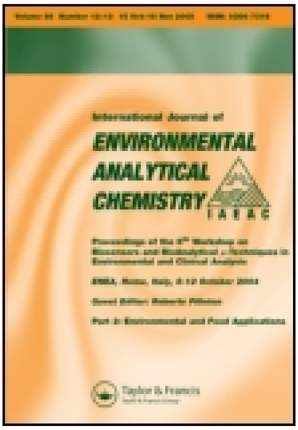


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

Square wave voltammetric determination of diafenthiuron and its application to water, soil and insecticide formulation

Recai İnam [a] & Funda Tekalp [a]

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

To cite this article: Recai İnam & Funda Tekalp (2012): Square wave voltammetric determination of diafenthiuron and its application to water, soil and insecticide formulation, International Journal of Environmental Analytical Chemistry, 92:1, 85-95

To link to this article: http://dx.doi.org/10.1080/03067319.2010.520126

Intern. J. Environ. Anal. Chem.
Vol. 92, No. 1, 15 January 2012, 85–95

Square wave voltammetric determination of diafenthiuron and its application to water, soil and insecticide formulation

Recai İnam* and Funda Tekalp

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

(*Received 10 March 2010; final version received 27 July 2010*)

A square wave cathodic stripping voltammetric (SWCSV) method has been developed for the determination of insecticide diafenthiuron. The procedure is based on controlled accumulation of the insecticide on a static hanging mercury drop electrode (SHMDE) at 0.00 mV (vs. Ag/AgCl) in Britton-Robinson buffer solution (pH 7.0). The insoluble mercury compound was reduced at $-510\,\mathrm{mV}$ during the cathodic potential scan. The peak currents were linearly related to insecticide concentration between 30.4 and $3200\,\mu\mathrm{g\,L^{-1}}$. The detection and quantification limit were $9.1\,\mu\mathrm{g\,L^{-1}}$ and $30.4\,\mu\mathrm{g\,L^{-1}}$, respectively. The proposed analytical procedure was applied to natural water and soil samples. The method was extended to direct determination of diafenthiuron in insecticide formulation Polo® 50 WP and average content of 50.3 ± 1.7 (m/m) at 90% confidence level, in close agreement with the 50.0% quoted by the manufacturer. HPLC comparison method indicated that accuracy was in agreement with that obtained by the proposed method.

Keywords: diafenthiuron; voltammetry; determination; insecticide formulation

1. Introduction

Pesticides are poisons designed to kill a variety of plants and animals such as insects (insecticides), weeds (herbicides), and mould or fungus (fungicides). Systemic or general insecticides are effective against a wide range of insects on fruits, vegetables and commercial crops. Diafenthiuron, 1-tert-Butyl-3-(2,6-diisopropyl-4-phenoxyphenyl) thiourea, is an insecticide and acaricide, whose structural formula is presented in Scheme 1.

It is an active agent against a wide range of sucking insects and some lepidopteron pests. The most important uses are the control of aphids and whiteflies in cotton, vegetable and other crops. Diafenthiuron is converted to the corresponding 1-*tert*-butyl-3-(2,6-di-isopropyl-4-phenoxyphenyl) carbodiimide which is probably responsible for its biological activity [1,2].

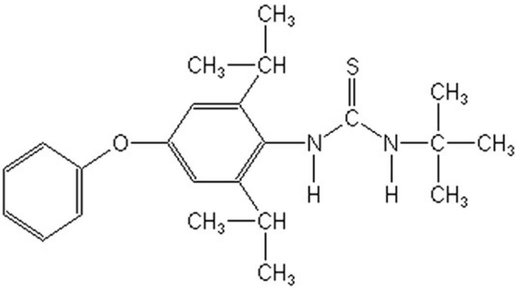
A wide range of analytical methods has been applied to the analysis of sulfonylurea or thiourea pesticides and most of them are based on chromatographic techniques [3–8]. While the use of electroanalytical techniques have also been suggested to analyse sulfonylurea pesticides [9–11], only a few methods are available for the electrochemical behaviour and determination of thiourea pesticides [12,13] and, to the best of our

---

*Corresponding author. Email: rinam@gazi.edu.tr

ISSN 0306–7319 print/ISSN 1029–0397 online

http://dx.doi.org/10.1080/03067319.2010.520126
http://www.tandfonline.com



Scheme 1. Structure of diafenthiuron.

knowledge, no publications dealing with the electroanalytical or voltammetric determination of diafenthiuron have appeared so far. Compared to chromatography, voltammetric techniques have several advantages such as low cost and possibility of analysis without the need of pre-treatments, as well as the short time required for the analysis.

The aim of the present work was to establish a new sensitive and selective square wave cathodic stripping voltammetric (SWCSV) method. Good recovery from real samples and commercial formula, and low relative standard deviations data, reflects the high accuracy and precision of the proposed SWS voltammetric method. Square wave stimulus offered the most favourable signal to noise characteristics and was used throughout because of better sensitivity as compared to linear scan or other electrochemical techniques. The selectivity of the proposed method for diafenthiuron was tested in the presence of relatively high concentrations of other pesticides and ions.

2. Experimental

2.1 *Reagents and solutions*

A stock solution of 400 µg L^{-1} diafenthiuron (with a purity of 99.7%) was prepared by dissolving diafenthiuron in 10.0 mL ethanol**.** Working solutions were prepared by diluting appropriate amount of this stock in ethanol. Salts used for supporting electrolyte, solvents and other reagents were of analytical reagent grade (Merck, Darmstandt, Germany). Britton-Robinson buffer (B-R buffer) solutions were prepared from a stock solution containing 0.04 M phosphoric, boric and acetic acids (Merck) by adding an appropriate amount of 2.0 M NaOH to obtain pH values ranging from 2 to 10.

2.2 *Apparatus*

The square wave voltammograms were obtained with a Bioanalytical Systems-epsilon potentiostat/galvanostat (BAS, West Lafayette, IN, USA) analyser coupled with a BAS-CGME (controlled growth mercury electrode) static mercury drop electrode stand. A three-electrode system was used, consisting of a platinum counter electrode, an Ag/AgCl (3 M NaCl) reference electrode and a static hanging mercury drop electrode (SHMDE) as a working electrode. All experiments were performed at room temperature. The HPLC system (Agilent 1100 HPLC system, Agilent Technologies, USA) consisted of a quaternary pump, a Rheodyne injector equipped with a 20 µL sample loop, 150 mm Zorbax Eclipse

XDB C18 5 μm column, and a model of L-7455 diode array and multiple wavelength UV–vis detector (200 nm) controlled by Agilent Chem. Station Software.

2.3 *Procedures*

The working electrode was placed in the voltammetric cell filled with 10 mL of a working electrolyte (8.0 mL B-R buffer solution and 2.0 mL ethanol) containing a known amount of diafenthiuron, after which the experimental and voltammetric parameters were studied. The solution was deoxygenated with a high purity of nitrogen (99.999%) for 300 s before recording the voltammogram. The selected accumulation potential ($E_{acc} = 0.0$ mV) was applied during the accumulation period ($t_{acc} = 220$ s) while the solution was kept under stirring and nitrogen atmosphere. Stirring was stopped and after 15 s equilibrating time, a potential scan was performed from the accumulation potential of 0.0 mV to −2000 mV by using square wave voltammetry (Osteryoung version). The square wave parameters used were a frequency (f) of 350 Hz, pulse amplitude (ΔE) of −200 mV, and staircase step (ΔE_s) of 15 mV. The quantifications were performed by the standard addition method, from the SW peak obtained at −510 mV versus Ag/AgCl (pH 7.0; 20 ± 2°C).

3. Results and discussion

3.1 *Cyclic voltammetry*

The cyclic voltammetric curve recorded by the potential scan on SHMDE within the potential range of 0.00 to −1700 mV (pH 7.0, scan rate = 250 mV s^{-1}), exhibited a cathodic peak at −640 mV (Figure 1). No anodic peak appeared on the reverse scans, which confirms the non-reversibility of the electrode process. On the other hand, a differential pulse polarogram obtained for diafenthiuron on dropping mercury elelectrode (DME) did not give any response. This phenomenon is attributed to the formation of the insoluble complexes with stationary mercury electrode. A potential scan rate was carried out to assess whether the processes diffusion or adsorption controlled. Using the concentration of 40 μg mL^{-1} diafenthiuron in B-R buffer at pH 7.0, the voltammetric peak currents were recorded as the scan rate over the range of 250 mVs^{-1} and 8000 mVs^{-1}. As a function of the scan rate, a plot of the logarithm of the peak current ($\log I_p$) versus the logarithm of the scan rate ($\log v$) gave a straight line with a slope of 0.54, close to the theoretical value of 0.5, which is expected for an ideal diffusion controlled reaction of solution species [14]. When the scan rate increased the peak potential (E_p) shifted in the negative direction, and the corresponding equation for E_p *vs.* $\log v$ plot confirmed the irreversibility of the electrode process.

3.2 *Square wave cathodic stripping voltammetry*

In the preliminary work, the polarographic investigation of a 4.0 μg mL^{-1} diafenthiuron showed no peak on dropping mercury electrode (DME) over the pH range 1.0–8.0 in Britton-Robinson (BR) buffer solution. However, it is well known that thiourea and its derivatives form insoluble mercury salts during the electro-deposition step, which can be determined by cathodic stripping voltammetry (CSV) at a static hanging mercury drop electrode (SHMDE) [12,15,16]. Accordingly, an accumulation potential of $E_{acc} = 0.0$ mV

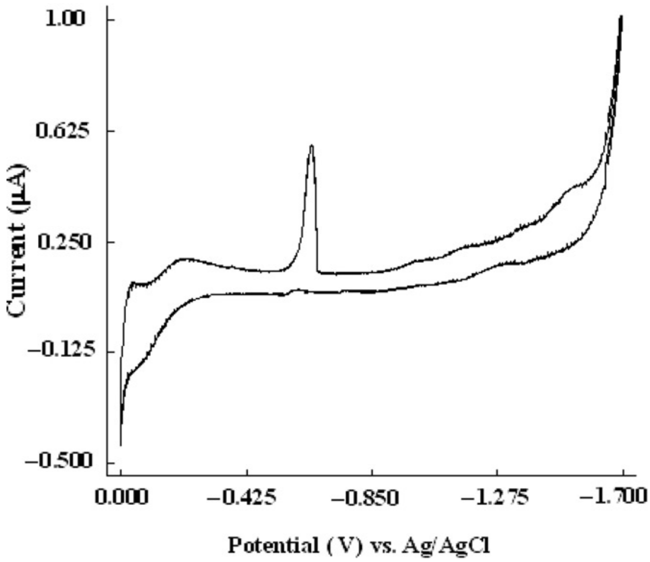
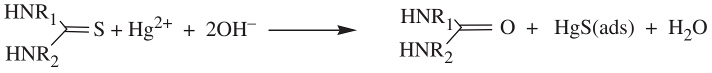
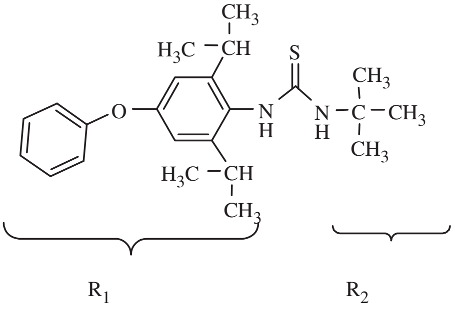


Figure 1. Cyclic voltammogram of $40\,\mu g\,mL^{-1}$ diafenthiuron at pH 7.0 with Britton-Robinson buffer, scan rate $= 250\,mV\,s^{-1}$.

was applied for the electro-deposition of $40.0\,\mu g\,L^{-1}$ on SHMDE electrode during the accumulation period, $t_{acc} = 220\,s$. The SWS voltammetric curve obtained for this insecticide gives rise to a single peak at about −510 mV versus Ag/AgCl at pH 7.0. This process occurs according to the following reaction and involves mercury ions produced by the anodic reaction of the mercury electrode:



$$(HNR_1)(HNR_2)C{=}S + Hg^{2+} + 2OH^- \longrightarrow (HNR_1)(HNR_2)C{=}O + HgS(ads) + H_2O$$



Mercury ion reduction in HgS is responsible for the occurrence of peak −510 mV versus Ag/AgCl at pH 7.0. This view agrees with that of Stara and Kopanica [16] who proved that HgS results as the product of the deposition step in an alkaline medium, whereas the thiourea derivative is stable enough and is included in a mercury complex at $pH < 7$ only. The influence of pH on peak current of diafenthiuron was investigated in the

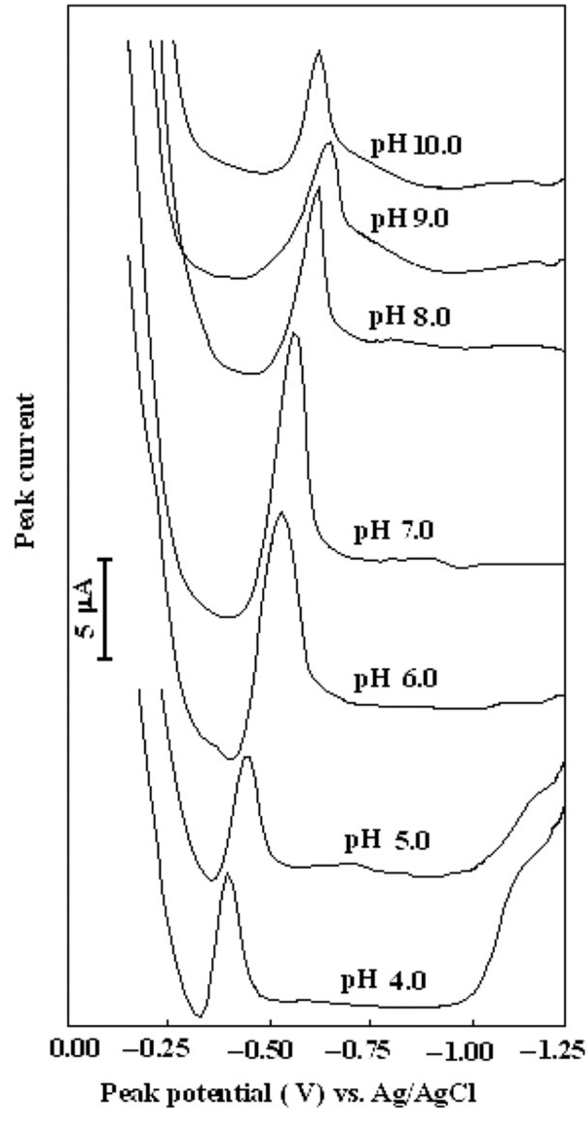


Figure 2. Effect of pH for the square wave voltammetric determination of 40 μg L^{-1} diafenthiuron. ($E_{acc} = 0.00$ mV, $t_{acc} = 220$ s, $\Delta E_s = 15$ mV, $f = 350$ Hz, $\Delta E = -200$ mV).

pH range of 4–10 (Figure 2). In acidic solutions at $pH \leq 3$, diafenthiuron had no peak. When the pH value exceeded the 3.0 the peak current began to appear and exist until the pH 10. For pH values higher than 10.0, no peak was observed. Regarding the relation *pH* vs. *Ip* a maximum current intensity was obtained at a pH value of 7.0. The cathodic response obtained at pH 7.0 was well defined, had a peak potential at −510 mV and was selected for further studies. The peak potential, E_p, shifted towards more negative values as the pH increased. The value $\Delta E_p/\Delta pH$ over the pH range studied was 52.8 mV pH^{-1}, indicating that the electrode process involves H^+ coupled with the reduction process.

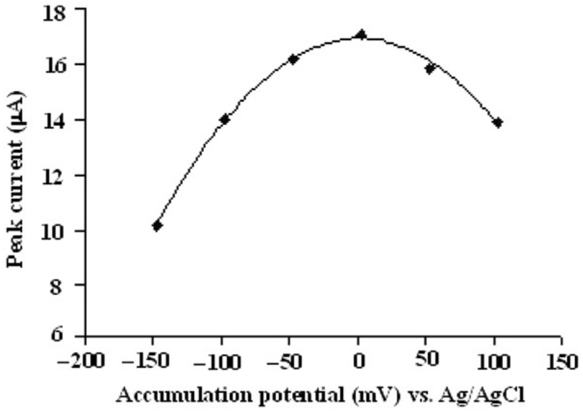


Figure 3. Influence of the accumulation potential (E_{acc}) on peak current (I_p) of 40 μg L^{-1} diafenthiuron (pH 7.0).

Electrode reaction mechanism for the diafenthiuron determination by SWCSV was probably the formation of insoluble mercury compound (HgS) during the accumulation step, which was subsequently stripped out on scanning the potential in a cathodic direction.

$$H_gS(ads) + 2e^- + 2H^+ \longrightarrow H_g(l) + H_2S$$

The mercury ion reduction in the insoluble compounds was then responsible for the occurrence of the voltammetric stripping peaks. The square wave stimulus offered the most favourable signal to noise characteristics and was used throughout because of better sensitivity as compared to linear scan or other electrochemical techniques.

The first parameter to be optimised for the determination of diafenthiuron employing SWSV was accumulation potential (E_{acc}) and time (t_{acc}). For 40 μg L^{-1} diafenthiuron, the dependence of the stripping peak current on the accumulation potential was studied over the range +100 to −150 mV and highest peak intensity was obtained for an E_{acc} of 0.00 mV (Figure 3). The dependence of peak current on accumulation time at 20 μg L^{-1} of diafenthiuron was also studied. A gradual increase in peak current intensity was observed between 100 and 220 s starting to decrease in a roughly linear manner, probably due to the saturation of the mercury electrode at a higher electro-deposition time. The optimal accumulation potential and time of 0.00 mV and 220 s were chosen respectively, because the well-defined peak shape and maximum developed peak current were achieved. Optimum conditions selected for square wave frequency, step potential (ΔE_s) and the pulse amplitude (ΔE) were 350 Hz, 15 mV and 200 mV, respectively.

3.2.1 *Analytical methodology*

Using the obtained optimised parameters, a standard addition curve was obtained for diafenthiuron in an electrolyte of pH 7.0 B-R buffer solution. Aliquots from the stock solution were consecutively added to the voltammetric cell (Figure 4). The peak currents obtained from voltammograms were linearly related to pesticide concentration between

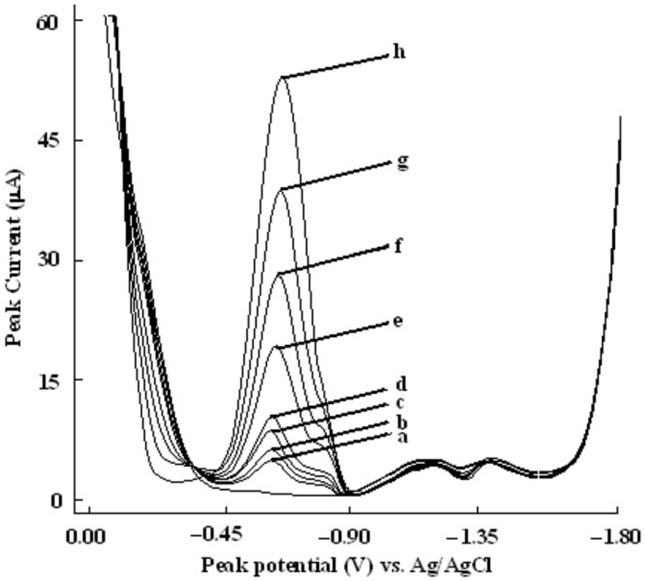


Figure 4. Square wave stripping voltammograms for linear calibration curve in pH 7.0 B-R buffer solution (a) 32 μg L^{-1} (b) 40 μg L^{-1} (c) 200 μg L^{-1} (d) 400 μg L^{-1} (e) 800 μg L^{-1} (f) 1200 μg L^{-1} (g) 1600 μg L^{-1} (h) 3200 μg L^{-1}. ($E_{acc} = 0.00$ mV, $t_{acc} = 220$ s, $\Delta E_s = 15$ mV, $f = 350$ Hz, $\Delta E = -200$ mV).

30.4 and 3200 μg L^{-1}. The detection limit (LOD) and quantification limit (LOQ) of the procedures were calculated according to the 3s/m and 10s/m criterions, respectively, where *s* is the standard deviation of the peak currents for the fortified blank solution containing 20 μg L^{-1} diafenthiuron (12 runs) and *m* is the slope of related calibration graph [17]. The obtained values of LOD and LOQ were 9.1 μg L^{-1} and 30.4 μg L^{-1}, respectively. The high values of the slope (1.58×10^{-2} μA $\mu g^{-1} L^{-1}$) and correlation coefficient ($r = 0.9924$) reflected the sensitivity of the proposed method. The reproducibility of the proposed methodology was determined from the 12 different measurements of the 20 μg L^{-1} diafenthiuron and the relative standard deviation was obtained as 2.14%.

3.3 *Interference effect*

The performance of the voltammetric determination of diafenthiuron was evaluated in presence of some potential-interfering pesticides, such as alanycarb, cyclosulfamuron and thifensulfuron). These pesticides are selected by considering some criteria such as their common usage and electroactivity. In the preliminary experiments, 40 μg L^{-1} alanycarb and thifensulfuron did not give any peak response under the same conditions. On the other hand, cyclosulfomuron generated a cathodic peak at −1300 mV, but did not seriously interfere with the analyte signal at −510 mV. As shown in Figure 5, 40 μg L^{-1} diafenthiuron in the presence of 40 μg L^{-1} alanycarb, cyclosulfomuron and thifensulfuron mixture was simultaneously determined as 39.0 ± 2.4 with a recovery of 97.5% ($n = 4$, 90% confidence level).

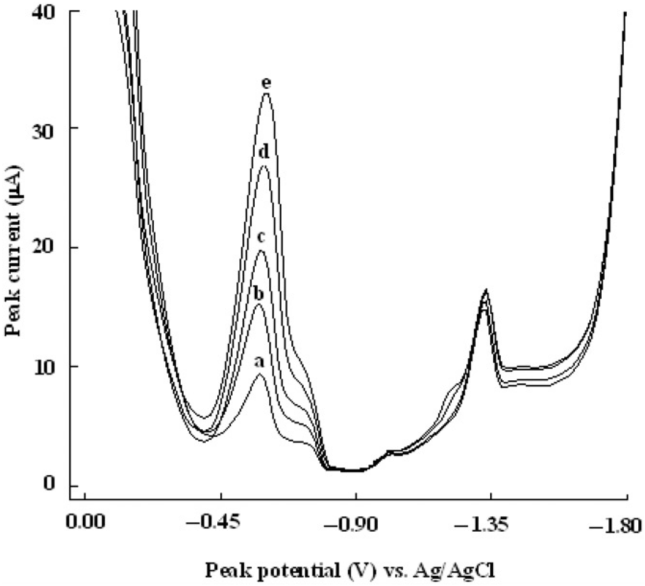


Figure 5. Determination of 40 µg L^{-1} diafenthiuron (target molecule) in the presence of some potential-interfering pesticides (a) pH 7.0 BR buffer solution + 40 µg L^{-1} diafenthiuron + 40 µg L^{-1} alanycarb + 40 µg L^{-1} cyclosulfamuron; (b) 80 µg L^{-1} diafenthiuron (c) 120 µg L^{-1} diafenthiuron (d) 160 µg L^{-1} diafenthiuron (e) 200 µg L^{-1} diafenthiuron. ($E_{acc} = 0.00$ mV, $t_{acc} = 220$ s, $\Delta E_s = 15$ mV, $f = 350$ Hz, $\Delta E = -200$ mV).

The selectivity of the proposed method for diafenthiuron was tested in the presence of relatively high concentrations of Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, K^+, Na^+ CN^-, NO_3^- and Cl^-. These co-existing ions are chosen mostly electro-active (produce a peak current), e.g. Ni^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+}. $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, NaCl and KCN salts were used for the preparation of co-existing ions. The co-existing ions were taken as 100-fold excess of diafenthiuron by considering high tolerance limit. The recoveries of 200 µg L^{-1} diafenthiuron in the presence of 100-fold excess of Ni^{2+}, Co^{2+}, Cd^{2+}, Pb^{2+}, Na^+ and CN^- were 103.7 ± 8.2, 101.0 ± 3.2, 114.6 ± 1.5, 99.3 ± 0.9, 96.4 ± 9.6 and 93.5 ± 1.4% (n = 3 at 90% confidence interval), respectively.

3.4 *Applications*

Tap water samples sprinkled with 40 to 400 µg L^{-1} diafenthiuron were placed in a temperature controlled water-bath (shaker) at 20°C and shaken for 2 h. From the supernatant, aliquots were transferred to the voltammetric cell and pesticide determination was performed from the peak current generated at −525 mV vs. Ag/AgCl. The peak displacement of −510 mV to −525 mV could be attributed to pH effect or can also be an effect of humic substances that could interact with the pesticide causing a local change of pH. For soil analysis, 2.0 g of ground and dried soil samples were spiked with a 10.0 mL stock diafenthiuron solution at concentration levels of 200–2000 µg kg^{-1}. After homogenising the samples, they were placed in a temperature controlled water-bath (shaker) at

Table 1. The values obtained for the determination of spiked diafenthiuron at some selected concentrations in tap water and soil samples.

Added		Found* $\overline{X} \pm \frac{t.s}{\sqrt{n}}$		Recovery* (%) $\overline{X} \pm \frac{t.s}{\sqrt{n}}$	
Tap water ($\mu g\,L^{-1}$)	Soil ($\mu g\,kg^{-1}$)	Tap water ($\mu g\,L^{-1}$)	Soil ($\mu g\,kg^{-1}$)	Tap water	Soil
–	–	N.D.	N.D.	N.D.	N.D.
40	200	41 ± 3	200 ± 20	103 ± 7	99 ± 8
200	1000	207 ± 8	995 ± 75	104 ± 4	99 ± 7
400	2000	420 ± 20	1935 ± 105	105 ± 5	97 ± 1

*$t = 90\%$ confidence level, $n = 3$. N.D. not determined.

20°C and shaken for 2 h, centrifuged for 10 min at 3000 rpm. From the supernatant, aliquots were transferred to the voltammetric cell and pesticide determination was performed from the peak current generated at −450 mV *vs.* Ag/AgCl. The same procedure was applied for pesticide free samples and no interferences were observed in a blank extracted from the soil or water. The mean results for three determinations were $198 \pm 12.5\,\mu g\,kg^{-1}$, which is very close to the diafenthiuron added soil ($200\,\mu g\,kg^{-1}$), with a recovery of 99.0%. The results for the recoveries of various spiked concentrations are presented in Table 1. The sufficiently good recoveries and low relative standard deviations (RSD) data reflects the high accuracy and precision of the proposed SWCS voltammetric method.

Insecticide formulation Polo® 50 WP (50% diafenthiuron by mass) was provided by Syngenta Crop Protection AG (Basel, Switzerland). Pesticide formulation equivalent to $400\,\mu g\,L^{-1}$ diafenthiuron was accurately prepared in a 10.0 mL of ethanol solution, and sonicated 5 min. A quantity of 10 μL of an aliquot of this clear supernatant liquor was added to 10.0 mL of the pH 7.0 B-R buffer solution containing 2.0 mL ethanol in the electrochemical cell and peak responses were measured at −510 mV under optimised conditions. The diafenthiuron in insecticide formulation was analysed, by the standard addition method. These data gave an average diafenthiuron content of 50.1 ± 2.6 ($n = 4$)% at 90% confidence level, in close agreement with the 50% quoted by the manufacturer. The results obtained were compared with an HPLC method. The method involves the use of acetonitrile / H_2O (90:10, (v/v) % as the mobile phase and 150 mm Zorbax Eclipse XDB C18 (5 μm particle size) column. Diafenthiuron was determined by HPLC using diode array and multiple wavelength UV–vis detectors at 200 nm. The diafenthiuron content in the Polo® 50 WP (50% diafenthiuron by mass) 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 2). 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 diafenthiuron analysis of commercial formulations.

Table 2. Assay results from the insecticide formulation Polo® 50 WP.

	SWSV	HPLC
Labeled claim (% m/m)	50.0	50
Amount found (% m/m)	50.3	49.8
R.S.D. (%)	1.7	0.6
Relative error (%)	0.7	0.4
Student's *t*-test	0.61* [2.65]	
Variance ratio *F*-test	8.62* [9.28]	

*The figures in parenthesis are the tabulated values of *t* and *F* at 95% confidence level ($n = 5$) for SWSV and 4 for HPLC.

According to the Japan Food Chemical Research Foundation, maximum residue limit (MRLs) values were presented as 0.02 ppm ($\approx$20 μg kg^{-1}) for a wide range of food, e.g. wheat, potatoes, cabbages, onions, melons, lemons, etc. [18]. Accordingly, the obtained values of LOD and LOQ (9.1 μg L^{-1} and 30.4 μg L^{-1}) and determination of 40 μg L^{-1} diafenthiuron in real samples such as water, soil extract and commercial formulation reflects adequate sensitivity and applicability of the method in real samples.

4. Conclusion

The square wave cathodic stripping voltammetric method developed was found applicable for the rapid determination of diafenthiuron insecticide in commercial formulation and in some natural samples. The influences of some pesticides and various ions as potentially interfering were investigated. The main advantages of the new method are higher sensitivity and less influence of the matrices effect. When compared to chromatography, the proposed voltammetric method has several advantages, i.e. their low cost, lower pollution and the possibility of analysis without extraction, or pre-concentration, as well as the short time required for analysis. The results obtained by the proposed method were in good agreement with those obtained by the HPLC method.

References

[1] H.A. Kadir and C.O. Knowles, J. Econ. Entomol. **84**, 780 (1991).

[2] F.J. Ruder and H. Kayser, Pestic. Biochem. Phys. **46**, 96 (1993).

[3] P. Degelmann, S. Egger, H. Jurling, J. Muller, R. Niessner, and D. Knopp, J. Agr. Food Chem. **54**, 2003 (2006).

[4] E.G. Cotterill, Pest. Sci. **34**, 291 (1992).

[5] R. Carabias-Martinez, E. Rodriguez-Gonzalo, E. Herrero-Hernandez, and J. Hernandez-Mendez, Anal. Chim. Acta **517**, 71 (2004).

[6] Q. Yan, S.J. Li, C.R. Zhan, and T. Peng, Anal. Chem. **32**, 1436 (2004).

[7] N. Wang and W.L. Budde, Anal. Chem. **73**, 997 (2001).

[8] L. Debbarh and N. Moore, J. Anal. Toxicol. **26**, 216 (2002).

[9] R. İnam, E.Z. Gülerman, and N. Uncu, Int. J. Environ. Anal. Chem. **86**, 1135 (2006).

[10] C. Olmedo, L. Deban, M. Coca, M. Vega, and F. delaRosa, J. Anal. Chem. **357**, 962 (1997).

[11] T. Sarıgül and R. İnam, Bioelectrochem. **75**, 55 (2009).

[12] M.R. Smyth and J.G. Osteryoung, Anal. Chem. **49**, 2310 (1977).
[13] F. Manea, C. Radovan, and J. Schoonman, J. Appl. Electrochem. **36**, 1075 (2006).
[14] E. Laviron, L. Roullier, and C. Degrand, J. Electroanal. Chem. **112**, 11 (1980).
[15] M. Fedorenko, O. Manousek, and P. Zuman, Chem. Listy **49**, 1494 (1953).
[16] V. Stara and M. Kopanica, Anal. Chim. Acta **159**, 105 (1984).
[17] L.A. Currie, Anal. Chim. Acta **391**, 103 (1999).
[18] The Japan Food Chemical Research Foundation**,** Table of MRLs for agricultural chemicals, diafenthiuron, <http://www.ffcr.or.jp/>.