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# Determination of Diethofencarb (Isopropyl 3,4-Diethoxyphenylcarbamate) by Square Wave Voltammetry Using Multiwall Carbon Nanotube Paste Electrode

Nur AKBAŞ and Recai İNAM\*

*Gazi University, Faculty of Science, Department of Chemistry, 06500 Ankara, Turkey*

## Abstract

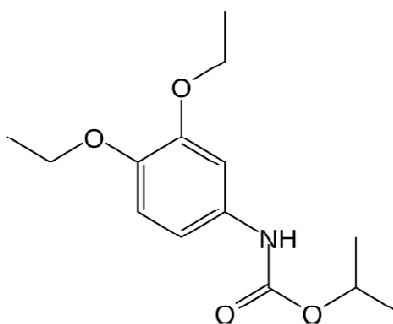
Diethofencarb fungicide has been studied by square wave voltammetry (SWV) on multi wall carbon nanotube paste electrode (MWCNTPE). The peak potentials have been shifted to more negative direction with increasing pH, showing us a maximum peak response at + 861 mV (vs.Ag/AgCl) and pH 2.0. Operational parameters affecting sensitivity and selectivity such as accumulation potential ( $E_{acc}$ ), accumulation time ( $t_{acc}$ ), frequency ( $f$ ) and pulse amplitude have been optimized. The constructed calibration curve was linear within the concentration range of  $2.50 \mu\text{g mL}^{-1}$  and  $30.5 \mu\text{g mL}^{-1}$ . The calculated limit of detection (LOD) and limit of quantification (LOQ) values were  $0.77 \mu\text{g/mL}$  and  $2.57 \mu\text{g/mL}$ , respectively. Its determination were realized in the presence various fungicides to put forth the selectivity, accuracy and applicability of the recommended method. The spiked tomato juice samples with  $2.50 - 7.50 \mu\text{g mL}^{-1}$  diethofencarb were subjected to the proposed method and recoveries over 97% and relative standard deviations less than 3.8% reflected a high degree of accuracy and precision.

**Keywords:** Diethofencarb; Fungicide; Determination; Voltammetry; Carbon nanotube paste electrode.

\* Corresponding author. Tel.: +90 312 202 11 25; Fax: +90 312 212 22 79; E-mail address: rinam@gazi.edu.tr ( R. İnam)

## 1. Introduction

Diethofencarb (isopropyl 3,4-diethoxyphenylcarbamate, DFC) is a fungicide and derivative of N-phenylcarbamate presenting potent effects to cope with several fungal species, particularly *Botrytis spp.*, *Cercospora spp.*, and *Venturia spp.*, which are resistant to benzimidazole fungicides [1]. The structural formula of diethofencarb is shown in Scheme 1.



**Scheme 1** Structure of diethofencarb

Diethofencarb is one of the most widely used carbamate pesticide for fruit and vegetable cultivation without harmful effects of various fungus species mentioned above, and therefore, to ensure the safety of our food supplies, it is necessary to develop fast, simple, accurate and sensitive analytical methods for its quantitation. The limit of detection obtained in this method (0.77  $\mu\text{g/mL}$ ) is compatible with the lower maximum recommended limits (MRLs) of apples, pears, wine grapes and tomatoes (0.8, 0.8, 0.9 and 0.7 mg/kg) established by the European Food Safety Authority (EFSA)[2]. Up to now, chromatographic methods were largely used for the determination of diethofencarb, but well, these methods are tedious, time-consuming, and often require large volumes of toxic organic solvents. In the previous studies octadecyl modified graphene was used as a novel adsorbent for the isolation of metolcarb, carbaryl, isoprocarb, and diethofencarb from vegetables prior to determination by high-performance liquid chromatography [3]. In the study performed by Zho et al. graphene's powerful adsorptive properties together with  $\text{TiO}_2$  nanotube were used for the separation and determination of carbamate pesticides, including metolcarb, carbaryl, isoprocarb, and diethofencarb using high performance liquid chromatography [4]. Ionic liquid-based ultrasound-assisted emulsification microextraction (IL-USAEME) combined with high performance liquid chromatography has been reported for the determination of azoxystrobin, diethofencarb, pyrimethanil and kresoxim-methyl in water samples [5]. For the determination of diethofencarb and pyrimethanil in aqueous samples, a dispersive liquid-liquid

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3 microextraction method was developed and limits of detection for diethofencarb and  
4 pyrimethanil were 0.24 and 0.09  $\mu\text{L}^{-1}$ , respectively [6].  
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7 Despite the use of voltammetric methods for the determination of carbamate pesticides in  
8 general [7-12], no work is available for diethofencarb in this regard. To our knowledge, this is  
9 the first voltammetric report for determination of diethofencarb using multiwall carbon nano  
10 tube paste electrode (MWCNTPE). The unique characteristics of carbon nanotubes such as  
11 electrical conductivity, mechanical strength, and a wide viable potential range make them  
12 reasonably attractive for constructing chemical sensors [13-17]. Furthermore, carbon  
13 nanotubes have some advantages with respect to electroanalytical chemistry, for instance,  
14 small size with large surface area, high sensitivity, rapid response, and enhanced electron  
15 transfer when used as electrodes in electrochemistry.  
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22 Finally, the objective of this study is to formulate a carbon paste electrode using multiwall  
23 nanotube powder and determine trace amounts of diethofencarb with lower cost and less time  
24 consumption.  
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## 28 **2. Experimental**

### 29 **2.1. Instrumentation**

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32 Electrochemical measurements were performed on a Bioanalytical Systems-Epsilon  
33 potentiostat/galvanostat (BAS, Epilson) analyzer connected with a BAS C-3 solid electrode  
34 cell stand. BAS MF-2010 model carbon nanotube paste electrode ( $\text{Ø}=3$  mm,  $A=0.071$  cm<sup>2</sup>)  
35 was used as a working electrode, a platinum wire (BASMW1032) as the counter electrode,  
36 and an Ag/AgCl (3 mol L<sup>-1</sup> KCl) was used as a reference electrode. pH measurements were  
37 performed by a Hanna pH meter with combined glass electrode. All experiments were  
38 performed under room conditions.  
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### 46 **2.2. Reagents**

47 Supporting electrolytes with a pH 1 and 2 were prepared using H<sub>2</sub>SO<sub>4</sub>. The following 0.04 M  
48 H<sub>3</sub>BO<sub>3</sub>, 0.04 M H<sub>3</sub>PO<sub>4</sub> and 0.04M CH<sub>3</sub>COOH were used to prepare Britton–Robinson buffer  
49 (BR buffer) solutions extending from pH 3.0 to 10.0. All chemicals were provided from  
50 Merck, Darmstadt, Germany. MWCNT powder (mesh size, -270, <53  $\mu\text{m}$ ) was obtained from  
51 Merck. Diethofencarb stock solution was prepared freshly by dissolving 5.0 mg  
52 Diethofencarb(C<sub>14</sub>H<sub>21</sub>O<sub>4</sub>; Mwt: 267.32 g/mol) in 10.0 mL solvent consisting of 50% acetone  
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and 50% distilled water and kept in refrigerator to avoid possible photo or thermal decomposition. Dilute solutions were prepared freshly by distilled water prior to experiments.

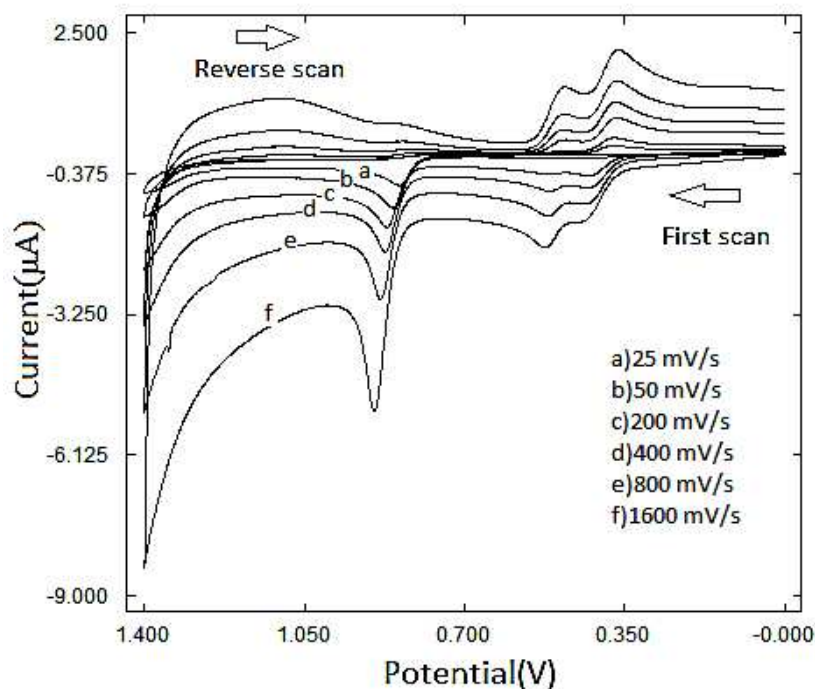
### 2.3. Preparation of the multi wall carbon nanotube paste electrode (MWCNTPE)

MWCNT and mineral oil were mixed with 70% and 30 % mass percentages, respectively and the homogenized paste was inserted in a plastic syringe needle using a 3-mm diameter copper wire (BAS MF 2010). The prepared paste in the electrode surface was smoothed with a spatula. Then, a few cycles of cyclic voltammetric procedure was applied for the surface treatment before recording of voltammograms for the fungicide molecule.

## 3. Results and Discussion

### 3.1. Cyclic voltammetry

In order to elucidate the electro-activity of the diethofencarb fungicide on the MWCNTPE, cyclic voltammetric experiments were primarily conducted. Diethofencarb gave a single anodic wave at about + 860 mV in 0.01 M sulphuric acid solution in the first scan toward anodic direction and none of the cathodic peak was observed in the subsequent second or reverse scan(**Fig.1**).



**Figure 1.** Cyclic voltammograms obtained for 5  $\mu\text{g mL}^{-1}$  diethofencarb at some selected scan rates within 25 and 1600  $\text{mV s}^{-1}$ .

Cyclic voltammetric measurements recorded with 5  $\mu\text{g mL}^{-1}$  diethofencarb in 0.01 M  $\text{H}_2\text{SO}_4$  solution showed a non-reversible nature of the peak at + 860 mV on MWCNTP electrode in the range of scan rates comprised between 25 and 1600  $\text{mV s}^{-1}$ . The influence of the potential scan rate within 25 and 1600  $\text{mV s}^{-1}$  on the peak potential and the peak current of diethofencarb were evaluated to assess whether the processes on MWCNTP electrode seem to be under diffusion or adsorption controlled. The linear increments in the oxidation peak intensity with the logarithm of the scan rate ( $\log v$ ) having a slope of 0.411 (correlation coefficient 0.986), evinced the diffusion control process.

$$\log i_p (\mu\text{A}) = 0.411 \log v (\text{mVs}^{-1}) - 0.817 \quad r = 0.986$$

This value is very close to the theoretical one of 0.5 which has been accepted for an ideal diffusion-controlled electrode process. The increments of scan rates from 25.0 to 1600  $\text{mVs}^{-1}$  caused the peak potentials to shift linearly in the positive way.

$$E(\text{mV}) = 0.0350 (\text{mV/ mVs}^{-1}) v (\text{mVs}^{-1}) + 843.3(\text{mV})$$

( scan rate: 25 – 1600  $\text{mVs}^{-1}$ )

A positive shift of + 60 mV in the peak potentials upon the scan rate treatments within 25 and 1600  $\text{mV s}^{-1}$  together with a plot of  $\log$  of peak intensity versus  $\log$  of scan rate with a slope of 0.411 confirmed both irreversibility and diffusion nature of the electrode process, respectively.

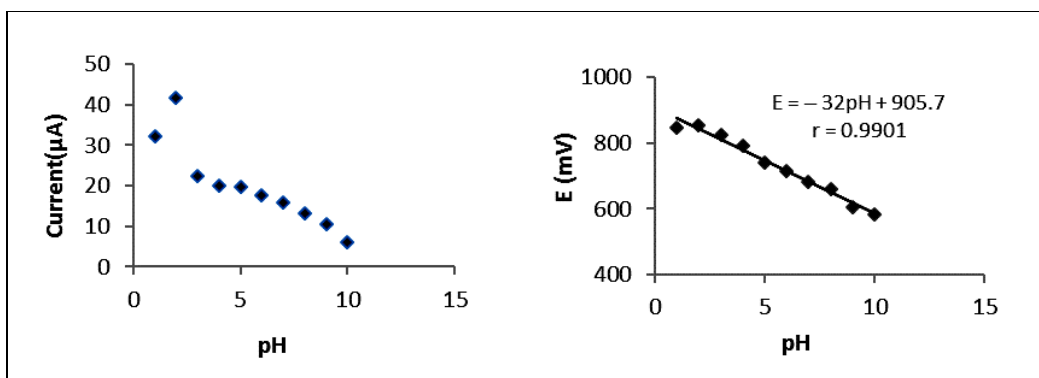
### 3.2. Effect of pH

The electrode reaction for diethofencarb was also investigated over pH range 1.0–10 in  $\text{H}_2\text{SO}_4$  and B-R buffer media. The effect of pH on the peak intensity showed a maximum at pH 2.0 (**Fig.2**), thus this pH value was preferred to carry out the electro-analytical works. The peak potential was slightly pH dependent with a negative slope of – 32 mV/ pH unit (**Fig.2**).

$$E(\text{mV}) = -32 (\text{mV/pH}) \text{pH} + 905.7(\text{mV}) \quad r = 0.9901$$

A linear potential shift to the less positive potentials could be attributed to the coupling of  $\text{H}^+$  with the electrooxidation process as expected for various organic compounds. Moreover, the

oxidation of organic compounds involving the loss of protons with electrons could be displayed simply by  $R-H \rightarrow R + H^+ + e^-$  and this justifies the pH dependency with a negative slope of  $-32 \text{ mV/pH}$ .



**Figure 2.** Effect of pH on the peak intensity and peak potential for the square wave voltammetric determination of  $5 \mu\text{g mL}^{-1}$  diethofencarb (BR buffer for pH 3.0 to 10.0 and  $\text{H}_2\text{SO}_4$  for pH 1 and 2;  $E_{\text{acc}} = 100 \text{ mV}$ ,  $t_{\text{acc}} = 60 \text{ s}$ ,  $f = 100 \text{ Hz}$ ,  $\Delta E = 40 \text{ mV}$ ).

### 3.3. Optimization of operational parameters

**Figure 3** shows the influence of initial potential, accumulation time, square wave frequency and pulse amplitude on the peak sensitivity for  $5 \mu\text{g mL}^{-1}$  diethofencarb, respectively. The effect of initial or accumulation potential on the diethofencarb peak was studied from 0.0 to +800 mV for 60 s. The peak intensity was significantly increased up to +100 mV and then dramatically decreased. The initial potential was therefore applied as +100 mV for further experimental works. The equilibrating or accumulation time was studied in the range of 20.0 to 200 s for  $5.0 \mu\text{g mL}^{-1}$  diethofencarb in 0.01 M  $\text{H}_2\text{SO}_4$  solution. The peak intensity increased sharply up to 60 s whereas at higher accumulation time the peak intensity versus time plots started to slightly decrease, meaning that equilibrium was achieved at the electrode surface. 60 s was therefore chosen as an optimum equilibration time. Since the frequency determines the intensity of the current signal and, in turn, the sensitivity of the method, the square wave frequency on the current response was studied in the range of 25-500 Hz. The peak intensity was gradually increased with frequency up to 100 Hz and then distorted. 100 Hz was therefore used in subsequent studies. The plot of  $\log f$  versus peak potential (mV) in



0.01 M H<sub>2</sub>SO<sub>4</sub> was linear with a slope of 50.4 mV s<sup>-1</sup> as stated by the following linear equation:

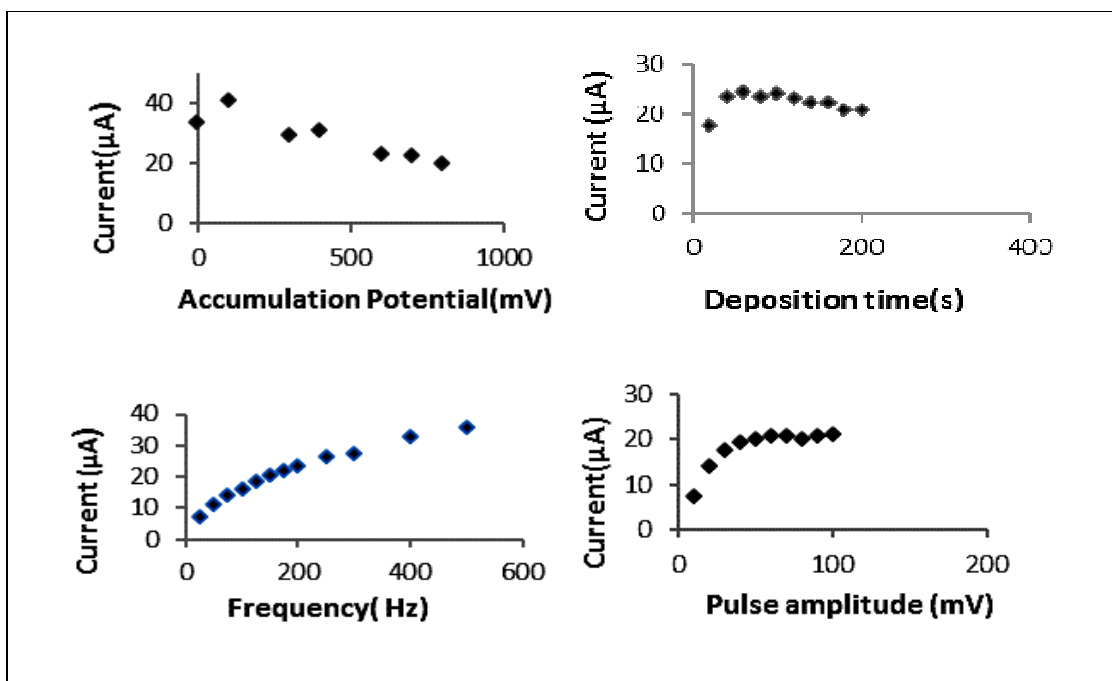
$$E_p \text{ (mV)} = 50.4 \log f + 780.3 \text{ (mV)}$$

The peak potential should shift linearly with the *log* of frequency as stated in the following equation [18]:

$$\frac{\Delta E_p}{\Delta \log f} = \frac{2.303RT}{\alpha nF}$$

where  $\alpha$  and  $n$  are the transfer coefficient and number of electrons, respectively. If we equate the experimentally obtained slope to the  $2.3RT/\alpha nF$ ,  $\alpha n$  is calculated as 1.1. The transfer coefficient value could be accepted as 0.5 for the irreversible electrode process, accordingly the number of transferred electrons were 2.2, which was close to  $n \sim 2$ .

The influence of the square wave pulse height on the peak sensitivity was studied in the range from 10 to 100 mV and the peak current were significantly increased up to 40 mV, then it reached equilibrium.



**Figure 3.** Effect of initial potential(mV) (a); equilibration time(s) (b); square wave frequency(Hz) (c); pulse amplitude (d); for 5 µg mL<sup>-1</sup> diethfencarb.



### 3.4. Validity of the method

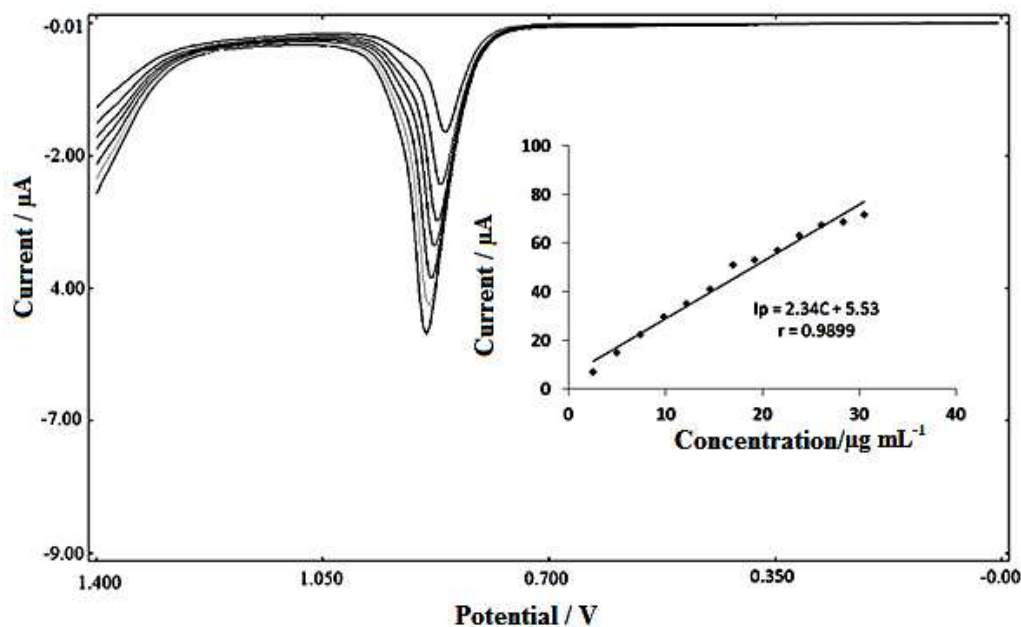
The validity of the proposed electro-analytical method was proved with respect to parameter such as limit of quantitation (LOQ), limit of detection (LOD), selectivity, accuracy, precision and repeatability.

#### 3.4.1. Linearity range

The calibration equation was carried out by the standard addition of diethfencarb solutions and the linearity was evaluated by linear regression analysis. The calibration curve constructed for diethfencarb was linear within the concentration range of  $2.50 \mu\text{g mL}^{-1}$  and  $30.5 \mu\text{g mL}^{-1}$  and given by the following equation:

$$I (\mu\text{A}) = 2.34 (\mu\text{A}/\mu\text{g mL}^{-1}) C (\mu\text{g mL}^{-1}) + 5.53 (\mu\text{A}) \quad r = 0.9899$$

The square wave voltammograms recorded in the optimized conditions were presented in **Figure 4**. The LOD and LOQ values were calculated from the peak intensity by use of the equations  $\text{LOD} = 3s/m$  and  $\text{LOQ} = 10s/m$ , where  $s$ , the standard deviation for fortified blank solution corresponding to  $2.50 \mu\text{g mL}^{-1}$  (ten runs) and  $m$  is the slope of the calibration curve. The calculated LOD and LOQ values were  $0.77 \mu\text{g/mL}$  and  $2.57 \mu\text{g/mL}$ , respectively. The analytical characteristics are summarized in **Table 1**.



**Figure 4.** SW voltammograms for the calibration curve of diethofencarb at  $\text{pH} \approx 2.0$  with  $\text{H}_2\text{SO}_4$   $E_s = 6 \text{ mV}$ ;  $f = 100 \text{ Hz}$ ;  $\Delta E = 40 \text{ mV}$ ;  $t_{\text{acc}} = 60 \text{ s}$ ;  $E_{\text{acc}} = +100.0 \text{ mV}$

**Table 1.** Some analytical features of diethofencarb calibration plot in 0.01 M H<sub>2</sub>SO<sub>4</sub>.

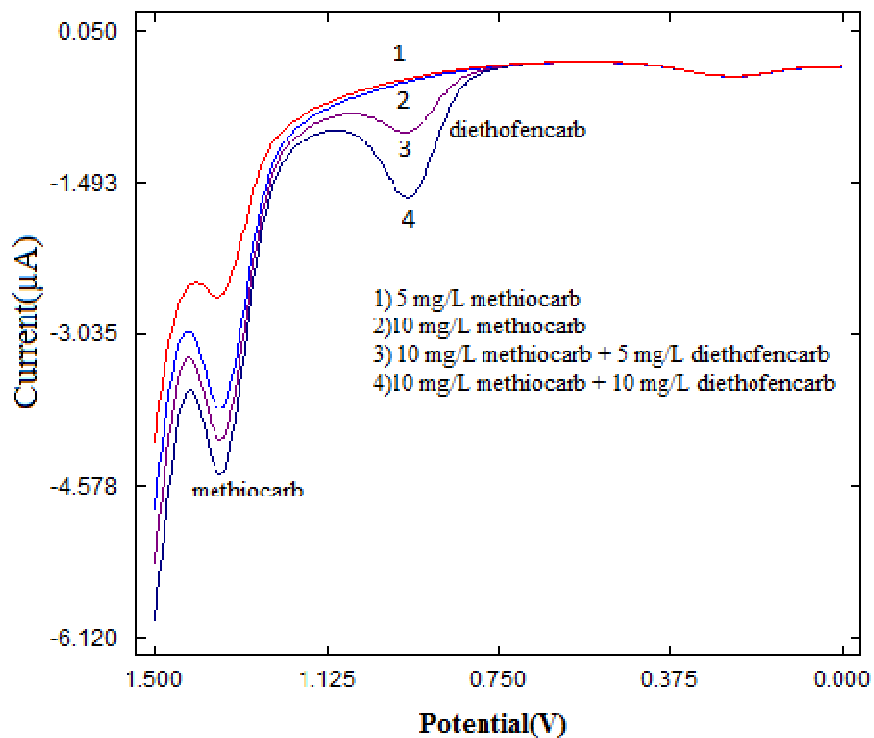
Parameters	Performance data*
Peak potential(mV)	+861
Linearity range ( $\mu\text{g mL}^{-1}$ )	2.50 – 30.51
Slope ( $\mu\text{A}/\mu\text{g mL}^{-1}$ )	2.34
Intercept( $\mu\text{A}$ )	5.53
Correlation coefficient	0.9899
Limit of detection(LOD) $\mu\text{g mL}^{-1}$	0.77
Limit of quantification(LOQ) $\mu\text{g mL}^{-1}$	2.57
Repeatability of peak potential (RSD %)	0.32
Repeatability of peak current (RSD %)	3.84

\*n=10

### 3.4.2. Selectivity

One of the main aims of analytical methods is to determine pesticides at trace level concentration in real matrices, hence, under the selected optimum conditions, the recommended method was applied to diethofencarb determination in the presence of various pesticides.

Diethofencarb determination were realized in the presence various fungicides to put forth the selectivity, accuracy and applicability of the recommended method. The selectivity was evaluated by means of recovery tests. The degree of interference was estimated by comparing the assay results in the presence of various fungicide species to that in their absence. The recovered mass percentages from 4.95  $\mu\text{g mL}^{-1}$  diethofencarb in the presence of penconazole, difenoconazole, cymoxamil, bendiocarb, kresoxim-methyl, desmedipham and methiocarb were presented in **Table 2**. The only electroactive species in the studied potential ranges were desmedipham and methiocarb having the oxidation peak potentials of +1266 mV and +1300 mV, respectively. Cymoxamil, bendiocarb, kresoxim-methyl and desmedipham did not cause a considerable influence on the determination of diethofencarb, and their resulting recoveries were between 93.2% and 99.6 % when the mass ratio 1:1. **Figure 5** displays the determination of diethofencarb next to the methiocarb and the resulting recoveries justify the relatively good selectivity of the proposed method.



**Figure 5.** Square wave voltammograms for determination of diethofencarb next to the methiocarb in 0.01 M H<sub>2</sub>SO<sub>4</sub>.

**Table 2** Interference effect of some pesticides on the determination of 4.95  $\mu\text{g mL}^{-1}$  diethofencarb in 0.01M  $\text{H}_2\text{SO}_4$ .

Interfering species*	Mass ratio of 1 : 1 Recoveries (%)	Mass ratio of 1 : 3 Recoveries (%)	Mass ratio of 1 : 5 Recoveries (%)
Penconazole	86.3	72.9	63.1
Difenoconazole	76.2	54.5	46.1
Cymoxamil	97.7	92.7	80.8
Bendiocarb	93.2	79.3	68.6
Kresoxim-Methyl	94.8	80.6	73.8
Desmedipham**	99.6	75.0	55.6
Methiocarb***	98.5	94.1	88.0

\* dissolved in acetone. \*\*1266 mV. \*\*\* 1300 mV.

### 3.4.3. Analytical application, accuracy and precision

The method was checked by performing recovery tests and the associated accuracy and precisions were both evaluated. To achieve this, tomato juice samples containing 2.50 – 7.50  $\mu\text{g mL}^{-1}$  diethofencarb were subjected to the proposed method. The voltammetric peak obtained at about + 860 mV (vs Ag/AgCl) was used for the determination of diethofencarb in spiked tomato juice. The accuracy was given by calculating the percent recoveries of the diethofencarb in spiked tomato juice matrices. The precision of the method was specified by calculating the relative standard deviation (%RSD). The samples analyzed with great success in 0.01 M  $\text{H}_2\text{SO}_4$  and their sufficiently precise and accurate results were presented in **Table 3**. The experimental values for tomatoes juice samples spiked with 2.50, 5.0 and 7.50  $\mu\text{g mL}^{-1}$  diethofencarb were  $2.43 \pm 0.062$ ,  $4.89 \pm 0.018$  and  $7.35 \pm 0.030$  at 90% confidence level, respectively. The adequately recoveries over 97% and relative low standard deviations less than 3.8% reflected a high degree of accuracy and precision of the recommended square wave voltammetric method.

**Table 3.** Recovery values for the diethofencarb in spiked tomatoes juice.

Spiked ( $\mu\text{g mL}^{-1}$ )	Found( $\mu\text{g mL}^{-1}$ )		Recovery (%)	% RSD	% Relative Error
	$\bar{X} \pm S$	$\bar{X} \pm \frac{t \cdot s}{\sqrt{n}}$			
2.5	$2.43 \pm 0.092$	$2.43 \pm 0.062$	97.2	3.80	-2.8
5.0	$4.89 \pm 0.027$	$4.89 \pm 0.018$	97.8	0.55	-2.1
7.50	$7.35 \pm 0.045$	$7.35 \pm 0.030$	98.0	0.61	-2.0

$n=8$ , % 90 Confidence level

## Conclusion

Voltammetric analysis of diethofencarb fungicide was realized on a newly prepared muttivalled carbon nanotube paste electrode. These composite electrodes have some advantages with respect to electroanalytical chemistry, for instance, small size with large surface area, high sensitivity, rapid response, and enhanced electron transfer when used as electrodes in electrochemistry. The accuracy and precision was shown by calculating the percent recoveries of the diethofencarb in spiked tomatoes juice. The applicability and selectivity of the developed method were proved in the presence of some coexisting pesticides. The adequately recoveries over 97% and relative low standard deviations less than 3.8% reflected a high degree of accuracy and precision.

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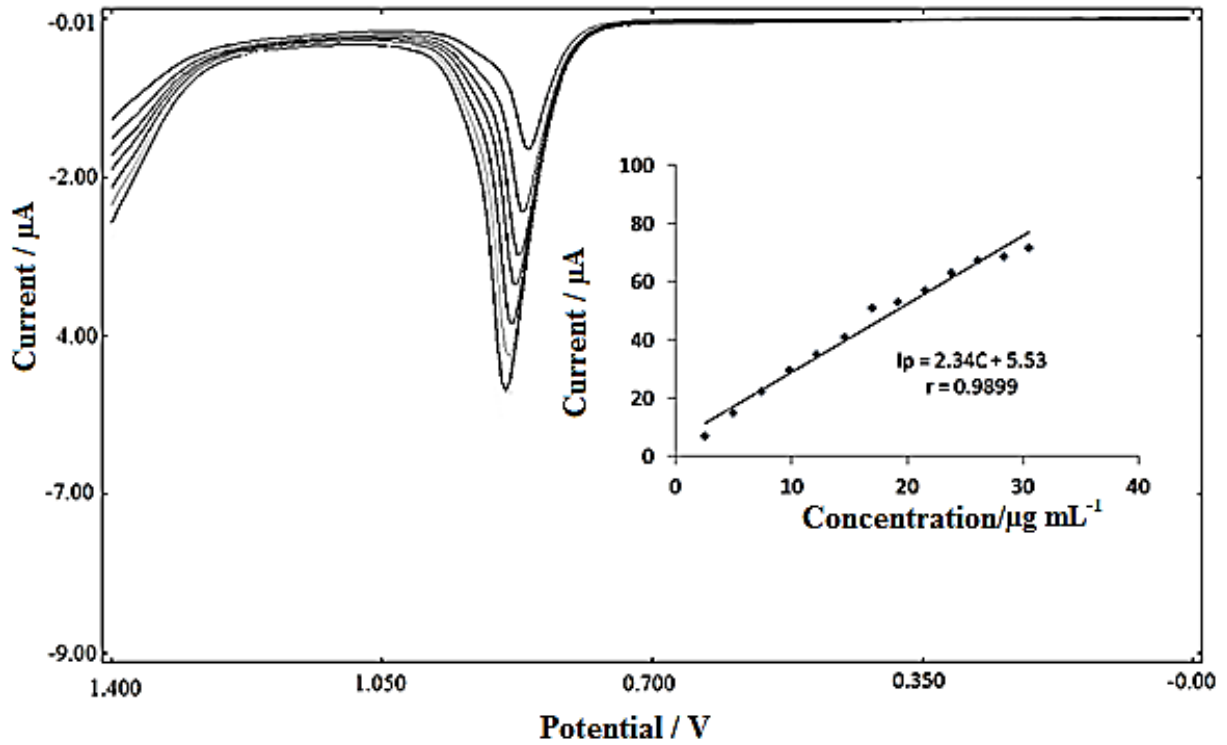
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A new sensitive square wave anodic peak on a newly prepared carbon nanotube electrode at +861 mV provided diethofencarb fungicide determination.