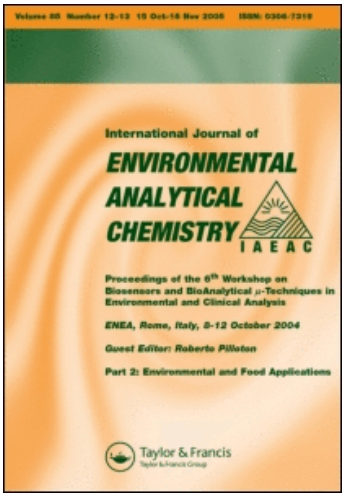


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Polarographic determination of herbicide thifensulfuron methyl/application to agrochemical pesticide, soil, and fruit juice

Recai İnam[a]; Tuba Sarİgül[a]; Ebru Zeynep Gülerman[a]; NazlI Uncu[a]
[a] Faculty of Art & Science, Department of Chemistry, Ankara, Turkey

To cite this Article İnam, Recai , Sarİgül, Tuba , Gülerman, Ebru Zeynep and Uncu, NazlI(2006) 'Polarographic determination of herbicide thifensulfuron methyl/application to agrochemical pesticide, soil, and fruit juice', International Journal of Environmental Analytical Chemistry, 86: 15, 1135 — 1149
To link to this Article: DOI: 10.1080/03067310600797606
URL: http://dx.doi.org/10.1080/03067310600797606

Intern. J. Environ. Anal. Chem.
Vol. 86, No. 15, 20 December 2006, 1135–1149

Taylor & Francis
Taylor & Francis Group

Polarographic determination of herbicide thifensulfuron methyl/application to agrochemical pesticide, soil, and fruit juice

RECAI İNAM*, TUBA SARİGÜL, EBRU ZEYNEP GÜLERMAN and NAZLI UNCU

Faculty of Art & Science, Department of Chemistry, Gazi University, 06500, Ankara, Turkey

(*Received 31 January 2006; in final form 21 April 2006*)

A novel, sensitive, simple, fast, and fully validated differential pulse polarographic (DPP) method for the determination of trace amounts of thifensulfuron-methyl in pesticide formulation, soil, and orange juice is reported. This procedure was based on a highly sensitive peak formed due to the reduction of thifensulfuron-methyl on a dropping mercury electrode over the pH range 1.00–10.00 in Britton–Robinson buffer. The polarographic reduction exhibits only a single peak in the pH ranges $pH \geq 3.0$ and $pH \leq 6.0$ and $pH = 10.0$ located at potential values of −1.010, −1.350, and −1.610 V (*vs.* SCE), respectively. The single peak appeared as a maximum at pH 3.0 (−1.010 V) was well resolved and suitable to be investigated for analytical use. This peak showed quantitative increments with the additions of standard thifensulfuron-methyl solution under the optimal conditions, and the cathodic peak current was linearity proportional to the thifensulfuron-methyl concentration in the range of 2×10^{-7}–5×10^{-5} M. The limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.05×10^{-7} and 3.50×10^{-7} M, respectively, according to the relation $k \times SD/b$ (where $k = 3$ for LOD, $k = 10$ for LOQ, SD is the standard deviation of the blank, and b is the slope of the calibration curve). The proposed method was applied to pesticide formulation (Harmony® Extra), and the average percentage recovery was in agreement with that obtained by the spectrophotometric comparison method, 97.82 and 102.6%, respectively. The method was extended to determination of thifensulfuron-methy in spiked soil and orange juice, showing a good reproducibility and accuracy with a relative standard deviation of 4.55 and 1.40%, and relative errors of +2.80 and +1.90%, respectively.

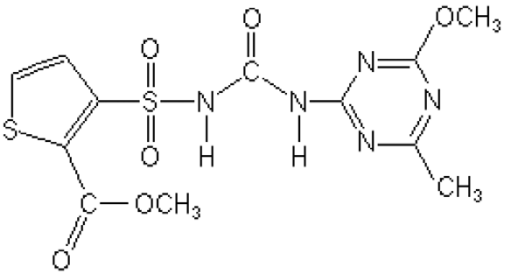
Keywords: Polarography; Pesticide; Thifensulfuron-methyl

1. Introduction

Sulphonylureas are a class of herbicides used for crop protection. Chlorsulphuron, metsulphuron-methyl, tribenuron-methyl, and thifensulfuron-methyl belong to the group of sulphonylurea herbicides characterized by low application rates (active ingredients 2–40 g ha^{-1}) and phytotoxicity [1, 2]. This provides a good crop selectivity

*Corresponding author. Fax: +90-312-212-22-79. Email: rinam@gazi.edu.tr

ISSN 0306-7319 print/ISSN 1029-0397 online © 2006 Taylor & Francis
DOI: 10.1080/03067310600797606



Scheme 1. Structural formula of thifenilsulfuron-methyl.

and is commercialized for use in wheat, barley, rice, corns, soybeans, and oilseed rape. Despite their low application rates, there is a need to establish to what extent sulphonylurea herbicides may leach from soil to water. It is also known that contamination by pesticides is not restricted only to soil, but also to the consumption of contaminated foods [3, 4] and water [5].

Thifensulfuron methyl (DPX-M6316) [methyl 3-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulphamoyl)] is a compound of the family of sulphonylureas, whose general structure is shown in scheme 1. It is an ingredient of a herbicide known as DPX-M6316 and is selective for weed control in cereals and other crops in which it controls adventitious wide leaved plants. The molecular structure of thifensulfuron methyl is characterized by an s-triazinic ring bonded through an urea bridge to a hetero-aromatic sulphonamide. The degradation of thifensulfuron methyl in soil, leading to the formation of the herbicidally inactive thifensulfuron acid, is due to microbial carboxyesterase activity [6]. Several oxidation processes able to destroy and, eventually, mineralize organic pollutants have been proposed [7, 8]. These processes involve either environmentally safe oxidants (like ozone or H_2O_2) [8] or photocatalysis [9, 10]. The bacterial mineralization of sulphonylurea herbicides in soil also plays an important role in their degradation. The highest mineralized amount in 126 days was observed for metsulphuron-methyl (40%) followed by tribenuron-methyl (25%) and thifensulfuron-methyl (11%) [11].

The increase in agricultural production promotes an equivalent increase in the level of pesticide in waters, soils, and foodstuff. The extensive development of the pesticide field requires more rigorous analytical methods for the control of drugs. In this respect, new analytical methods to monitor different types of pesticides and their residues in biological and environmental interest have become very important. Therefore, there is a need for a simple, sensitive, accurate, and time-saving method for its evaluation in pure solutions, soil, irrigation water, and fruit juices. For the present purposes, the analysis technique for thifensulfuron-methyl should be rapid, simple, and highly sensitivity. Electroanalytical techniques have been shown to be excellent for the determination of pharmaceutical and pesticide compounds in different matrix.

The most analytical procedures for the determination of sulphonylurea pesticides are the chromatographic procedures [12–14], but electroanalytical techniques have also been used for the determination and study of several pesticides in different matrixes like water, soils, plants, and food [15–18]. Tribenuron is also a compound of the family of sulphonylurea, whose electrochemical behaviour and assay of commercial samples were described using the polarographic technique [19]. However, no work has been reported

in the literature dealing with polarographic behaviour as well as the polarographic determination of the thifensulfuron-methyl in commercial formulation, water, and fruit juices. Thus, the polarographic behaviour of thifensulfuron-methyl was studied, and a new method for the determination of thifensulfuron-methyl in the pesticide formulation Harmony® Extra, spiked soil, and orange juice was developed. The electroanalytical or polarographic technique has several advantages over traditional methods. It is possible to perform the analysis directly with the formulation, without any extraction, clean-up, or pre-concentration steps. The advantages of experimental electrochemical techniques in the field of drug analysis are their simplicity, low cost, and relatively short analysis time when compared with the other techniques [20–22].

2. Experimental

2.1 *Chemicals and reagents*

Thifensulfuron-methyl [$C_{12}H_{13}N_5O_6S_2$, M_w: 387.394, 97.0% purity] was kindly provided by duPont (Nambsheim, France). Stock solutions of thifensulfuron-methyl (1.0×10^{-3} M) were prepared in 50% ethanol solution and kept in the dark in a refrigerator. The supporting electrolyte, namely Britton–Robinson buffer (B–R buffer, 0.04 M, pH 2–12), was prepared in doubly distilled water. Working solutions were prepared by dilution of the stock solution with the selected supporting electrolyte to give the solution containing thifensulfuron-methyl in the concentration range of 2.0×10^{-7} to 1.0×10^{-4} M. The agrochemical pesticide formulation Harmony® Extra (50% thifensulfuron methyl and 25% tribenuron methyl, by mass) was obtained from ordinary dealers of agrochemicals (Bay-Tar, Antalya, Turkey). Salts used for supporting electrolyte, solvents, and other reagents were of analytical reagent grade (Merck or Sigma). All solutions were protected from light and were 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 to confirm the absences of impurities. B–R buffer solution was prepared by dissolving 2.3 mL of glacial acetic acid, 2.7 mL of phosphoric acid, and 2.4720 g by dilution with water to 1.0 L. Fifty millilitre portions of this solution were taken, and the desired pH was adjusted between 2.0 and 10.0 by addition of the appropriate amount of 2.0 M NaOH.

2.2 *Apparatus*

A Princeton Applied Research Company (PAR) model 174A polarographic analyser system, equipped with a PAR mercury drop timer, was used. A Kalousek electrolytic cell with reference-saturated electrode (SCE), separated by a 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^{-1}). 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. Absorption spectra and absorbances were recorded using UNICAM UV 2–100, double beam UV-visible spectrophotometer.

2.3 *Procedures*

2.3.1 Polarographic measurements of thifensulfuron-methyl. The polarographic response of thifensulfuron-methyl at the dropping mercury electrode (DME) was analysed in 0.04 M B–R buffer with pH varying in the range of 2.0–10.0 in a 1.0×10^{-5} M thifensulfuron-methyl solution. HCl solution (0.10 M) was used for pH 1.0. The optimum pH for the thifensulfuron-methyl analysis was selected by the maximum peak current value obtained.

For this purpose, 10.0 mL of supporting electrolyte solution of B–R buffer was put into the polarographic cell and de-oxygenated with high-purity nitrogen (99.999%) for about 5 min. The analytical curves for thifensulfuron-methyl were obtained by standard addition of the pesticide to the electrolyte and evaluation of the peak currents in the DPP experiments, in the linear concentration range 2.0×10^{-7}–5.0×10^{-5} M and 9.9×10^{-7}–1.9×10^{-5} M at pH 3.0 and 10.0, respectively. The background polarograms were obtained by scanning the potential from 0.0 V to about −1.5 to −2.0 V (*vs.* SCE) depending on the pH of the solution.

Thifensulfuron methyl hydrolyses readily at high and low pH, and the hydrolysis rate is pH-dependent following pseudo-first-order kinetics with a half-life of 28.8 and 97.6 h at pH 4.0 and 9.0, respectively [23]. It is much more stable at a neutral pH, and the half-life at pH 7 is 250 h. At alkaline pH, thifensulfuron methyl hydrolysed to thifensulfuron, which was slowly transformed by sulphonylurea bridge cleavage and demethylation of the methoxy group. The stability of thifensulfuron methyl solutions was also investigated at pH 3.0 and 10.0 by using a polarographic control. The degree of degradation during the analysing period (about 10 min) was 1.6 and 2.4% at pH 3.0 and 10.0, respectively. Stock solutions of thifensulfuron-methyl (1.0×10^{-3} M) were prepared in 50% ethanol solution at neutral pH and kept in the dark in a refrigerator, in order to prevent hydrolysis. Application of the method to spiked soil and orange juice was also carried out at neutral pH, and therefore degradation was negligible.

The optimum conditions for the analytical determination of the investigated compound by DPP were found to be: pHs 3.0 and 10, peak potentials of −1.010 and −1.590 V, scan rate of 50 mV s^{-1}, and a pulse amplitude of 50 mV with pulse duration of 50 ms at an ambient temperature of 25 ± 3°C. A pH of 10.0 was chosen for the determination of thifensulfuron-methyl in pesticide formulation, since the tribenuron peak interferences appeared also at pH 3.0.

2.3.2 Formulation assay procedure. A suitable amount of pesticide formulation Harmony® Extra (50% thifensulfuron-methyl and 25% tribenuron) equivalent to 1×10^{-3} M thifensulfuron-methyl was accurately measured and transferred into a 100 mL calibrated flask, made up to the mark with 50% ethanol solution, and sonicated for 15 min. In the DPP experiments, 200 μL of an aliquot of this clear supernatant liquor was added to 10.0 mL of the buffer in the electrochemical cell (previously

de-aerated for 5 min with humidified, 99.999% ultra-pure nitrogen) and measured under calibration conditions, with the exception of choosing pH 10.0 instead of pH 3.0, since the interferences of the tribenuron peak was observed at pH 3.0. The thifensulfuron-methyl in pesticide formulation was analysed in the potential range of −0.8 to −1.8 V, by the standard addition method. The same procedure was employed in the UV-visible spectrophotometric analyses (performed at 225 nm, the maximum absorbance).

2.3.3 Analysis of soil and orange juice sample

- Soil sample: Two grams of soil (ground and dried) was weighed and spiked with thifensulfuron-methyl at concentration levels of 3.0×10^{-7}–9.0×10^{-5} M in 20.0 mL of 50% ethanol solution. After homogenizing the samples for 10 min, they were placed in centrifuge tubes, shaken for 2 h, and centrifuged for 10 min at 3000 rpm. From the supernatant, 1.0 mL aliquots were collected, transferred to the polarographic cell containing 9.0 mL of pH 3.0 B–R buffer solution. The thifensulfuron-methyl in soil was analysed in the potential range of −0.5 to −1.2 V, by the standard addition method. The same procedure was employed in the UV-visible spectrophotometric analyses (performed at 225 nm, the maximum absorbance).
- Orange-juice sample: The same electroanalytical procedure described above was used for the determination of thifensulfuron-methyl in orange juice with the exception of UV-visible spectrophotometric analyses. For this purpose, 10.0 mL of juice was extracted from an orange without any pre-separation or pre-concentration. The juice sample was spiked with thifensulfuron-methyl at concentration levels of 1.0×10^{-6}–2.0×10^{-5} M in 20.0 mL 50% ethanol solution. After completing the above procedure, 1.0 mL aliquots then added to the electrochemical cell containing 9.0 mL pH = 3.0 B–R buffer solution. The thifensulfuron-methyl in orange juice was analysed in the potential range of −0.5 to −1.3 V, by the standard addition method.

3. Results and discussion

3.1 *Polarographic behaviour*

For control of pH, a range of possible reagents, hydrocholoric acid, phosphoric acid, acetic acid, boric acid and B–R buffers, were tested. No major differences were observed between the different buffers, and eventually the B–R buffer (0.04 M) was chosen for its wide pH range applicability. Thifensulfuron-methyl exhibited single or double well-defined DP peaks depending on the pH of the B–R buffer solution. Figure 1(a) and (b) shows typical DP polarograms of 1.0×10^{-5} M thifensulfuron-methyl within the pH range of 1.0–10.0. As shown in figure 1, the polarographic reduction exhibits only a single peak in the pH ranges pH ≥ 3.0 and pH ≤ 6.0, pH 10.0, located at −1.010, −1.350, and −1.610 V (*vs.* SCE), respectively. However, in the pH range of 1.0–2.0 and 7.0–9.0, two polarographic peaks are observed, located

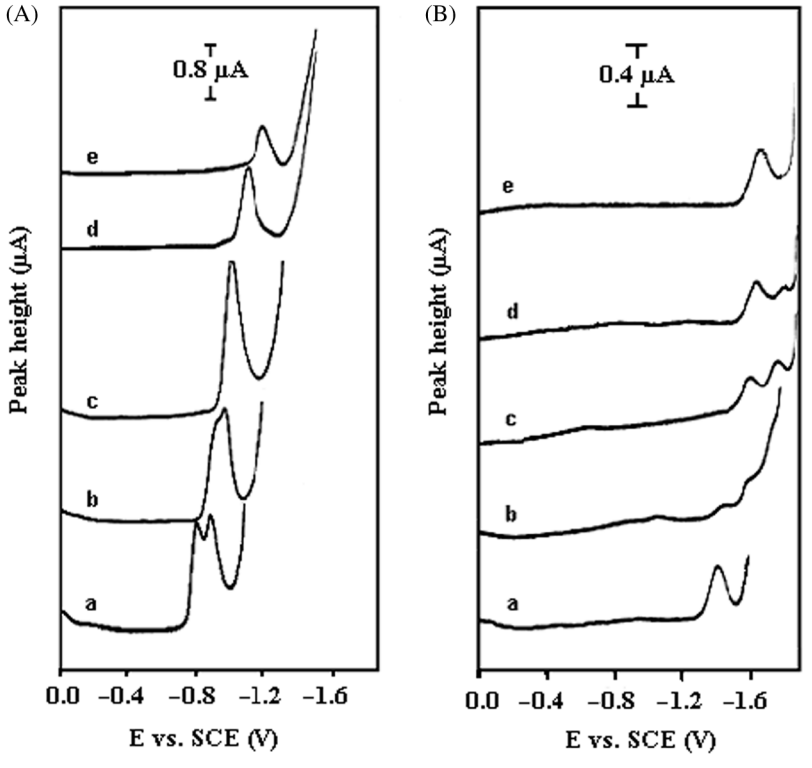


Figure 1. (A) DPP polarogram of 1.0×10^{-5} M thifensulfuron-methyl in pH 1.0–5.0 B–R buffer solution. (a) pH 1.0, (b) pH 2.0, (c) pH 3.0, (d) pH 4.0, and (e) pH 5.0. (B) DPP polarogram of 1.0×10^{-5} M thifensulfuron-methyl in pH 6.0–10.0 B–R buffer solution. (a) pH 6.0, (b) pH 7.0, (c) pH 8.0, (d) pH 9.0, and (e) pH 10.0.

at −0.830 V, −0.910 V/−0.920 V, −0.960 V and −1.400 V, −1.550 V/−1.590, and −1.730 V (*vs.* SCE), respectively.

As shown in figure 2, the peak potentials of the first and second peaks were shifted to more negative values with increasing pH. The first peak was found between pH 1.0 and 10.0, and its reduction potential was shifted to more negative values with increasing pH, showing a single linear segment with a slope of 93.7 mV in this pH range. The linear segments can be expressed by the following regression equations:

$$E_p(\text{mV}) = -93.7\,\text{pH} - 742.7(\text{pH } 1.0 - 10.0)(r = 0.993).$$

This behaviour indicated the involvement of protons in the rate-determination step, and proton transfer precedes the electron transfer. The peak current of the first peak was recorded between the pH 1.0 and 10.0, and showed a maximum at pH 3.0 (−1.010 V) corresponding to the $pK_a \pm 1$ of thifensulfuron-methyl ($pK_a = 4.0$) [24]. However, this peak decreased sharply with further increasing pH, diminished to about zero at pH 7.0, and then increased slightly up to pH 10.0 (figure 3). We found that the peak at pH 3.0 was well resolved and appeared to be suitable for analytical use, showing quantitative increments with the additions of standard thifensulfuron-methyl solution.

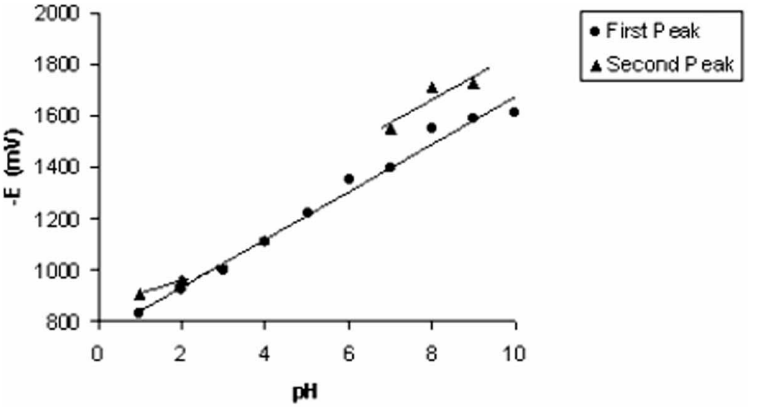


Figure 2. Dependence of the peak potential of the DP peak of 1.0×10^{-5} M thifensulfuron-methyl on pH.

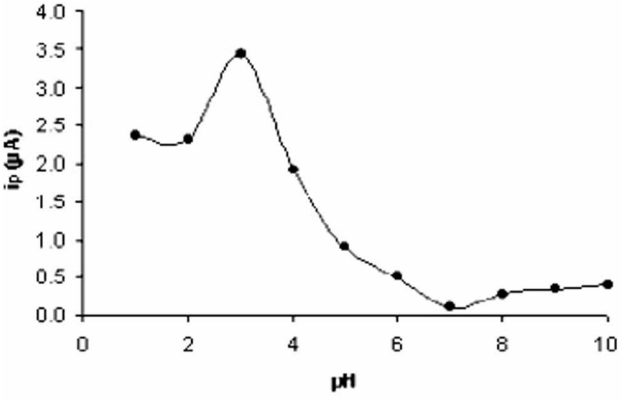


Figure 3. Dependence of the peak height of the DP peak of 1.0×10^{-5} M thifensulfuron-methyl on pH.

Since thifensulfuron-methyl and tribenuron both belong to sulphonylurea families showing large values of $\Delta E_p/\Delta$pH, and the model compound of tribenuron gave the same DP peak height as thifensulfuron-methyl at pH 3.0, the first peak for thifensulfuron-methyl should be due to the reduction of the C–N centre. Coulometric measurements for tribenuron under a controlled potential indicated that the electroactivity is due to the C–N bonds of the urea and reduction peak corresponding to the reduction of the C–N centre of the urea bridge via the $4e^-/4H^+$ [19] mechanism. On the other hand, we determined that while tribenuron has only one peak at pH 1.0–2.0, thifensulfuron-methyl has two peaks in this pH range. The second peak in more acidic buffer solutions could be attributed to thiophene moiety.

3.2 *Analytical curves in pure supporting electrolyte*

The optimum conditions for the analytical determination of the thifensulfuron-methyl compound by DPP were found to be pH 3.0 at a reduction potential of −1.010 V and

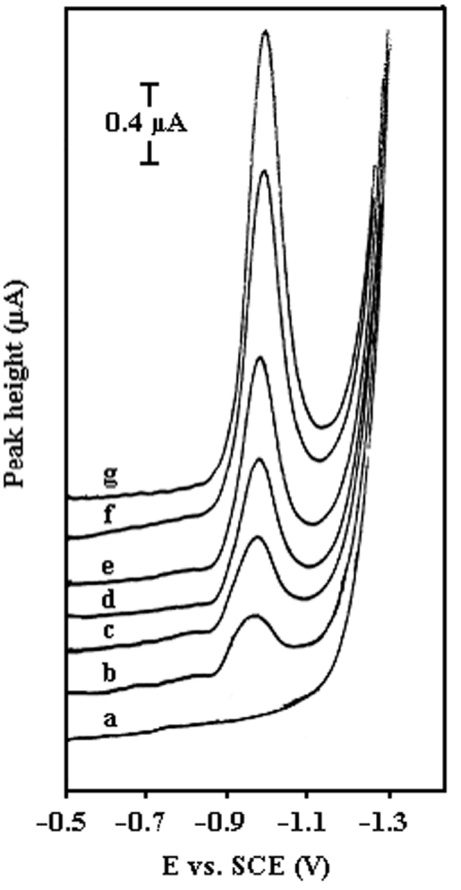


Figure 4. DPP responses for several concentrations of thifensulfuron-methyl in B–R buffer at pH 3.0. (a) 10.0 mL blank (pH 3.0 B–R buffer), (b) a + 50 µL 1.0×10^{-4} M thifensulfuron-methyl, (c) b + 50 µL 1.0×10^{-4} M thifensulfuron-methyl, (d) c + 10 µL 1.0×10^{-3} M thifensulfuron-methyl, (e) d + 10 µL 1.0×10^{-3} M, (f) e + 10 µL 1.0×10^{-3} M, and (g) f + 10 µL 1.0×10^{-3} M thifensulfuron-methyl.

50 mV pulse amplitude, with a 5 mV s^{-1} sweep rate and 1 s drop time, at 25 ± 3°C. The consecutive additions of thifensulfuron-methyl to the 0.04 M B–R buffer (pH 3.0) prepared with bi-distilled water gave the DPP response shown in figure 4. The peak currents obtained from the polarograms were linearly related to the pesticide concentration between 2×10^{-7} and 5×10^{-5} M, with the analytical equation given by:

$$I_p/\mu A = 5.15 \times 10^5 C(M) - 0.28 \; r = 0.997 (n = 10).$$

where I is the current intensity, and C is the molar concentration. The limit of detection (LOD) and limit of quantification (LOQ) were obtained as 1.05×10^{-7} M and 3.50×10^{-7} M, respectively, according to the relation $k \times SD/b$ (where $k = 3$ for LOD and $k = 10$ for LOQ, SD is the standard deviation of the blank, and b is the slope of the calibration curve). The straight line has a slope of 5.15×10^5 µA M^{-1}, an intercept of 0.28 µA, and a correlation coefficient of 0.997. The high sensitivity of differential pulse

polarography is accompanied by a very good repeatability. The precision from five repeated measurements of electrochemical signal of 5×10^{-7} M thifensulfuron-methyl solution for supporting electrolyte and soil was 5.40 and 9.50%, respectively, and 6.50% for orange juice of 1×10^{-6} M linearity (table 1). These values confirmed the sensitivity of the proposed method for the determination of thifensulfuron-methyl.

3.3 *Interference study*

The effect of the other commonly used pesticide tribenuron on thifensulfuron-methyl determination has been evaluated. The addition of equal amounts of tribenuron increased the thifensulfuron-methyl peak height by 100% at pH 3.0. This could be attributed to the overlapping of the peak current of tribenuron over thifensulfuron-methyl. Although no interference was observed with the addition of equal amounts of tribenuron at pH 10.0 (since tribenuron has no peak at pH 10.0). The selectivity could be achieved by changing pH when these two pesticides coexist in the same pesticide formulation, as in the case of Harmony® Extra. The interference effects of 2.0×10^{-5} M cations Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, and Cr^{3+} were investigated for the determination of 2.0×10^{-5} M thifensulfuron-methyl. Most of these ions are commonly present in soil or orange juice in trace amounts. Pb^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} exhibit cathodic reduction peaks at a more positive potential compared with the peak potential of thifensulfuron-methyl. According to the results, these metal ions exert no interference in the determination of thifensulfuron-methyl. As is well known, Mg^{2+} is an electroinactive species and has no interference effect. However, the polarographic reduction of Zn^{2+} showed a cathodic peak at about -0.93 V, very close to the thifensulfuron-methyl peak, and interfered with the investigated pesticide compound.

The interference effects of 2×10^{-5} M anions, such as $Cr_2O_7^{2-}$, I^-, SO_4^{2-}, F^-, Cl^-, and NO_3^-, were also investigated for the determination of 2×10^{-5} M thifensulfuron-methyl. Some of these ions, e.g. SO_4^{2-}, F^-, Cl^-, and NO_3^-, had no serious effect on the DPP current of thifensulfuron-methyl. In the presence of a relatively higher concentration of $Cr_2O_7^{2-}$ and I^-, the peak height changed to some extent (± 10). This could be explained by the oxidative properties of the $Cr_2O_7^{2-}$ and I^- ions.

3.4 *Determination of thifensulfuron-methyl in agrochemical products, soil, and orange juice*

Validation of the proposed cathodic differential pulse polarographic method for the assay of thifensulfuron-methyl in agricultural dosages, soil, and orange juice was carried out by estimating the range of linearity, LOD, LOQ, repeatibility, accuracy, and selectivity (table 1). The accuracy of the developed method was checked by calculating the recovery of a known amount of added thifensulfuron-methyl to the agrochemical pesticide formulation Harmony® Extra or soil and orange juice, and analysed via the optimized differential pulse polarographic procedure (tables 2 and 3).

Table 1. Regression data of the calibration lines for quantitative determination of thifensulfuron-methyl by DPP at pH 3.0 (B–R buffer).[a]

Parameters	Supporting electrolyte		Soil	Orange juice
	pH 3.0	pH 10.0		
Measured potential (V)	−1.010	−1.590	−1.030	−1.090
Linearity range (M)	2×10^{-7}–5.0×10^{-5}	9.9×10^{-7}–1.9×10^{-4}	3.0×10^{-7}–9.0×10^{-5}	1×10^{-6}–2.0×10^{-5}
Slope ($\mu A\, M^{-1}$)	5.15×10^{5}	2.39×10^{4}	1.26×10^{5}	1.34×10^{5}
Intercept (μA)	−0.28	0.0543	0.43	0.098
Correlation coefficient	0.997	0.999	0.998	0.997
LOD (M)	1.05×10^{-7}	6.60×10^{-7}	9.37×10^{-8}	4.1×10^{-7}
LOQ (M)	3.50×10^{-7}	2.20×10^{-6}	3.12×10^{-7}	1.37×10^{-6}
Repeatability of peak potential (RSD%)	0.359	0.62	0.42	0.68
Repeatability of peak current (RSD%)	5.40	5.40	9.50	6.50

[a]Each value is the mean of five experiments.

Table 2. Assay results from agrochemical pesticide formulation Harmony® Extra and mean recoveries in the spiked formulation.

	DPP	UV
Labelled (%)	50.00	50.00
Amount found (%)	49.55	50.94
RSD%	1.47	3.63
Bias (%)	−0.90	+1.88
Student's *t*-test	1.13 [2.45][a]	
Variance ratio *F*-test	6.24 [9.12][a]	
Added (mg)	77.48	193.70
Found (mg)[b]	75.79	198.64
Recovery (%)	97.82	102.6
RSD of recovery (%)	1.49	2.63
Bias (%)	−2.18	2.55

[a]Figures in parentheses are the tabulated values of t and F at the 95% confidence interval.
[b]Each value is the mean of five experiments.

Table 3. Application of the DPP and UV methods to the determination of thifensulfuron-methyl in spiked soil and orange juice sample.

	DPP		UV	
	Soil	Orange juice	Soil	Orange juice
Added (M)	1.05×10^{-5}	1.05×10^{-5}	5.0×10^{-5}	nd
Found (M)[a]	1.08×10^{-5}	1.07×10^{-5}	5.48×10^{-5}	nd
Recovery (%)	102.8	101.9	109.6	nd
RSD (%)	4.55	1.40	4.37	nd
Bias (%)	2.80	1.90	9.60	nd

[a]Each value is the mean of five experiments.

3.4.1 Agrochemical pesticide. There was no peak for the interfering species of tribenuron at pH 10.0. The thifensulfuron-methyl peak at this pH was high enough for its determination in agrochemical pesticide. Figure 5 shows the differential pulse polarograms corresponding to the determination of thifensulfuron-methyl concentration in Harmony® Extra. As can be seen in figure 5, well-defined polarographic peaks allowed pesticide determination without any interference effect of tribenuron. 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 analysed formulation of thifensulfuron-methyl. Each measurement was repeated five times. These data gave an average thifensulfuron-methyl content of $49.55 \pm 1.47\%$ for DPP, in close agreement with the 50.0% quoted by the manufacturer. The nominal content of the compound was calculated from the corresponding regression equation. The proposed polarographic method used for the analysis of Harmony® Extra needs no filtration of pesticide extract from undissolved recipients; only dilution of an aliquot from the supernatant layer with the pH 10.0 B–R buffer solution is required before each measurement.

The UV-visible spectrophotometric method was also applied to the formulation Harmony® Extra and soil to check the validity of the proposed method. Thifensulfuron-methyl absorption spectra exhibited three well-resolved maxima at 225, 245, and 286 nm. The maxima at 225 nm showed a better absorption and had

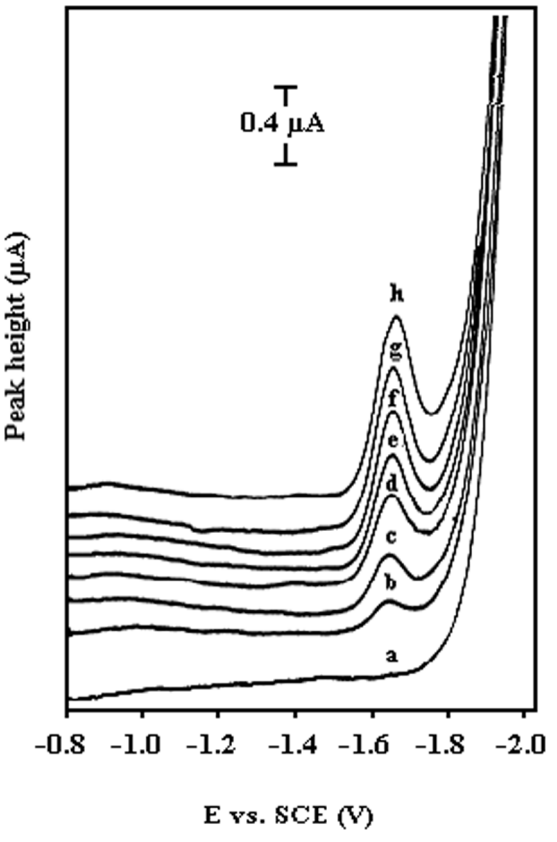


Figure 5. DP polarograms obtained for the determination of thifensulfuron-methyl in agrochemical pesticide (Harmony® Extra extract sample) at pH 10.0 B–R buffer. (a) 10 mL blank (pH 10.0 B–R buffer), (b) a + 100 µL 1.0×10^{-3} M thifensulfuron-methyl in Harmony® Extra extract, (c) b + 100 µL of 1.0×10^{-3} M thifensulfuron-methyl, (d) c + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, (e) d + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, (f) e + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, (g) f + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, and (h) g + 100 µL 1.0×10^{-3} M thifensulfuron-methyl.

a linear dependence on thifensulfuron-methyl concentration. The linear domain range was 5.0×10^{-6}–1.0×10^{-4} M for thifensulfuron-methyl, with a correlation coefficient of 0.999, and this can be expressed by the following regression equation:

$$A = 1.67 \times 10^{4} C(\mathrm{M}) - 0.0163,$$

where A is the absorbance of moxifloxacin at 225 nm, and C is the molar concentration.

The results obtained were compared statistically with the spectrophotometric (UV) method using Student's t-test and the variance ratio F-test (table 2). Statistical analysis of the results by both methods using these tests shows no significant differences in performance of the two methods regarding accuracy and precision, respectively. The experimental values of t and F at the 95% confidence level did not exceed the theoretical values, thus indicating good agreement with the spectrophotometric method. On the other hand, the main advantage of the proposed DPP method over the UV method is

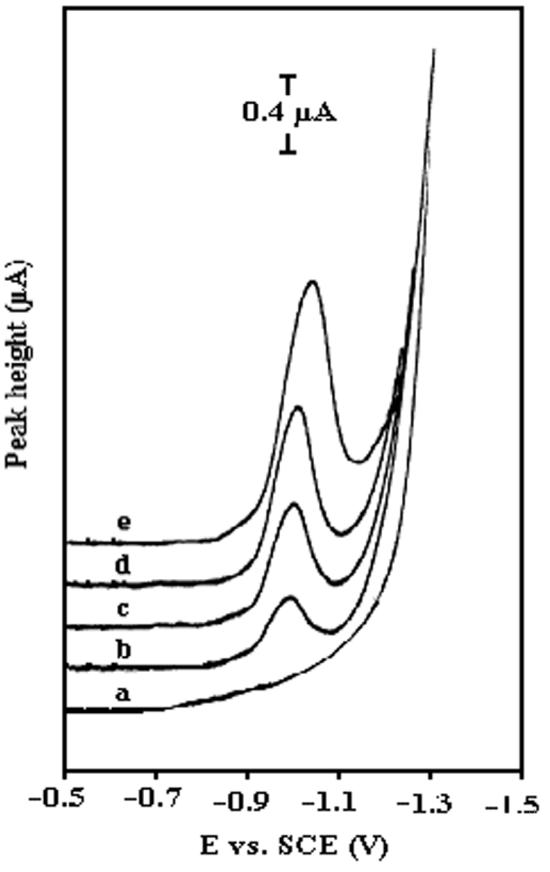


Figure 6. DP polarograms obtained for the determination of thifensulfuron-methyl in spiked soil at pH 3.0 B–R buffer. (a) 9.0 mL blank (pH 3.0 B–R buffer), (b) a + 1.0 mL 1.0×10^{-5} M thifensulfuron-methyl in soil extract, (c) b + 100 µL 1.0×10^{-4} M thifensulfuron-methyl, (d) c + 100 µL 1.0×10^{-4} M thifensulfuron-methyl, and (e) d + 100 µL 1.0×10^{-4} M.

that the DPP method offers a high sensitivity, low limit of determination, easy operation, and simple instrumentation.

3.4.2 Spiked soil and orange juice. The present optimized procedures were also successfully used to determine thifensulfuron-methyl spiked to soil and orange juice. The regression lines, calculated using the least-squares method for soil and orange juice, were:

$$I_p/\mu A = 1.26 \times 10^5 C(M) + 0.430 \ (r = 0.997) \text{ (for soil)}$$
$$I_p/\mu A = 1.34 \times 10^5 C(M) + 0.098 \ (r = 0.997) \text{ (for orange juice).}$$

In order to test the accuracy of the developed method, several aliquots of thifensulfuron-methyl standard solutions were added to soil and orange juice samples in different proportions. The recoveries were estimated by measuring the peak heights

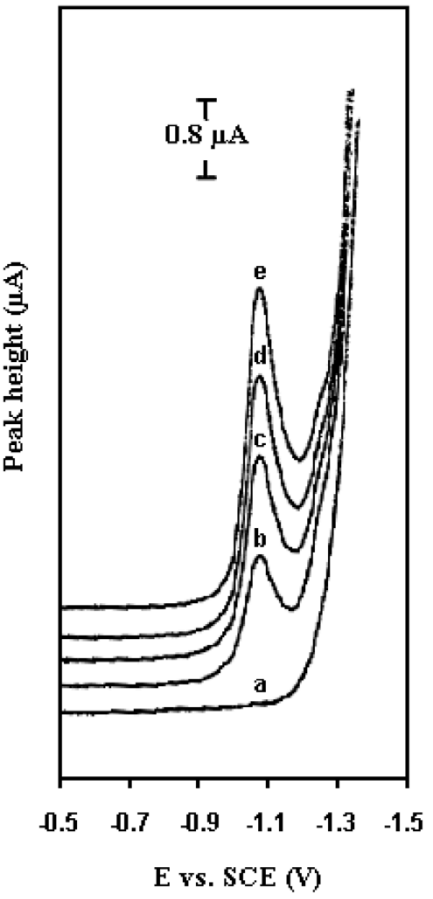


Figure 7. DP polarograms obtained for the determination of thifensulfuron-methyl in spiked orange juice at pH 3.0 with B–R buffer. (a) 9.0 mL blank (pH 3.0 B–R buffer), (b) a + 1.0 mL 1.0×10^{-4} M thifensulfuron-methyl in orange-juice extract, (c) b + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, (d) c + 100 µL 1.0×10^{-3} M thifensulfuron-methyl, and (e) d + 100 µL 1.0×10^{-3} M.

of extracted spiked soil or orange juice samples and comparing them with the peak heights obtained after standard additions of the same concentrations. Recoveries calculated from soil and orange juice samples spiked with 1.05×10^{-5} M are 102.8 and 101.9%, with relative standard deviations of 4.55 and 1.40%, respectively.

Figures 6 and 7 show differential pulse polarograms corresponding to the determination of thifensulfuron-methyl at selected concentrations in soil and orange juice, respectively. As can be seen, well-defined polarographic peaks were obtained in both samples. The results obtained for the determination of thifensulfuron-methyl in soil and orange samples are given in table 3. This table exhibits good recoveries for thifensulfuron-methyl determination that were obtained by differential pulse polarography for both samples as in the case of the spectrophotometric method. On the other hand, spectrophotometric determination could not be achieved for the determination of thifensulfuron-methyl in orange juice. This could be attributed basically to the vitamin C and citric acid.

4. Conclusion

The differential pulse polarographic method presented for the quantitative determination of thifensulfuron-methyl provides accurate determination in pesticide formulation, soil, and orange juice samples, and was found to be simple and highly sensitive. The main advantage of such a procedure is the possibility of determining the concentration of the active component directly from the pesticide formulation, without the need for any prior steps such as extraction, clean-up, or pre-concentration, which are tedious, time-consuming, and also polluting. The present method could possibly be applied for the determination of thifensulfuron-methyl in environmental samples as well as for quality-control laboratories.

References

[1] M.E. Beyer, H.M. Brown, M.J. Duffy. *Br. Crop Protect.*, **2**, 531 (1987).
[2] H.M. Brown. *Pestic. Sci.*, **29**, 263 (1990).
[3] A. Saba, F. Messina. *Food Qual. Prefer.*, **14**, 637 (2003).
[4] H.G.J. Mol, R.C.J. Van Dam, O.M. Steijer. *J. Chromatogr. A.*, **1015**, 119 (2003).
[5] E. Ballesteros, M.J. Parrado. *J. Chromatogr. A*, **1029**, 267 (2004).
[6] H.M. Brown, M.M. Joshi, A.T. Van, T.H. Carski, J.J. Dulka, M.C. Patrick, R.W. Reiser, R.S. Livingston, J. Doughty. *J. Agric. Food Chem.*, **45**, 955 (1997).
[7] D.F. Ollis, H. Al-Ekabi. *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam (1993).
[8] O. Legrini, E. Oliveros, A.M. Braun. *Chem. Rev.*, **93**, 671 (1993).
[9] F. Fresno, C. Guillard, J.M. Coronado, J.M. Chovelon, D. Tudela, J. Soria, J.R. Heffmann. *J. Photochem. Photobio. A*, **173**, 13 (2005).
[10] E. Vulliet, C. Emmelin, J.M. Chovelon, C. Guillard, J.M. Herrmann. *Appl. Catal. B Environ.*, **38**, 127 (2002).
[11] S.M. Andersen, P.B. Hertz, T. Holst, R. Bossi, C.S. Jacobsen. *Chemosphere*, **45**, 775 (2001).
[12] Q. Yan, S.J. Li, C.R. Zhan, T. Peng. *Chinese J. Anal. Chem.*, **32**, 1436 (2004).
[13] E. Ayano, H. Kanazawa, M. Ando, T. Nishimura. *Anal. Chim. Acta*, **507**, 211 (2004).
[14] J.B. Chao, J.F. Liu, M.J. Wen, J.M. Liu, Y.Q. Cai, G.B. Jiang. *J. Chromatogr. A*, **955**, 183 (2002).
[15] M.S. Ibrahim, K.M. Al-Magboul, M.M. Kamal. *Anal. Chim. Acta*, **432**, 22 (2001).
[16] M. Drevinek, V. Horak. *J. Electroanal. Chem.*, **423**, 83 (1997).
[17] W. Szczepaniak, B. Czyzowicz, M. Ren. *Anal. Chim. Acta*, **305**, 207 (1995).
[18] E.M. Garrido, C. Delerue-Matos, J.L.F.C. Lima, A.M.O. Brett. *Anal. Lett.*, **37**, 1755 (2004).
[19] C. Olmedo, L. Deban, M. Coca, M. Vega, F. Rosa. *Fresenius J. Anal. Chem.*, **357**, 962 (1997).
[20] B. Uslu, S.A. Özkan. *Electrochim. Acta*, **49**, 4321 (2004).
[21] S.A. Özkan, B. Uslu, P. Zuman. *Anal. Chim. Acta*, **501**, 227 (2004).
[22] S.A. Özkan, B. Uslu, Z. Senturk. *Electroanalysis*, **16**, 231 (2004).
[23] J.P. Cambon, J. Bastide. *J. Agric. Food Chem.*, **44**, 333 (1996).
[24] E.M. Beyer, M.J. Duffy, J.V. Hay, D.D. Schlueter. *Herbides Chemistry, Degradation and Mode of Action*, Vol. 5, Dekker, New York (1988).