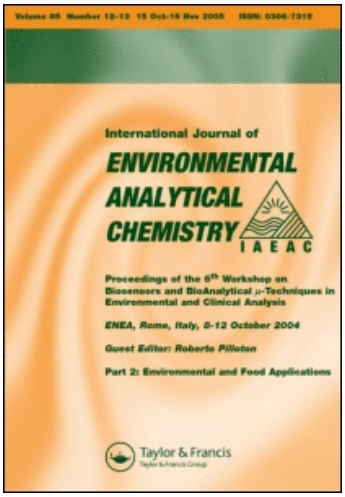

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Differential pulse polarographic behaviour of thiazopyr herbicide and application to its determination in fruit juice and soil samples

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Differential pulse polarographic behaviour of thiazopyr herbicide and application to its determination in fruit juice and soil samples

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A differential pulse polarographic method for the determination of the herbicide thiazopyr has been developed. The polarographic study of thiazopyr exhibited two well-defined cathodic peaks within the pH range of 1.0 to 8.0. The variation of pH and polarographic parameters indicated that the optimum conditions under which thiazopyr could be reduced were a pH 7.0 BR buffer solution, a reduction peak potential of −1270 mV (*vs.* SCE), scan rate of $5\,mV\,s^{-1}$, pulse amplitude of 50 mV with pulse duration of 50 ms at an ambient temperature of $25 \pm 3°C$. The main reduction peak was characterised by cyclic voltammetry as being irreversible and diffusion-controlled. A linear relationship between the peak current and the concentration of thiazopyr was obtained in the range of 0.43–38.6 $\mu g\,mL^{-1}$, with a detection limit of $0.127\,\mu g\,mL^{-1}$. The proposed method was successfully applied to the determination of thiazopyr in spiked fruit juice and soil samples. The mean recoveries of the $19.8\,\mu g\,g^{-1}$ and $3.96\,\mu g\,mL^{-1}$ thiazopyr spiked to soil and orange juice were $20.2 \pm 1.0\,\mu g\,g^{-1}$ and $3.84 \pm 0.12\,\mu g\,mL^{-1}$, at 95% confidence level, respectively. The sufficiently good recoveries and low relative standard deviation (RSD) data confirm the high accuracy and precision of the proposed method. The interferences effects of several commonly used pesticides and inorganic species were also studied. Interfering effects were eliminated either by providing selectivity with pH, or using EDTA as complexing agent.

Keywords: thiazopyr; herbicide; differential pulse polarography; soil

1. Introduction

Pesticides are widely used at various stages of cultivation and during post-harvest storage to protect fruits and vegetables against a range of pests and fungi or to preserve quality. The risk of pesticide residues depends on their ability to cause adverse health effects and the potential human exposure to their residues in the diet. Therefore, reliable analytical procedures are needed for their determination.

Thiazopyr, methyl-2-difluoromethyl-5-(4,5-dihydro-1,3-thiazol-2-yl)-4-isobutyl-6-trifluoromethylnicotinate (IUPAC) (Figure 1), is a new pre-emergence herbicide of the pyridine family, exhibiting a broad spectrum weed control activity. It will be

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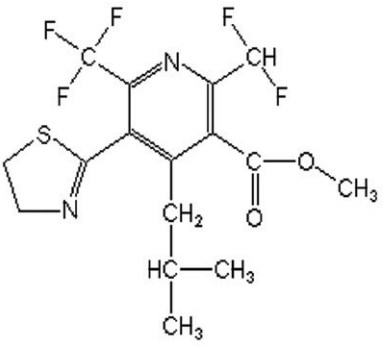

Figure 1. Structure of thiazopyr.

a useful addition for weed control in citrus growing areas, particularly where annual grass pressures are high, because it provides control against aggressive grass weeds at significantly lower use rates than existing products. It has a new unique mode of action and offers benefits in integrated pest management programs to counter the potential for weed resistance. Thiazopyr is extremely safe around citrus trees, including young citrus trees. Therefore, permanent tolerances have been established for residues in orange (whole fruit) at $0.05\,\mu g\,g^{-1}$ and grapefruit (whole fruit) at $0.05\,\mu g\,g^{-1}$ [1]. Hydrolysis of thiazopyr was observed at pH 7 and 9, with predicted half-life of 3,394 days and 64 days, respectively. In both cases, the hydrolysis product was thiazopyr monoacid. Thiazopyr degrades very slowly in soil, with an extrapolated half-life of 1,373 days [2].

As pesticide concentrations in agricultural and environmental samples are in general rather low, sensitive analytical methods are needed for their correct determination. So far, chromatographic techniques have been the most widely used [3–5], but electroanalytical techniques have also been used for their determination in different matrices like water, soil, plants and food [6–9]. Only few analytical procedures for the determination of thiazopyr were found in the literature and those are mostly chromatographic techniques [10–12]. A review of the literature revealed that no reports have been published on the electrochemistry or polarographic activity of thiazopyr. Moreover, none of the electroanalytical techniques such as stripping, cyclic or square wave voltammetry have been used for its determination in formulations or different matrices like water, soil, plants or food.

The polarographic technique presents some advantages in relation to many other analytical techniques. Progress made in pulse voltammetric techniques has increased the range of practical applications by enabling determinations of electroactive species at trace levels [13]. When compared to chromatography, the polarographic procedures have several other advantages such as their low cost, short time required for analysis, broad intervals of contents determined and selectivity [14–16]. On the other hand, electroanalytical methods offer useful applications in kinetic and equilibrium studies.

The aim of the present work was to study the polarographic and cyclic voltammetric behaviour of thiazopyr, and to develop a differential pulse polarographic method for its determination in soil and orange juice.

2. Experimental

2.1 *Materials*

Thiazopyr was provided by Dow AgroSciences LLC, USA Ltd., with a purity of 99.6%. Stock solutions of thiazopyr ($3.96 \times 10^2\,\mu g\,mL^{-1}$) were daily prepared in 50% ethanol solution and kept in the dark in a refrigerator. Thiazopyr is stable in sterile aqueous buffered solutions at pH 4 and 5. In the present work, the stability of thiazopyr solutions was also investigated at pH 3.0 and pH 7.0 by applying a DPP control and no degradation was observed during the short analysing and spiked periods.

A stock Britton Robinson buffer (BR buffer, 0.04 M, pH 2–11) was prepared by dissolution of 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid and 2.4720 g boric acid in 1 L aqueous solution. 50 mL portions of this solution were taken and the desired pH was adjusted between 2.0 and 12.0 by addition of the appropriate amount of 2M NaOH. A pH 1.0 solution was prepared from the dilution of 12 M HCl. The working (standard) solutions were prepared by dilution of thiazopyr stock solution with BR buffer of selected pH value, to give the concentration range of 39.6 to $3.96\,\mu g\,mL^{-1}$. 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 to 6 h after preparation to avoid possible decomposition.

The mercury (pro-analysis) was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through 3M HNO_3 and water columns in the form of fine droplets using a Pt fine sieve. The collected mercury was dried between sheets of filter paper. Before use, a differential pulse polarogram of this mercury was recorded at pH 3.0 and 7.0 BR buffer solution in order to confirm the absence of impurities.

2.2 *Apparatus*

A differential pulse polarographic (DPP) analyser system (PAR 174 A model, Princeton Applied Research Company, USA), 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 working and counter electrodes were a mercury dropping electrode (MDE) and a platinum wire, respectively. The natural drop time of the mercury electrode was 3.2 s ($2.04\,mg\,s^{-1}$). Cyclic voltammograms were obtained on the hanging mercury drop electrode (HMDE). 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.

2.3 *Procedures*

2.3.1 *Polarographic procedure*

The supporting electrolyte (10 mL), BR buffer solution, was put into the polarographic cell. The background polarograms were recorded after deoxygenating with a stream of high purity nitrogen (99.999%), by scanning the potential from 0.0 mV to about −1200 or −2000 mV depending on the pH of the solution. The analytical curves for the determination of thiazopyr were obtained by its standard addition. The linear concentration range was obtained at pH 3.0 and 7.0, from the evaluation of the peak

currents in the DPP experiments. The optimum conditions for the analytical determination of the investigated compound by DPP were found to be: pH 7.0 with the peak potentials of −1270 mV. The potential scan rate was 5.0 mV s^{-1} together with a pulse amplitude of 50 mV and pulse duration of 50 ms at an ambient temperature of 25 ± 3°C.

2.3.2 *Procedure for analysis of soil and orange samples*

Soils used in this study were collected in the city of Ankara (University Campus). Two grams of soil samples (ground and dried) were spiked with 39.6, 118.8 and 198 μg of thiazopyr stock solutions. The same procedure was also followed in parallel for a pesticide-free soil sample. After homogenizing the samples, they were inserted into the water-bath and shaken for 24 h at 35°C. The dried samples were extracted with 10 mL ethyl acetate and centrifuged for 5 min at 3000 rpm. After decantation of the supernatant, the soil sample was re-extracted with another 10 mL ethyl acetate. Sample extracts were filtered through filter paper and washed with 5 mL ethyl acetate. The collected filtrates were evaporated at 35°C and residue was dissolved in 10 mL 50% ethanol solution. From the supernatant, 1 mL of herbicide-free or spiked aliquots was transferred to the polarographic cell containing 9 mL pH 7.0 BR buffer solutions. Polarograms were recorded using the differential pulse polarographic (DPP) mode to get the calibration graph. However, the recoveries of the thiazopyr were calculated from peak current at about −1280 mV (*vs.* SCE), using the multiple standard additions.

25 mL of juice was extracted from an orange without any pre-separation or pre-concentration and spiked with thiazopyr at a concentration level of 3.96 to 19.8 μg mL^{-1}. After homogenizing the spiked samples, they were placed in a water-bath, shaken for 0.5 h and centrifuged for 5 min at 3000 rpm. From the supernatant, 1 mL aliquots were collected and transferred to the polarographic cell containing 9 mL pH 7.0 BR buffer solutions. After the polarographic procedure, thiazopyr in orange juice was analysed from the peak obtained at −1240 mV, by the standard addition method.

3. Results and discussion

3.1 *Polarographic behaviour of thiazopyr*

The polarographic investigation of a 7.76 μg mL^{-1} thiazopyr solution showed double well-defined differential pulse peaks over the pH 1.0–8.0 range in Britton-Robinson (BR) buffer solution (Figure 2). Ill defined peaks within the pH 9.0–12.0 range were not further evaluated. The pH effect on the peak current and potential was studied in BR buffer (0.04 mol L^{-1}) because of its wide pH range applicability. As seen from the Figure 2, the reduction peaks of thiazopyr on the dropping mercury electrode were found to be strongly pH dependent. The pH dependence could be attributed to a reduction process involving addition of H^+ to the oxidised species. According to pH dependency and the structure of the herbicide molecule, the first peak may correspond to the reduction of azomethine of the thiazole group [17]. The second peak, appearing at more negative potential compared to the first one, has also pH dependency and, may be generated due to the reduction of the azomethine group of the pyridine moiety.

The reduction potentials for both peaks shifted to more negative values with increasing pH and showed a single linear segment with their slopes of 42.3 and 45.2 mV/pH within the

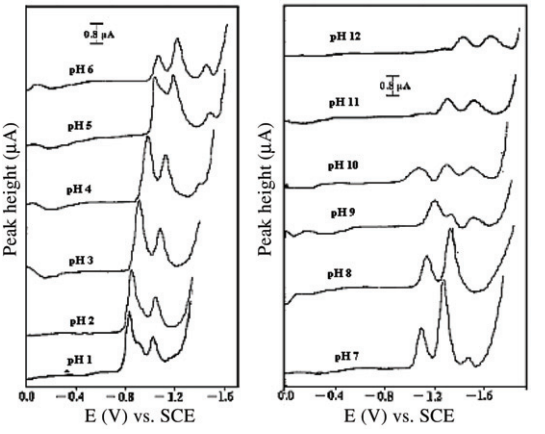

Figure 2. Effect of pH on the differential pulse polarographic peak of 7.76 μg mL^{-1} thiazopyr solution.

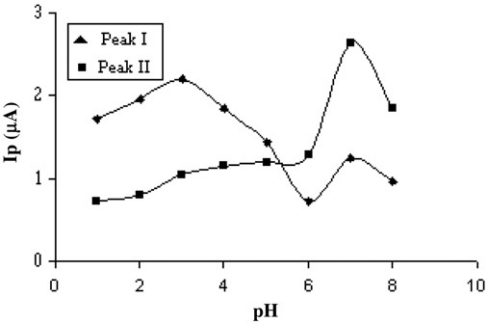

Figure 3. Effect of pH on the peak current of differential pulse polarographic peak obtained for a 7.76 μg mL^{-1} solution of thiazopyr.

pH 1.0–8.0 range. The relationship between E_p and pH for the first and second peak is expressed by the following equations:

$$-E_p\,(\text{mV}) = 42.3\ \text{pH} + 951 \quad \text{first peak} \quad (r = 0.994) \tag{1}$$

$$-E_p\,(\text{mV}) = 45.2\ \text{pH} + 765 \quad \text{second peak} \quad (r = 0.992) \tag{2}$$

Figure 3 shows the dependence of peak currents of thiazopyr on the pH of the BR buffer solution within the pH 1.0–8.0 range. The maximum sensitivity and response peak currents for the first and second peaks were found at pH 3.0 and pH 7.0, respectively. The sensitivity of the peak currents in more acidic solution decreases slightly due to the background discharge at lower pH. As the pH approaches to neutral or moderately basic region, the second peak reaches its maximum value at pH 7.0. Nevertheless, the first peak has its maximum value at pH 3.0. The peaks obtained between pH 9.0 and 12.0 have irregular and undefined shapes for the quantification of the target molecule. The reduction peaks decrease in basic solution, because of the controlling of the overall rate by protonation kinetics.

3.2 *Cyclic voltammetry*

A cyclic voltammogram of a 39.6 μg mL^{-1} solution of thiazopyr at HMDE was recorded in order to elucidate further electrode reaction. As shown in Figure 4, cyclic voltammogram of thiazopyr yields two well-defined reduction peaks at about −1.04 V and −1.22 V in BR buffer solution at pH 7.0. However, no oxidation peak was observed during the reverse scan, which corresponds to the characteristic well-known irreversible processes. The peak potentials displayed a catholic shift on increasing the scan rate from 20 to 500 mV s^{-1} prove also the irreversible nature of the reduction process.

$$-E_p\,(\text{mV}) = 0.119\,\upsilon\,(\text{mV s}^{-1}) + 1024.1 \quad \text{first peak} \quad (r = 0.981) \tag{3}$$

$$-E_p\,(\text{mV}) = 0.074\,\upsilon\,(\text{mV s}^{-1}) + 1206.3 \quad \text{second peak} \quad (r = 0.928) \tag{4}$$

Potential scan rates were evaluated to assess whether the reduction process on mercury electrode was diffusion or adsorption controlled. The function of the current intensity (I_p) *versus* the square root of the scan rate ($\upsilon^{1/2}$) was plotted. Linear plots were obtained for the first and second peaks, demonstrating the diffusion mass transport of the electroactive species to the HMDE surface. In the 20–500 mV s^{-1} ranges, the relations obey Equations (5) and (6):

$$I_p\,(\mu\text{A}) = 0.129\,\upsilon^{1/2}\,(\text{mV s}^{-1}) + 0.677 \quad \text{first peak} \quad (r = 0.976) \tag{5}$$

$$I_p\,(\mu\text{A}) = 0.379\,\upsilon^{1/2}\,(\text{mV s}^{-1}) + 2.811 \quad \text{second peak} \quad (r = 0.979) \tag{6}$$

A plot of logarithm of peak currents ($\log I_p$) *versus* logarithm of scan rate ($\log \upsilon$) for the first and second peaks gave a straight line with slopes of 0.36 and 0.31, respectively, close to the theoretical value of 0.5, which is expected for an ideal diffusion controlled reduction [18]. Equations (7) and (8), obtained for thiazopyr, indicate that the electrode process was controlled by diffusion.

$$\log I_p\,(\mu\text{A}) = 0.36 \log \upsilon\,(\text{mV s}^{-1}) - 0.428 \quad (r = 0.986) \tag{7}$$

$$\log I_p\,(\mu\text{A}) = 0.31 \log \upsilon\,(\text{mV s}^{-1}) + 0.203 \quad (r = 0.989) \tag{8}$$

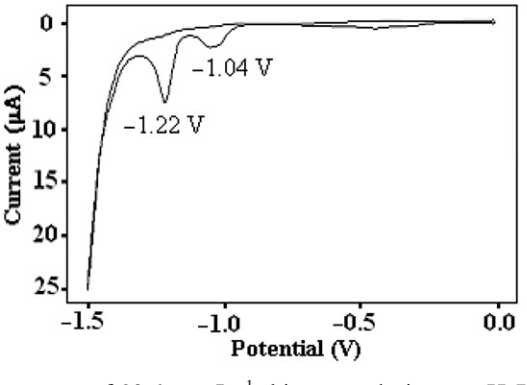

Figure 4. Cyclic voltammogram of 39.6 μg mL^{-1} thizopyr solution at pH 7.0 BR buffer (scan rate: 100 mV s^{-1}).

3.3 *Analysis of thiazophyr by DPP method*

The optimum pH for the analytical determination of the thiazopyr herbicide was 7.0 (at −1270 mV). However, pH 3.0 buffer solution was also used when the thiazopyr peak coincided with the peaks due to the co-existing-ions or some other pesticides. As displayed in Figure 5, the consecutive additions of thiazopyr caused proportional increments in the peak currents. The peak currents obtained from the polarograms were linearly related to

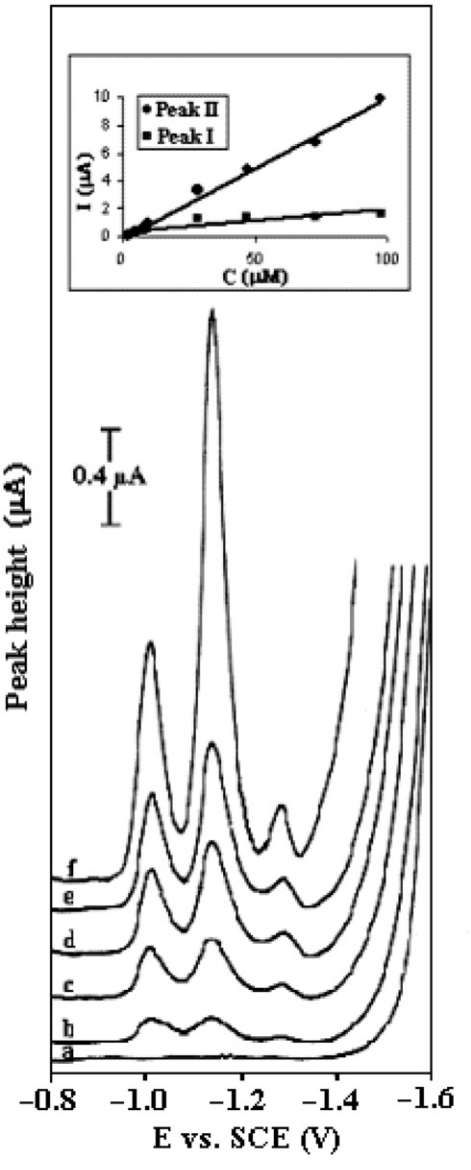

Figure 5. Calibration curves for thiazopyr in supporting electrolyte (BR buffer) at pH 7.0.
Notes: (a) 10 mL pH 7.0 BR buffer; (b) 7.92 μg thiazopyr; (c) 19.8 μg thiazopyr; (d) 31.7 μg thiazopyr; (e) 39.6 μg thiazopyr; (f) 118.8 μg thiazopyr.

Table 1. Statistical parameters for the polarogaraphic determination of thiazopyr.

	BR Buffer solution[a]		Soil	Orange juice
Parameter	pH 3	pH 7	pH 7	pH 7
Measured potential (mV)	−900	−1270	−1280	−1240
Linearity range ($\mu g\,mL^{-1}$)	1.73–25.6	0.43–38.6	13.2–146.5[b]	0.91–35.9
Slope ($\mu A/\mu g\,mL^{-1}$)	0.222	0.252	0.057[c]	0.192
Intercept (μA)	0.443	0.060	0.537	0.104
Correlation coefficient	0.993	0.997	0.999	0.993
LOD ($\mu g\,mL^{-1}$)	0.519	0.127	3.960[b]	0.269
LOQ ($\mu g\,mL^{-1}$)	1.73	0.430	13.20[b]	0.910
Repeatability of peak potential (RSD%)	0.73	0.480	0.66	0.65
Repeatability of peak current (RSD%)	2.86	3.60	2.96	3.68

Notes: [a]Britton–Robinson buffer solution; [b]Units in $\mu g\,g^{-1}$; [c]Units in $\mu A/\mu g\,g^{-1}$.

the herbicide concentration between 1.73 and 25.6 $\mu g\,mL^{-1}$ for the first peak at pH 3.0 and 0.43 to 38.6 $\mu g\,mL^{-1}$ for the second peak at pH 7.0, with the analytical Equations (9) and (10) given by:

$$I_p\,(\mu A) = 0.222\ C\ (\mu g\,mL^{-1}) + 0.4425 \quad r = 0.993,\ \text{pH } 3.0\ (n = 10) \tag{9}$$

$$I_p\,(\mu A) = 0.252\ C\ (\mu g\,mL^{-1}) - 0.0603 \quad r = 0.997,\ \text{pH } 7.0\ (n = 10) \tag{10}$$

The limit of detection (LOD) and limit of quantification (LOQ) were obtained for the experimental conditions employed using the equations $LOD = 3S_b/b$ and $LOQ = 10S_b/b$ from IUPAC [19], where S_b is the standard deviation of 0.77 $\mu g\,mL^{-1}$ thiazopyr for an average of ten values of current and b is the slope of the calibration curve. For the second peak at pH 7, the observed values of LOD and LOQ were 0.127 $\mu g\,mL^{-1}$ and 0.43 $\mu g\,mL^{-1}$, respectively. For the first peak at pH 3, LOD and LOQ values were 0.519 $\mu g\,mL^{-1}$ and 1.73 $\mu g\,mL^{-1}$, respectively.

The high sensitivity of differential pulse polarography is accompanied by very good repeatability. To estimate the repeatability of the proposed method, the RSD of ten times successful measurements of peak currents of 0.77 $\mu g\,mL^{-1}$ thiazopyr solution was calculated to be 3.60, 2.96 and 3.68% for BR buffer, soil and orange samples, respectively (see Table 1).

3.4 *Interference study*

The influence of some other commonly used pesticides, e.g., atrazine, acifluorfen and azinphos-methyl on the determination of thiazopyr was also examined (Table 2). Under the experimental conditions (pH 7.0) atrazine was electro inactive but acifluorfen and azinphos-methyl generated signals at −500 mV and −820/−1110 mV, respectively. Atrazine did not seriously interfere with the analyte signal up to ten-fold excess since it did not show electroactivity. The peak generated at – 500 mV due to the acifluorfen was located far away from the peak potential of thiazopyr at −1100 and −1270 mV. Therefore, acifluorfen had no significant effect on the polarographic peak of thiazopyr. The relatively large interference effect for azinphos-methyl could be attributed to its cathodic reduction peak, very close to

Table 2. Influence of some other commonly used pesticides on the recovery of 3.96 μg mL^{-1} thiazopyr solution.

Interfering pesticides	Concentration (μg mL^{-1}) ($\bar{x} \pm ts/\sqrt{N}$)[a]	Recovery (%)
[a]Atrazine	2.16	96.3 ± 0.1
	10.70	100.6 ± 2.3
	21.60	95.4 ± 1.8
[a]Acifluorfen	3.8	97.3 ± 0.7
	19.20	99.3 ± 2.6
	38.30	101.0 ± 1.9
[b]Azinphos methyl	3.17	99.0 ± 1.2
	15.90	96.4 ± 4.2
	31.70	95.2 ± 0.7

Notes: [a]DPP determination of thiazopyr at pH 7.0; [b]DPP determination at pH 3.0 due to the coincidence with that peak of thiazopyr at pH 7.0; 95% confidence level ($n = 4$).

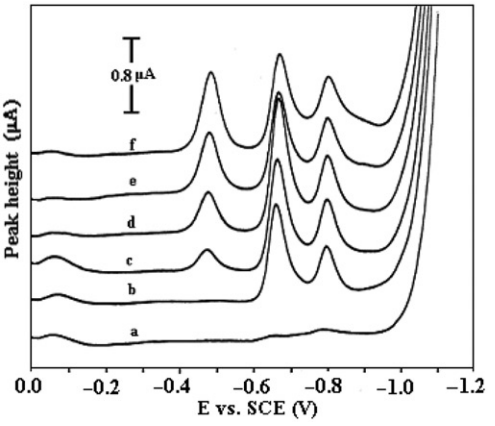

Figure 6. Determination of thiazopyr next to azinphos-methyl at pH 3.0 BR buffer.
Notes: (a) 10 mL pH 3 BR buffer; (b) a + 39.6 μg thiazopyr; (c) b + 31.7 μg azinphos-methyl, (d) b + 63.4 μg azinphos-methyl; (e) b + 95.1 μg azinphos-methyl; (f) b + 126.8 μg azinphos-methyl.

the thiazopyr peak, and therefore overlapping to some extent at pH 7.0. On the other hand, the resolution of the peak potentials between azinphos-methyl (−850 mV) and thiazopyr (−900/−1090 mV) at pH 3.0 were sufficient for the accurate determination of the thiazopyr (Figure 6). The recoveries of the 3.96 μg mL^{-1} thiazopyr next to 31.7 μg mL^{-1} azinphos-methyl were 95.2% with the relative standard deviations of 0.7% at 95% confidence level ($n = 4$). The results obtained for the recoveries of thiazopyr in the presence of several pesticides are presented in Table 2. The results are satisfactorily accurate and precise.

The selectivity of the proposed method for thiazopyr was investigated in the presence of some inorganic ions found mostly in soil and irrigation water. Some of these co-existing ions are electroactive (produce a peak current), e.g., Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, Cd^{2+} and some electroinactive (produce no peak current), e.g., K^+, Mg^{2+} and Ca^{2+}. The ions K^+, Ca^{2+}, Mg^{2+} and Fe^{3+} were prepared from their chloride salts. $CdSO_4$ was used

Table 3. Influence of interfering ions on the recovery of 3.96 μg mL^{-1} thiazopyr solution at pH 7.0.

Interfering ions	Concentration (μg mL^{-1})	Recovery (%)[a] of thiazopyr ($x \pm ts/\sqrt{N}$)	Interfering ions	Concentration (μg mL^{-1})	Recovery (%)[a] of thiazopyr ($x \pm ts/\sqrt{N}$)
Ni^{2+}	0.58	99.7 ± 3.2	Cu^{2+}	0.64	99.1 ± 2.0
	5.57	98.2 ± 3.7		6.35	94.7 ± 3.0
	29.4	98.0 ± 1.6		31.8	99.2 ± 2.5
	58.7	98.5 ± 2.3		63.6	97.1 ± 4.8
Pb^{2+}	2.07	99.0 ± 7.7	Zn^{2+}	0.65	99.5 ± 2.1
	20.7	99.1 ± 2.2		6.54	101.3 ± 4.3
	103.5	98.3 ± 3.2		32.7	103.4 ± 2.6
	207	102.3 ± 6.7		65.4	102.5 ± 13
Cr^{3+}	0.52	98.9 ± 1.3	K^{+}	0.39	98.4 ± 3.3
	5.20	100.6 ± 2.1		3.90	98.9 ± 1.6
	26.0	100.1 ± 1.2		19.5	98.3 ± 1.2
	52.0	102.3 ± 2.5		39.0	98.3 ± 1.5
Mg^{2+}	0.24	101.1 ± 7.5	Ca^{2+}	0.40	100.5 ± 1.8
	2.43	97.5 ± 2.4		4.01	99.8 ± 2.3
	12.2	99.0 ± 2.7		20.1	99.9 ± 1.9
	24.3	100.8 ± 0.7		40.1	100.9 ± 1.7
Fe^{3+}	0.56	101.2 ± 1.2	Cd^{2+}	1.12	97.9 ± 3.7
	5.56	102.4 ± 2.3		11.2	99.6 ± 3.9
	27.9	99.6 ± 2.8		56.0	98.5 ± 3.7
	55.8	103.7 ± 3.1		112.4	101.2 ± 2.8

Note: [a]Mean of four determination at 95% confidence level.

for preparing Cd^{2+} solution. Nitrate salts were used to obtain all the remaining interfering ions. The co-existing ions were taken as 1, 10, 50 and 100-fold molar excess and the results are summarised in Table 3. The degrees of interfering effects were treated as the recoveries (by percentage) of 3.96 μg mL^{-1} thiazopyr solution in the presence of the interfering ions.

Cu^{2+} and Cd^{2+} appeared at more positive potentials (−170 and −700 mV, respectively) than thiazopyr (−1100 and −1270 mV). Thus, the polarographic peaks of these ions did not overlap the herbicide peak and therefore they had no marked effect on the polarogram of thiazopyr. The recoveries of 3.96 μg mL^{-1} thiazopyr in the presence of 63.6 μg mL^{-1} Cu^{2+} and 112.4 μg mL^{-1} Cd^{2+} were 97.12 ± 4.8 and 101.20 ± 2.8 ($n = 4$; 95% confidence interval), respectively. Pb^{2+} did not produce a polarographic peak at pH 7.0 due to the lead-acetate generated from the equilibrium of one of the buffer components. There was no peak for Fe^{3+} as expected for neutral or basic media.

On the other hand, the polarographic peaks for Ni^{2+} at −1140 mV and Zn^{2+} at −1130 mV overlapped intensively with the double peaks of thiazopyr at −1100 mV and 1270 mV. Fortunately, the interfering effect of Ni^{2+} and Zn^{2+} has been eliminated by the addition of EDTA into the solution. The peak currents of these ions immediately disappeared because the peak potentials of Ni-EDTA or Zn-EDTA shifted to more negative potentials that permitted the accurate determination of thiazopyr without interference effect. This can be explained with the relatively high stable complex of Ni-EDTA or Zn-EDTA, with conditional stability constants (at pH 7) of 2.02×10^{15}, 1.54×10^{13}, respectively. Finally, 3.96 μg mL^{-1} thiazopyr was successfully determined in presence of 58.7 μg mL^{-1} Ni^{2+} and 65.4 μg mL^{-1}Zn^{2+}, with a recovery of 98.5 ± 2.3 and

Table 4. Determination of spiked thiazopyr in soil and orange juice at some selected concentrations.

Sample	Added	Found[a] ($x \pm ts/\sqrt{N}$)	RSD[b] (%)	RE[c] (%)
Soil ($\mu g\,g^{-1}$)	–	ND	–	–
	19.8	20.2 ± 1.0	2.0	+2.0
	59.4	58.4 ± 3.5	2.4	−1.7
	99.0	100.5 ± 1.2	0.5	+1.6
Orange juice ($\mu g\,mL^{-1}$)	–	ND	–	–
	3.96	3.84 ± 0.12	1.9	−3.0
	11.9	11.9 ± 0.28	0.9	0.0
	19.8	19.7 ± 0.28	0.5	−0.5

Notes: [a]Three determination at 95% confidence level; [b]RSD: Relative standard deviation. [c]RE: Relative error. ND: not detected.

$102.5 \pm 1.3\%$ ($n = 4$; 95% confidence interval), respectively. Chromium ion did not show interfering effect because of ill-defined peak appeared at far higher, positive potential than thiazopyr.

Finally, Ca^{2+}, Mg^{2+} and K^+ are electro-inactive species and therefore had no marked effect on thiazopyr determination. According to the obtained results, the recoveries of $3.96\,\mu g\,mL^{-1}$ thiazopyr in presence of $40.1\,\mu g\,mL^{-1}$ Ca^{2+}, $24.3\,\mu g\,mL^{-1}$ Mg^{2+} and $39.0\,\mu g\,mL^{-1}$ K^+ were 98.3 ± 1.5, 100.6 ± 0.9 and $99.1 \pm 1.1\%$, respectively.

3.5 *Determination of thiazopyr in spiked soil and orange juice samples*

Calibration curves were obtained for thiazopyr in both soil and orange juice samples, considering the matrix effects of the real samples. Linear regression analysis of increasing amounts of the thiazoppyr in soil and orange juice samples gave, Equations (11) and (12), respectively:

$$I_p = 0.057\,\mu A/\mu g\,g^{-1}\,C + 0.5366 \quad (r = 0.999) \tag{11}$$

$$I_p = 0.192\,\mu A \mu g\,mL^{-1}\,C + 0.1045 \quad (r = 0.994) \tag{12}$$

where C is the concentration in $\mu g\,g^{-1}$ (soil) and $\mu g\,mL^{-1}$ (orange juice), I is the peak current in μA. The precisions obtained from ten repeated measurements of $3.85\,\mu g\,g^{-1}$ and $0.77\,\mu g\,mL^{-1}$ thiazopyr for soil and orange juice samples were 4.96% and 3.68%, respectively. These results confirmed the sensitivity of the proposed method.

The validity of the proposed method was proven by spiking thiazopyr to soil and orange samples over the ranges of 19.8 to $99.0\,\mu g\,g^{-1}$ and $3.96\,\mu g\,mL^{-1}$ to $19.8\,\mu g\,mL^{-1}$, respectively and subjecting the samples to the analytical procedure in Section 2.3.2. From the supernatant, 1 mL was transferred to the polarographic cell containing 9 mL of BR buffer solution with a pH of 7.0. Polarograms were recorded under the optimised conditions and the herbicide in soil and orange juice were determined from the peak currents generated at about −1280 mV and −1240 mV (*vs.* SCE), respectively, using multiple standard additions according to the procedure described in Section 2.3.2.

Table 4 shows the experimental results corresponding to the determination of spiked thiazopyr at selected concentrations in soil and orange juice samples. Recoveries calculated for soil and orange juice samples spiked with $19.8\,\mu g\,g^{-1}$ and $19.8\,\mu g\,mL^{-1}$ level were $20.2 \pm 1.0\,\mu g\,g^{-1}$ and $19.7 \pm 0.28\,\mu g\,mL^{-1}$ at 95% confidence level, respectively. The percentage recoveries for soil and orange juice samples were detected as 102.0% and 99.5%, with relative standard deviations of 2.0% and 0.5%, respectively. The sufficiently good recoveries and low relative standard deviation data reflects the high accuracy and precision of the proposed pulse differential polarographic method.

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