful applications in kinetic and equilibria studies, much more than HPLC or GC which often can perturb equilibria in the reaction mixture.

Only a few methods for analyzing pymetrozine compound can be found in the literature [13,14]. They are mainly based on high-performance liquid chromatography (HPLC). A review of the literature revealed that no reports have been published on the electrochemistry or polarographic activity of pymetrozine. The aim of the present work is to investigate the polarographic behaviour of the pymetrozine, find out optimum analysis conditions and apply the method for the determination of pymetrozine in commercial formulation, lake water and orange juice.

2. Experimental

2.1. Materials

Pymetrozine was provided by Ciba Geigy Ltd., Basle, Switzerland, with a purity of 99.7%. Agrochemical formulation Plenum® was provided by Syngenta Crop Protection AG., Basle, Switzerland. Stock solutions of pymetrozine (1.0×10^{-3} mol L^{-1}) were daily prepared in 30% ethanol solution and kept in the dark in a refrigerator. Supporting electrolyte namely Britton–Robinson buffer (B–R buffer, 0.04 M, pH 2-11) was prepared in doubly distilled water. Working solutions were prepared by dilution of the stock solution with selected supporting electrolyte to give the solution containing pymetrozine in the concentration range of 4.97×10^{-7} to 7.35×10^{-5} mol L^{-1}. Salts used for supporting electrolyte, solvents and other reagents were of analytical reagent grade (Merck or Sigma). All solutions were protected from light and used within 3–6 h to avoid possible decomposition.

The mercury (pro-analysis) was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute HNO_3 and water columns in the form of fine droplets. The collected mercury was dried between sheets of filter paper. Before use, a differential pulse polarogram of this mercury was recorded in order to confirm the absences of impurities. Britton–Robinson (B–R) buffer solution was prepared by dissolution of 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid and 2.4720 g boric acid in water to 1.0 L. 50.0 mL portions of this solution were taken and the desired pH was adjusted between 2.0 and 11.0 by addition of appropriate amount of 2.0 mol L^{-1} NaOH.

2.2. Apparatus

A PAR (Princeton Applied Research Company, USA) model 174A differential pulse polarographic (DPP) analyzer system, equipped with a PAR mercury drop timer, was used. A Kalousek electrolytic cell with reference-saturated calomel electrode (SCE), separated by liquid junction, was used in a three-electrode configuration. The counter electrode was platinum wire. The natural drop time of the mercury electrode was 3.2 s (2.04 mg/s). The polarograms were recorded with a Linseis LY 1600 X–Y recorder (Linseis, Selb, Germany). pH values were measured with a Hanna HI 8521 pH meter. The HPLC system (Agilent 1100 HPLC system, Agilent Tecnologies, USA) consisted of a quaternary pump, a Rheodyne injector equipped with a 20 μL sample loop, 150 mm Zorbax Eclipse XDB C_{18} 5 μm column, and a model of L-7455 diode array and multiple wavelength UV–vis detector controlled by Agilent Chem. Station Software.

2.3. Procedures

2.3.1. Polarographic measurements

A 10.0 mL of supporting electrolyte solution of Britton–Robinson (B–R) buffer was put into the polarographic cell and de-oxygenated with high-purity nitrogen (99.999%) for about 5 min. The background polarograms were obtained by scanning the potential from 0.0 mV to about −1200 or −2000 mV (versus SCE) depending on the pH of the solution. The analytical curves for the determination of pymetrozine were obtained by standard addition of the insecticide and evaluation of the peak currents. The optimum conditions for the analytical determination of the investigated compound by DPP were found to be: pH 2.0, peak potential −580 mV, scan rate of 2.0 mV/s, pulse amplitude of 50 mV with pulse duration of 50 ms at an ambient temperature of 25 ± 3 °C.

Pymetrozine hydrolyses readily at low pH and hydrolysis rate is pH dependent following pseudo-first order kinetics with an half-life of ≤14 days (pH 5; 25 °C), ≥80 days (pH 7; 25 °C) and ≥86 days (pH 9; 25 °C). Photolysis half-life in water and soil are 2 days (pH 7) and ≥30 days, respectively [15]. In the present work, the stability of pymetrozine solutions was also investigated at pH 3.0 and 7.0 by applying a polarographic control and no degradation was observed during the short analyzing and spiked periods. Stock solutions of pymetrozine (1.0×10^{-3} mol L^{-1}) were prepared daily in 50% ethanol solution at neutral pH and kept in the dark in a refrigerator, in order to avoid hydrolytic process.

2.3.2. Formulation assay procedure

A suitable amount of pesticide formulation Plenum® (50% pymetrozine by mass) equivalent to 1.0×10^{-3} mol L^{-1} pymetrozine was accurately measured and transferred into a 100.0 mL of calibrated flask and completed to the mark with 30% ethanol solution, and sonicated 5 min. In the DPP experiments, 100 μL of an aliquot of this clear supernatant liquor was added to 10.0 mL of the pH 2.0 B–R buffer solution in the electrochemical cell (previously de-aerated for 5 min with humidified, 99.999%

ultra-pure nitrogen.) and peak responses measured at −530 mV under calibration conditions The pymetrozine in pesticide formulation was analyzed, by the standard addition method. The results obtained were compared statistically with HPLC method using student *t*-test and variance ratio *F*-test.

2.3.3. Procedure for analysis of spiked orange juice and lake water samples

A 10.0 mL of juice was extracted from an orange without any pre-separation or pre-concentration. The juice sample was spiked with pymetrozine at concentration levels of 1.0×10^{-5} to 1.0×10^{-4} mol L^{-1} in 25.0 mL 30% ethanol solution. After homogenizing the samples, they were placed in centrifuge tubes, shaken for 30 min and centrifuged for 5 min at 3000 rpm. From the supernatant, 1.0 mL aliquots were collected, transferred to the polarographic cell containing 9.0 mL pH 2.0 B–R buffer solution. After the completion the above polarographic procedure for measurements, pymetrozine in orange juice was analyzed from the peak obtained at −540 mV, by the standard addition method.

A 10.0 mL of lake water (obtained from Göksu Lake, Ankara, Turkey) were taken from the sample without any pre-separation or pre-concentration. The samples were spiked with a stock pymetrozine solution at concentration levels of 1.0×10^{-5} to 1.0×10^{-4} mol L^{-1} in 25.0 mL 30% ethanol solution. After the completion the above procedure, 1.0 mL aliquots then added to the electrochemical cell containing 9.0 mL pH 2.0 B–R buffer solution. The determination of the insecticide in lake water was performed from the peak obtained at −530 mV, under the experimental conditions described above using multiple standard additions.

3. Results and discussion

3.1. Polarographic study

The B–R buffer (0.04 mol L^{-1}) was chosen as a supporting electrolyte because of its wide pH range applicability. There was a single or double reduction peaks depending on pH's. The only pH range that both peaks could be observable was limited within pH 1.0–6.0. Fig. 1 shows typical selected DPP polarograms for the first peak obtained from 3.0×10^{-5} mol L^{-1} pymetrozine in B–R buffer solution within the pH range of 2.0–11.0. As shown from this figure, the peak currents depend on the acidity of the medium and decrease in neutral or basic solutions.

It was found that the peak potentials of both peaks shifted to more negative values with increasing pH and peak current of the first peak decreased markedly until pH 4.0 and remained nearly constant up to pH 11. Fig. 2 shows the dependence of both peak currents of pymetrozine on the pH of B–R buffer solution within the pH range of 1.0–11.0. The maximum sensitivity and response peak current was found at pH 2.0 comparing with other pH's. As the pH approaches to neutral or moderately basic region, reduction peak decreases because of the controlling of the overall rate by protonation kinetics [16]. Therefore, we found that the first peak at pH 2.0 was optimum, not only because of its highest

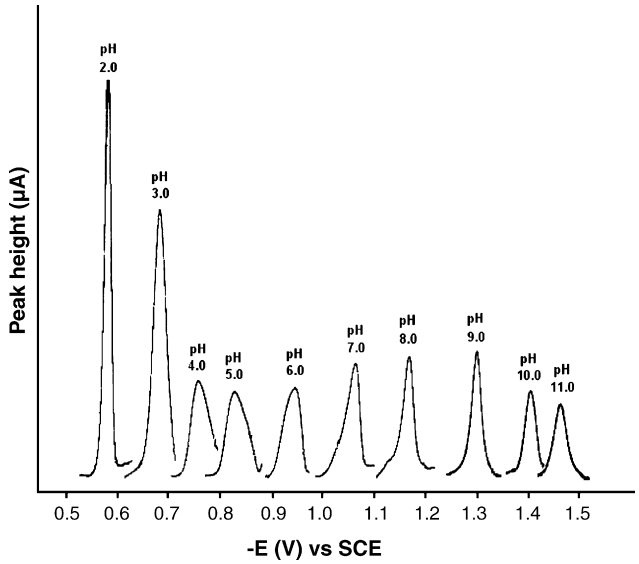

Fig. 1. DPP polarograms of 3.0×10^{-5} mol L^{-1} pymetrozine at some selected pH's.

sensitivity but also well-resolved characteristics and suitability for analytical use.

For the second peak, the maximum peak (Fig. 2) and a break between two segments (Fig. 3) at pH 3.0, which corresponds to the $pK_a \pm 1$ value of pymetrozine could be attributed to the acid-dissociation constant (pK_a) of pymetrozine. The reported pK_a of the pymetrozine was 3.07 [17]. As shown in Fig. 3, both peak potentials were strongly pH-dependent in that they shifted to more negative values with increasing pH and the first peak showed a linear segment with a slope of 98.4 mV in this pH range.

$$E_p\,(\text{mV}) = -98.4\text{pH} - 386\,(\text{pH}\ \ 1.0\text{–}11.0) \quad (r = 0.996)$$

This phenomenon shows a reduction process involving addition of H^+ to the oxidized species. According to the structure of the insecticide molecule, the peaks may correspond to the reduction of azomethine group via the well-known $2e^-/2H^+$ reduction

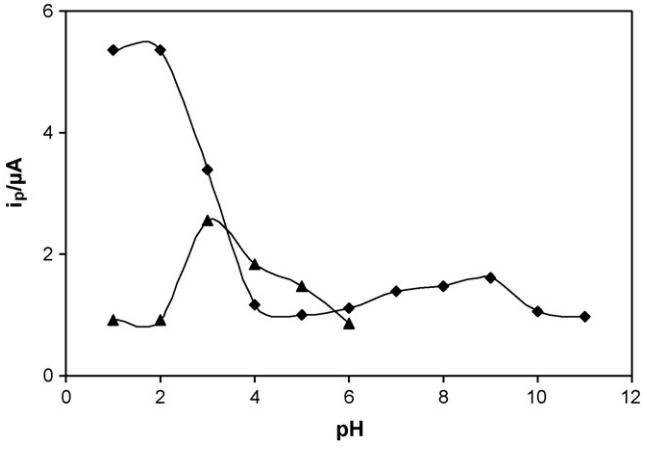

Fig. 2. Effect of the pH on the peak currents of differential pulse polarographic peaks obtained for the 3.0×10^{-5} mol L^{-1} pymetrozine ((■) first peak; (▲) second peak).

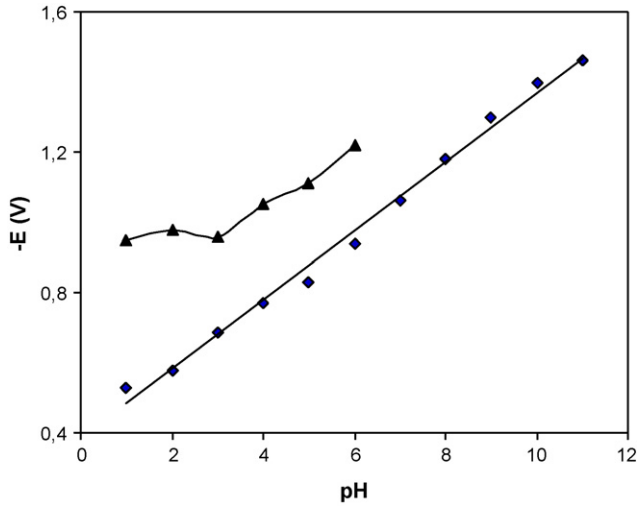

Fig. 3. Effect of the pH on the peak potentials of differential pulse polarographic peaks obtained for the 3.0×10^{-5} mol L^{-1} pymetrozine ((■) first peak; (▲) second peak).

mechanism of azomethine compounds [18]. On the other hand, the further mechanistic study was not pursued.

Increasing the mercury height (h) resulted in a corresponding increase in the wave height (w). Also a plot of log W versus log h gave a straight line with a slope of 0.83 ($r = 0.997$). Changing the buffer concentration over the range 0.03–0.12 M resulted in a negligible change in wave height. These two characteristics pointed out to diffusion-controlled process and adsorption phenomenon played a limited role in the electrode process.

3.2. Analytical methodology for the determination of pymetrozine in pure water

A calibration curve was obtained for pymetrozine in an electrolyte, B–R buffer solution, prepared with pure water. The optimum conditions for the analytical determination of pymetrozine compound by DPP were found to be pH 2.0 at a reduction potential of −580 and 50 mV pulse amplitude, 2 mV/s sweep rate, 1 s drop time, at 25 ± 3 °C. The consecutive additions of pymetrozine to the 0.04 mol L^{-1} B–R buffer (pH 2.0) prepared with double-distilled water resulted in the DPP response displayed in Fig. 4. Under optimized experimental conditions, a linear relationship between the peak current of pymetrozine at dropping mercury electrode and concentration can be established in the range of 4.97×10^{-7} to 7.35×10^{-5} mol L^{-1}. The linear regression equation was

$$I_p\,(\mu A) = 1.24 \times 10^5\, C\,(\text{mol L}^{-1}) + 0.224,$$

$$r = 0.995\,(n = 10)$$

The limit of detection (LOD) and limit of quantification (LOQ) were obtained for the experimental conditions employed using the following equations from IUPAC [19]:

$$\text{LOD} = \frac{3S_b}{b} \quad \text{and} \quad \text{LOQ} = \frac{10S_b}{b}$$

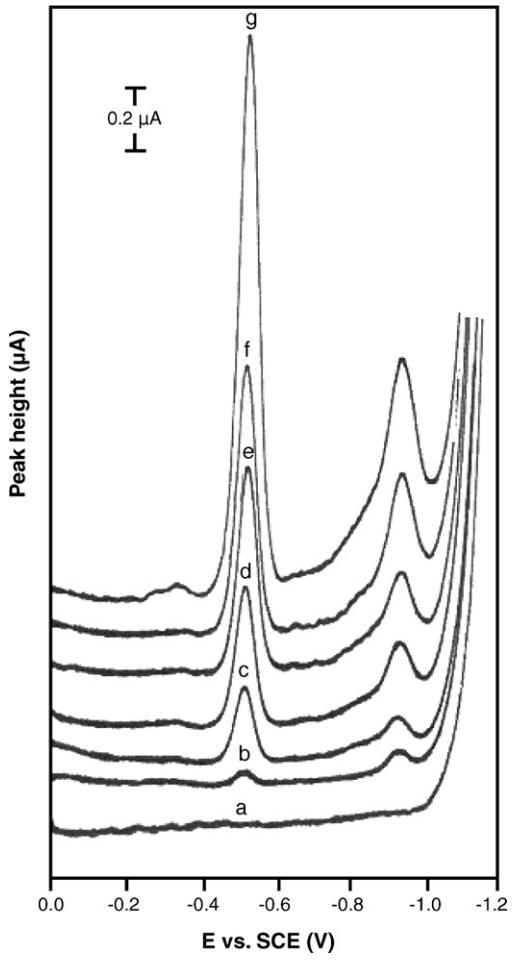

Fig. 4. DPP responses for several concentrations of pymetrozine at pH 2.0 B–R buffer solution. (a) 10.0 mL blank (pH 2.0, B–R buffer); (b) $a + 100\,\mu$L, 1.0×10^{-4} mol L^{-1} pymetrozine; (c) $b + 20\,\mu$L, 1.0×10^{-3} mol L^{-1} pymetrozine; (d) $c + 20\,\mu$L, 1.0×10^{-3} mol L^{-1} pymetrozine; (e) $d + 30\,\mu$L, 1.0×10^{-3} mol L^{-1}; (f) $e + 20\,\mu$L, 1.0×10^{-3} mol L^{-1} pymetrozine; (g) $f + 100\,\mu$L, 1.0×10^{-3} mol L^{-1} pymetrozine.

where S_b is the standard deviation of the blank for an average of ten values of current and b is the slope of the calibration curve. The observed values of LOD and LOQ were 1.48×10^{-7} and 4.93×10^{-7} mol L^{-1}, respectively. The straight line had a slope of 1.24×10^5 μA/mol L, an intercept of 0.224 μA and a correlation coefficient of 0.995. The high sensitivity of differential pulse polarography was accompanied by very good repeatability. To estimate the repeatability of the proposed method, the R.S.D. of fifth times successful measurement of peak current of 3.0×10^{-5} mol L^{-1} pymetrozine was calculated to be 3.98% (Table 1), which demonstrates the good repeatability of the method.

3.3. Interference study

The effects of other commonly used pesticides cyanazine and prometryn on the determination of pymetrozine has been evaluated. The cyanazine and prometryn were both polarographically active compounds and their reduction potentials measured at about −850 and −950 mV, respectively. These potentials did

Table 1
Analytical performance data of the proposed method

Parameters	Supporting electrolyte	Lake water	Orange juice
Measured potential (V)	−580 mV	−530 mV	−540 mV
Linearity range (mol L^{-1})	4.97×10^{-7} to 7.35×10^{-5}	4.97×10^{-7} to 9.09×10^{-6}	4.97×10^{-7} to 9.10×10^{-6}
Slope (μA/mol L)	1.24×10^{5}	3.31×10^{5}	7.43×10^{5}
Intercept (μA)	0.224	0.114	0.023
Correlation coefficient	0.995	0.997	0.993
S.E. of slope	4.7×10^{3}	1.4×10^{4}	1.1×10^{4}
S.E. of intercept	0.06	0.050	0.039
LOD (mol L^{-1})	1.48×10^{-7}	1.49×10^{-7}	1.53×10^{-7}
LOQ (mol L^{-1})	4.93×10^{-7}	4.96×10^{-7}	5.10×10^{-7}
LOD (ppb)	32.15	32.36	33.23
LOQ (ppb)	107.08	107.73	110.77
Repeatability of peak Potential (R.S.D.%,)	0.66[a]	0.61[b]	0.38[b]
Repeatability of peak Current (R.S.D.%)	3.98[a]	3.32[b]	2.63[b]

[a] Number of experiments, $n = 5$.
[b] Number of experiments, $n = 6$.

not fit into pymetrozine peak and the addition of up to three-fold cyanazine and prometryn on pymetrozine caused no change on the peak current.

The influence of some cationic and anionic species which are commonly found in soil and irrigation water on the polarographic determination of pymetrozine was investigated. The interference studies were performed using the various interfering ions, most of them being electroactive, e.g., Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Co^{2+} and the others inactive, e.g., Mg^{2+}, $SO_4{}^{2-}$, $NO_3{}^{-}$, F^{-} and Cl^{-}. The interfering ions were taken at equimolar concentration, 5 and 10 times the amount of pymetrozine. The degree of interference effects were shown as the ratio of the peak currents in the presence of the interfering ions to that in their absence (by percentage). The results are summarized in Table 2. Under the optimum polarographic conditions for the determination 2.0×10^{-5} mol L^{-1} pymetrozine, Cu^{2+} and Pb^{2+} appeared at less negative potentials, Ni^{2+} and Zn^{2+} at more negative potentials compared to the peak potential of pymetrozine. Thus, the polarographic peaks of these ions did not overlap the pesticide peak. It was found that an equimolar concentration or at even higher molar excess (10:1) of these ions had no distinct effect on the peak response of pymetrozine. The recovery of 2.0×10^{-5} mol L^{-1} pymetrozine in the presence of Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+} was 100, 97, 97 and 96%, even 10-fold of the mentioned ions. Serious effects were observed in the presence of relatively higher concentrations of Cr^{3+} since its reduction potential was coincided with that pymetrozine peak to some extent. This could be explained with the appearance of a shoulder near the triflumizole peak due to the higher concentration of Cr^{3+}, which prevents the peak intensity of the triflumizole. Co^{2+} did not seriously affect the pymetrozine peak, since there was no peak response for this cation at the studied pH and concentration. Mg^{2+}, $SO_4{}^{2-}$ and $NO_3{}^{-}$ are polarographically inactive species and therefore had no noticeable effect on the polarographic peak of pymetrozine. Therefore, the proposed method can be used as a selective method. On the other hand, relatively higher concentrations of F^{-} and Cl^{-} caused a significant effect and consequently the degrees of recoveries of triflumizole were 88 and 93% at their 10-fold concentrations.

3.4. Application of the methodology to agrochemical pesticide, lake water and orange juice

The applicability and validation of the proposed cathodic differential pulse polarographic method for the assay of pymetrozine in agricultural dosages, spiked lake water and orange juice were investigated via estimation of the range of linearity, the limit of detection (LOD), the limit of quantification (LOQ), repeatability, accuracy and selectivity (Table 1). The accuracy of the developed method was checked by calculating the recovery of known amount of added pymetrozine to the agrochemical pesticide formulation Plenum® or spiked lake water and orange juice and analyzed via the optimized differential pulse polarographic procedure (Tables 3 and 4).

Table 2
Influence of interfering ions on the peak current of 10 μmol L^{-1} pymetrozine

Concentrations of interfering ions (μmol L^{-1})	Interfering ions and their influence on signal ratio (%)										
	Ni^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cr^{3+}	Co^{2+}	Mg^{2+}	$SO_4{}^{2-}$	$NO_3{}^{-}$	F^{-}	Cl^{-}
10	100	100	100	100	96	100	100	103	100	96	98
50	100	100	100	98	92	94	98	103	100	96	97
100	97	100	97	96	85	94	98	104	100	88	93

Table 3
Assay results from agrochemical pesticide formulation Plenum®

	DPP ($n=4$)	HPLC ($n=6$)
Labeled claim (mass%)	50.00	50.00
Amount found (mass%)	49.66	49.13
R.S.D. (%)	1.89	0.92
Bias (%)	−0.68	−1.74
Student t-test	1.42 [2.31][a]	
Variance ratio F-test	4.36 [5.41][a]	

[a] The figures in parenthesis are the tabulated values of t and F at 95% confidence level.

3.4.1.1. Agrochemical pesticide

Pymetrozine peak at pH 2.0 was sufficiently high for its determination in agrochemical pesticide. Fig. 5 shows the differential pulse polarograms corresponding to the determination of pymetrozine content in Plenum®. As can be seen in Fig. 5, well-defined polarographic peaks allowed pesticide determination without interference effect of recipients in pesticide formulation. To study the accuracy of the proposed method, and to check the possible interferences from common recipients recovery studies were carried out. For these experiments, known amounts of the pure compound were added to the earlier analyzed formulation of pymetrozine. Each measurement was repeated five times. These data gave an average pymetrozine content of 49.66 ± 1.89% (by mass) for DPP, in close agreement with the 50.0% (by mass) quoted by the manufacturer. The nominal content of the compound was calculated from the corresponding regression equation. The proposed polarographic method applied for the analysis of Plenum® needed no filtration of pesticide extract from undissolved recipients; just a previous dilution of an aliquot from the supernatant layer with the pH 2.0 B–R buffer solution was required before each measurements.

The results obtained were compared with an HPLC method. The method involves the use of methanol/H_2O (60:40, (v/v)%) as the mobile phase and 150 mm Zorbax Eclipse XDB C_{18} (5 μm particle size) column. Pymetrozine was determined by HPLC using diode array and multiple wavelength UV–vis detector at 254 nm. The pymetrozine content in the Plenum® was calculated and compared statistically by student t-test for accuracy and variance ratio F-test for precision with the result obtained HPLC method (Table 3). Statistical analysis of the results by both methods using the student t-test and variance ratio F-test, show no significant difference between the performance of the two methods regarding the accuracy and precision, respectively. The experimental values of t and F at 95% confidence level did not exceed the theoretical ones indicating the good agreement with the HPLC method. Because the proposed method offers high sensitivity, low limit of determination, easy operation and simple instrumentation, it can be recommended for the pymetrozine analysis of agrochemical pesticides.

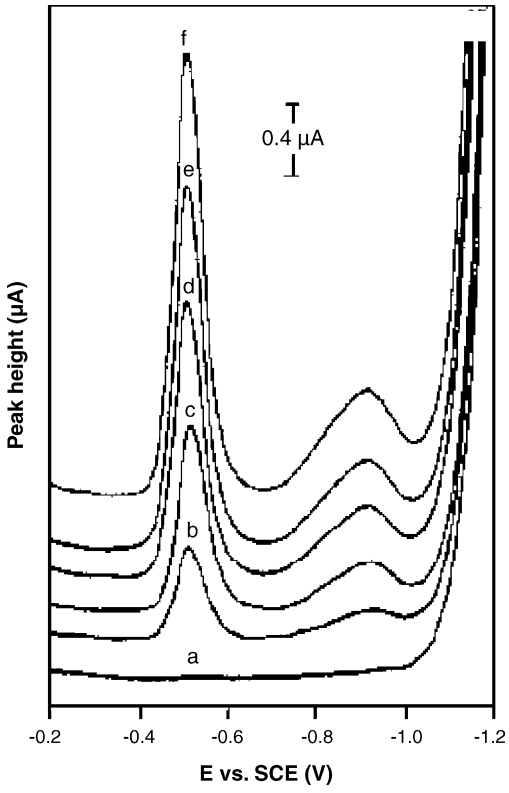

Fig. 5. DP polarograms obtained for the determination of pymetrozine in agrochemical pesticide (Plenum® extract sample) at pH 2.0. (a) 10.0 mL blank (pH 2.0, B–R buffer); (b) a + 50 mL μL, 1.0×10^{-3} mol L^{-1} Plenum® extract sample; (c) b + 50 μL, 1.0×10^{-3} mol L^{-1} pymetrozine; (d) c + 50 μL, 1.0×10^{-3} mol L^{-1} pymetrozine; (e) d + 50 μL, 1.0×10^{-3} mol L^{-1} pymetrozine; (f) e + 50 μL, 1.0×10^{-3} mol L^{-1} pymetrozine.

3.4.1.2. Lake water and orange juice

Recovery experiments were also performed in order to evaluate the interference of organic and inorganic components in natural water or orange juice matrices. A calibration curve was obtained for pymetrozine in both natural samples. The

Table 4
Application of the proposed method for the determination of pymetrozine in spiked lake water and orange juice

Added (mol L^{-1})	Found ($x \pm t \times s/\sqrt{n}$) (mol L^{-1})[a]		% Recovery		Relative error (%)	
	Lake water	Orange juice	Lake water	Orange juice	Lake water	Orange juice
1.0×10^{-6}	$(0.97 \pm 0.05) \times 10^{-6}$	$(0.98 \pm 0.04) \times 10^{-6}$	97.0	98.0	−3.0	−2.0
3.0×10^{-6}	$(2.88 \pm 0.17) \times 10^{-6}$	$(2.96 \pm 0.11) \times 10^{-6}$	96.0	98.7	−4.0	−1.3
5.0×10^{-6}	$(4.89 \pm 0.23) \times 10^{-6}$	$(4.97 \pm 0.19) \times 10^{-6}$	97.8	99.4	−2.2	−0.6
8.0×10^{-6}	$(8.32 \pm 0.20) \times 10^{-6}$	$(7.80 \pm 0.32) \times 10^{-6}$	104.0	97.5	+4.0	−2.5
1.0×10^{-5}	$(0.97 \pm 0.03) \times 10^{-5}$	$(0.98 \pm 0.02) \times 10^{-5}$	97.0	98.0	−3.0	−2.0

[a] Number of experiment, $n=6$ and t: 95% confidence level.

relationship between peak current (I_p) and concentration of pymetrozine was rectilinear for both lake water and orange juice over the range cited in Table 1. Linear regression analysis of the data gave the fallowing equations:

$$I_p = 3.31 \times 10^5 C + 0.1142 \, (r = 0.997)$$

For lake water and

$$I_p = 7.43 \times 10^5 C + 0.0232 \, (r = 0.993)$$

for orange juice, respectively; where C is the concentration in mol L^{-1} and I is the peak current in μA. The precision from six repeated measurements of electrochemical signal of 1.0×10^{-5} mol L^{-1} pymetrozine solution for lake water and orange juice were 3.32 and 2.63%, respectively. These values confirmed the sensitivity of the proposed method for the determination of pymetrozine in spiked samples.

The linearity range and reduction potential of pymetrozine in supporting electrolyte shows some differences compared to lake water and orange juice. This could be attributed to matrix effect or adsorption of some interfering ions on the electrode surface. The influence of some cationic, anionic or organic species which are commonly present in natural waters and fruit juices on the peak currents was probably narrowed the linearity range or shifted the potentials to more positive values (Table 1).

The accuracy of the proposed procedure for the determination of the pymetrozine in lake water and orange juice was checked using different amounts of spiked lake water and orange juice samples. Table 4 shows the experimental results corresponding to the determination of spiked pymetrozine at selected concentrations in lake water and orange juice samples. Unspiked samples (blanks) were previously analyzed with the polarographic method and no amount of tested insecticide compound was detectable. Following the procedure described in Section 2.3.3, the recoveries were estimated by measuring the peak heights of extracted spiked lake water or orange juice samples and comparing them with the peak heights obtained after the standard additions of known concentrations. The results are shown in Table 4. Recoveries calculated for lake water and orange juice samples spiked with 5.0×10^{-6} mol L^{-1} level were $(4.89 \pm 0.23) \times 10^{-6}$ and $(4.97 \pm 0.19) \times 10^{-6}$ M at 95% confidence level, respectively. The percent recoveries for lake water and orange juice were calculated as 97.8 and 99.4% with relative standard deviations of 4.49 and 3.64%, respectively. The results are satisfactorily accurate and precise.

4. Conclusion

A novel electro-analytical method involving DPP and dropping mercury electrode was proposed to determine pymetrozine content in agrochemical formulation, natural water and orange juice. The differential pulse polarographic method presented for the quantitative determination of pymetrozine allowed the accurate determination and was found to be rapid, simple and highly sensitive. The main advantage of such a procedure is the possibility to determine the concentration of the active component directly from the insecticide formulation and natural samples without any previous treatment, such as extraction, clean-up, derivatization or pre-concentration which are tedious, time consuming and also polluting. The present method could possibly be applied for the determination of pymetrozine in environmental samples as well as for quality control laboratories.

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