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Voltammetric determination of phenmedipham herbicide using a multiwalled carbon nanotube paste electrode

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Abstract: Phenmedipham is an herbicide used especially in the sugar beet harvest to fight against broad-leaved weeds and studies of its voltammetric behavior and detection have not been done before. The superior properties of carbon nanotubes such as electrical conductivity, mechanical strength, and wide potential ranges make them attractive for chemical sensors and the phenmedipham compound gave an oxidation peak at +1320 mV (vs. Ag/AgCl) on the nanostructured multiwalled carbon nanotube paste electrode. Square wave voltammetric measurements recorded for phenmedipham showed that the peak current increased linearly between 0.02 and 2.0 mg/L with a regression coefficient of $r = 0.9989$, and the limit of detection and limit of quantification were calculated as 6.96 μg/L and 23.2 μg/L, respectively. The applicability and the selectivity of the improved square wave voltammetric method for the phenmedipham assay were investigated in the presence of certain herbicides and fungicides such as carbendazim, benomyl, aclonifen, ethofumesate, metamitron, and p-acetanisidide (methacetin). Phenmedipham at 1 mg/L with the same amount of these pesticides was determined to have recoveries of 103.5 ± 0.7, 94.5 ± 2.8, 104.3 ± 1.8, 101.9 ± 3.1, 93.8 ± 1.7, and 101.3 ± 1.8, respectively (n = 3). The method was also applied to the phenmedipham assay in saturated tea sugar prepared as a spiked natural sample and 1.0 g/L phenmedipham in the sugar solution was successfully determined with a relative error of –5.0% and a relative standard deviation of 3.16%.

Key words: Square-wave voltammetry, phenmedipham herbicide, carbon paste electrodes, determination

1. Introduction

In almost all agricultural operations, pesticides are widely used as a strategy to boost yields and reduce costs. However, environmental and toxicological risks arise with the use of pesticides, and pollution of groundwater becomes a major concern. Carbamate compounds were synthesized at the beginning of the 1950s and are still used in pest control today due to their broad spectrum of biological activity.[1] Carbamate group pesticides are among the most important pesticides used as insecticides or fungicides to increase yield and quality in agricultural production[2] and their use increases with increasing demand for food.[3] They can be chemically classified as carbamate acaricides, carbamate fungicides, carbamate herbicides, carbamate insecticides, carbamate nematicides, carbanilate fungicides, carbanilate herbicides, and carbanilate rodenticides. The carbamate herbicides are further divided into carbamate and carbanilate, and phenmedipham is classified as a carbanilate herbicide. The most common pesticides in the carbanilate herbicide group are carbasulam, carbetamide, chlorbufam, chlorpropham, desmedipham, phenisopham, phenmedipham, and propham. Phenmedipham [3-

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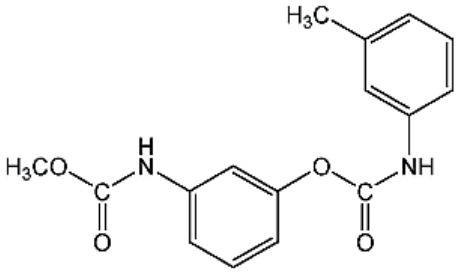
methoxycarbonylaminophenyl 3-methylcarbanilate] is an herbicide used especially in the sugar beet harvest to fight against broad-leaved weeds and its structural formula is presented in the Scheme.



Scheme. Phenmedipham. IUPAC: 3-Methoxycarbonylaminophenyl-3-methylcarbanilate.

Many analytical methods have been used in the determination of carbamates and the most common of these are chromatographic ones. High-performance liquid chromatography (HPLC) coupled with various detectors, i.e. ultraviolet (UV),[4–6] diode arrays,[7–9] chemiluminescence,[10–12] fluorescence,[13,14] and mass spectrometry,[15–17] are leading techniques in the determination of carbamate pesticides. However, these methods have some disadvantages, such as long analysis procedures, tedious and long sample preparation processes, time-consuming and complicated preprocessing steps, and expensive and toxic solvents used in preprocessing. They can also be determined frequently by electrochemical methods such as differential pulse voltammetry,[18] square wave voltammetry (SWV),[19–22] and amperometry.[23] An alternative to these analytical methods is the voltammetric methods, which have very high sensitivity and selectivity through the use of a wide variety of modified electrodes[18,19,21] and allow the determination of pesticides or environmental pollutant organic species over a wide range of concentrations.[24]

Although various electrochemical methods have been used for the extensive detection of pesticides included in the carbamate classification, this is not the case for the herbicide phenmedipham. According to our literature review, while there have been several studies of phenmedipham by HPLC,[25–27] no studies have reported the voltammetric characterization of this herbicide. The current study is the first voltammetric report on the determination of phenmedipham herbicide with multiwalled carbon nanotube paste electrode (MWCNTPEs). Nanoparticle paste electrodes prepared with carbon nanotubes have recently been used extensively in the electrochemical determination of pesticides[28–30] in terms of simplicity of paste preparation, low cost, easy surface renewal, fairly good stability, low residual current, easy portability and miniaturization. The superior properties of carbon nanotubes such as electrical conductivity, mechanical strength, and wide potential ranges make them attractive for chemical sensor construction.[31] In addition, carbon nanotubes are advantageous compared to other sensors in terms of electron transfer rate, sensitivity, and rapid response in analysis thanks to their small size.

2. Results and discussions

2.1. Voltammetric parameters and instrumental optimization

All analytical and instrumental parameters must be optimized prior to starting analytical determinations with square wave stripping voltammetry. Based on this consistency, parameters such as accumulation potential (E_{acc}) and time (t_{acc}), frequency (f), pulse amplitude (ΔE), step potential (ΔE_s), and pH were first optimized for phenmedipham determination. When working with analytical techniques done by voltammetric stripping

methods, the electrodeposition potential and the electrodeposition time should be optimized according to the electrochemical properties of the analyte so that the sensitivity and selectivity of the method can be improved.[31] The optimized instrumental parameters affecting SWV characteristics, such as accumulation potential (E_{acc}), accumulation time (t_{acc}), frequency (f), pulse amplitude (ΔE), and step potential (ΔE_s), were $E_{acc} = +$ 200 mV, $t_{acc} = 60$ s, $f = 60$ Hz, $\Delta E = 10$ mV, and $\Delta E_s = 60$ mV, respectively.

On the other hand, the peak potentials were shifted in the positive direction and the log f plot versus the peak potential (V) for phenmedipham in pH 2.0 B–R buffer solution was linear with the slope of 41.7 mV/s as expressed by the following linear equation:

$$E_p(mV) = 41.7 log f(s^{-1}) + 1232.4, \quad (1)$$

Since $\Delta E_p / \Delta \log f = 2.303RT/\alpha nF$, when the slope of the log f plot versus the peak potential (V) was equated to $2.303RT/\alpha nF$, αn could be obtained as 1.4.

2.2. Effect of pH on square wave voltammograms of phenmedipham

The electrochemical behavior of 5.0 mg/L phenmedipham on the MWCNTPE, depending on pH, was studied by SWV at pH 1.0 to 6.0 (Figure 1). Since preparation of the buffer solution at pH 1 and 2 was impractical, sulfuric acid solutions were used as a supporting electrolyte for these pH levels. B–R buffer solution was used as a supporting electrolyte for the voltammograms to be obtained between pH 2.0 and 6.0. Peaks recorded from pH 3.0 to 6.0 indicate that they are enlarging and their sharpness is decreasing. As the pH increases towards the more basic regions, the peaks shift towards less positive values and expand with another peak formation in the form of a shoulder. Since the phenmedipham voltammogram at +1320 mV obtained in pH 2.0 B–R buffer solution gives a single sharp peak, this medium is preferred for subsequent analytical determinations. In general, protonated compounds at low pH values are oxidized at the electrode surface and are responsible for the sensitivity of the peak currents.

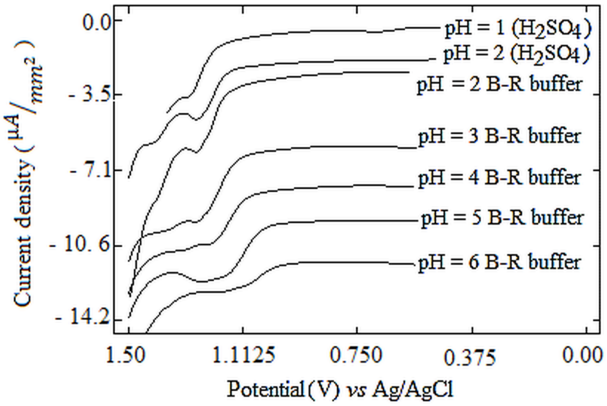


Figure 1. pH effect on the determination of 5.0 mg/L phenmedipham herbicide on MWCNTPE electrode ($\Delta E_s = 6$ mV; $f = 60$ Hz; $\Delta E = 10$ mV; $t_{acc} = 60$ s; $E_{acc} = +200$ mV).

2.3. The monitoring of electrochemical behavior with cyclic voltammetry

Cyclic voltammetry (CV) is a useful technique for elucidating the electrochemical behavior of organic species and that of the mechanisms of electrode reactions. As shown in Figure 2, 5.0 mg/L phenmedipham gave an oxidation

peak at +1320 mV and no cathodic peak occurred on inverse scans. This indicates that the oxidation peak is irreversible. Potential scans between 25 mV/s and 400 mV/s were performed to investigate the effect of these scan rates on peak potentials and peak currents. Peak potentials (E_p) shifted slightly to more positive values with increasing scanning rates (v). The effect of potential scanning speeds on the oxidation peak potentials for phenmedipham is given below:

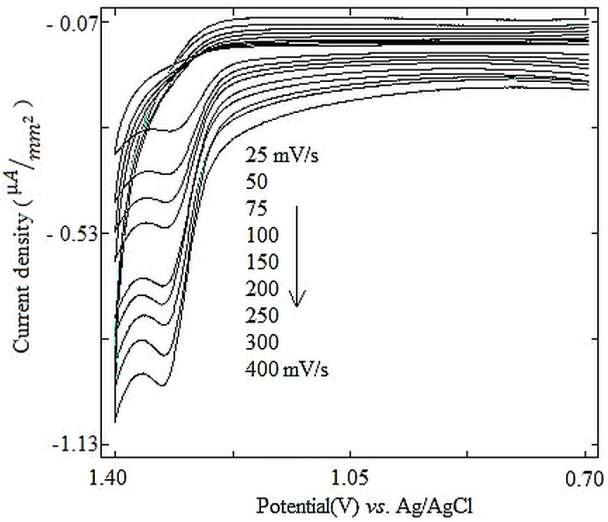


Figure 2. Effect of the potential sweep rate on the cyclic voltammogram of 5.0 mg/L phenmedipham herbicide (pH 2.0 B–R buffer solution).

$$E_p\,(mV) = 15.2 log v(mV/s) + 1342.3(mV), r = 0.9684. \quad (2)$$

The correlation and correlation coefficient between peak potential and log v are sufficiently good for this linearity. As seen in the above equation, when the potential scan rate is increased by 10 times, the peak potentials are shifted to 15.2 mV more positive values. This correlation obtained above is also evidence that the electrode response is irreversible.

In CV studies, the peak currents at potential scan rates ranging from 25 mV/s to 400 mV/s were measured to determine whether the electrooxidation process is diffusive or adsorptive-controlled. In order to evaluate how the peak currents function according to the square root or logarithm of the potential scan rate, the corresponding graphs were plotted and the following linear correlations were obtained. A logarithmic plot of peak intensities versus the logarithm of potential scan rate created a straight line with a slope of 0.5886. Since the experimental value can be regarded as close to the theoretical one of 0.5, it is expressed for an ideal reaction of the diffusion-controlled electrooxidation process.[32]

$$I_p(\mu A) = 2.903 v^{1/2}(V/s) + 0.001, r = 0.9840. \quad (3)$$

$$log I_p(\mu A) = 0.587 log v(mV/s) - 1.207, r = 0.9883. \quad (4)$$

Based on our experiments and the mechanistic approaches of voltammetric determinations of some carbamate pesticides,[33,34] phenmedipham oxidation gives a chemical coupling reaction, probably following a cationic radical formation.

2.4. Calibration curve

With the application of optimized experimental conditions and instrumental parameters SW voltammograms were recorded at various phenmedipham concentrations and then a calibration graph based on peak currents versus concentration was drawn (Figure 3). Square wave voltammetric measurements recorded for phenmedipham showed that the peak current increased linearly between 0.02 and 2.0 mg/L with a regression equation given as follows:

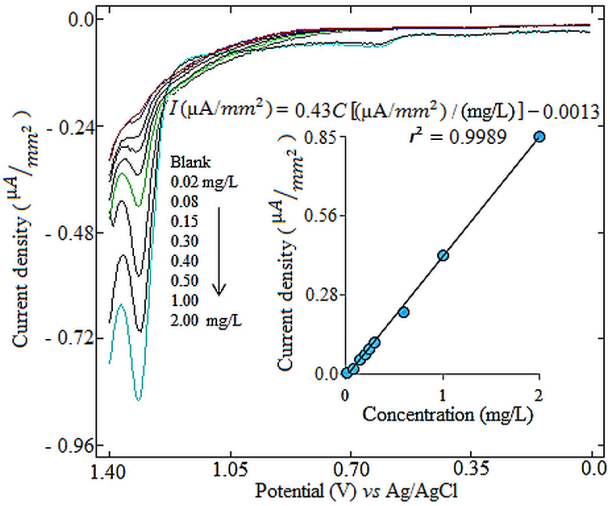


Figure 3. Square wave voltammograms and calibration graph for determination of phenmedipham herbicide on MWCTPE (pH 2.0 B–R buffer solution; ΔE_s = 6 mV; f = 60 Hz; ΔE = 10 mV; t_{acc} = 60 s; E_{acc} = +200 mV).

$$I_p\,(\mu A/mm^2) = 0.43C[(\mu A/mm^2)/(mg/L)] - 0.0013, r = 0.9989. \tag{5}$$

The limit of detection (LOD) and the limit of quantification (LOQ) of the developed method were calculated according to the following equations proposed by the IUPAC:[35]

$$LOD = 3S_b/m, \tag{6}$$

$$LOQ = 10S_b/m. \tag{7}$$

In the above equations, S_b is the standard deviation of the intersection point of the calibration curve and the term m indicates the slope of the calibration curve. Using these equations, the LOD and LOQ values of the square wave stripping voltammetry detection method developed for phenmedipham were calculated to be 6.96 μg/L and 23.2 μg/L, respectively. The detection and quantification limits can be compared to the values of 3.2 and 8.4 μg/kg, which are phenmedipham residues in sugar beet root samples[36] and an acceptable value of 0.1 mg/kg.[37] It is also reported that this voltammetric method gives an advantage over some chromatographic methods[25,26] in terms of detection and quantification limits. The reproducibility value in seven different measurements for 0.15 mg/L phenmedipham was calculated with a relative standard deviation of 1.56%. In experiments for the reproducibility of peak potentials, the reproducibility value was calculated in the same way and was obtained with a relative standard deviation of 0.23%. Accordingly, Table 1 summarizes the analytical performance data, with the method exhibiting fairly good precision, accuracy, and reproducibility.

Table 1. Analytical performance data for phenmedipham determination by SWSV.

Analytical parameters	SWSV[a]
Peak potential (mV)	+1320
Linearity range (mg/L)	0.02–2.0
Slope [(μA/mm^2)/(mg/L)]	0.43
Intercept (μA/mm^2)	–0.0013
Correlation coefficient	0.9989
Limit of determination, LOD (μg/L)	6.96
Limit of quantification, LOQ (μg/L)	23.20
Reproducibility of peak potential (RSD%)[a]	0.23
Reproducibility of peak current (RSD%)[a]	1.56

[a] n = 7 ; SWSV: Square wave stripping voltammetry.

2.5. Method selectivity and interference effect

One of the most important parameters that must be provided for an analytical method to be valid is selectivity: the analytical determination of the target species in the presence of other species should be accurate and reproducible. To ascertain this, the applicability and selectivity of the improved square wave voltammetric method for the phenmedipham assay have been investigated in the presence of certain herbicides and fungicides.

Since the phenmedipham herbicide studied in this work is of the carbamate class, the interference effects of other carbamate pesticides such as benomyl and carbendazim have been studied in particular. Benomyl is a fungicide of the benzimidazole carbamate class and formulas developed with benomyl as an active ingredient are used to fight black spots in apple and pear farming. It is also used against cherry flower monilia disease, peach monilia disease, and apple and peach shedding diseases. The electrooxidation of the benomyl fungicide was previously studied by square-wave adsorptive stripping voltammetry and the quantitation was performed using the peak generated at +1144 mV.[38] Carbendazim is a systemic fungicide of the benzimidazole family and used for the control of diseases in fruit trees, nut crops, vegetables, cereals, tropical crops and ornamentals, turf, and many field crops. The interfering effect of carbendazim on the phenmedipham peak is particularly important because the carbendazim peak at +1160 mV can be considered close to the peak of phenmedipham at +1320 mV. Electroanalytical investigation of carbendazim from the previous adsorptive stripping voltammetry[39] and square wave adsorptive stripping voltammetry[22] also confirms an electrooxidation peak at around +1100 mV.

On the other hand, despite the fact that benomyl does not have any peak in the working conditions, 1 mg/L phenmedipham could be determined with a relative error of –5.5% in the presence of 1 mg/L benomyl. When the amount of benomyl is increased by 5- and 10-fold, the interference increases and the error in the determination of 1 mg/L phenmedipham exceeds 15%.

Of the other herbicides studied, an interfering effect was found for aclonifen (nitrophenyl ether herbicides), widely used as an herbicide in chickpea cultivation. The square wave voltammetric method for the determination of aclonifen herbicide showed an oxidation peak at +1175 mV on the glassy carbon electrode (GCE) in a pH 4 B–R buffer solution.[40] Aclonifene was taken at the same concentration as phenmedipham (1 mg/L) and the relative error in recovery of phenmedipham was +4.3%. If the aclonifen concentration exceeded the phenmedipham concentration by 5- or 10-fold, the relative error in the phenmedipham assay was below the 5% tolerance limit.

Ethofumesate (benzofuranyl alkylsulfonate herbicides) is mostly used for the production of sugar beet in the struggle against narrow-leaved and broad-leaved weeds. Ethofumesate did not produce any peak in working conditions and the interference effect in the phenmedipham assay was minimal when compared to other pesticides. Recovery of 1 mg/L phenmedipham herbicide in the presence of ethofumesate herbicide at concentrations of 1, 5, and 10 mg/L was found to be +1.9%, –0.1%, and –0.9%, respectively. Since phenmedipham and ethofumesate are used to combat broad-leaved weeds in sugar beet production, the relatively low relative error observed in codeterminations is superior to this method.

Metamitron (triazinone herbicides) is an herbicide effective against grass and broad-leaved weeds in beet crops. p-Acetanisidide (methacetin) is an anilide herbicide for a wide variety of crops, including potatoes, cotton, rice, and corn. While the relative error in the recovery of 1 mg/L phenmedipham herbicide in the presence of metamitron herbicide at a concentration of 1 mg/L was below 10%, it approached 60% upon increasing the metamitron concentration by 5- and 10-fold. In other words, there is a serious interference effect in the determination of phenmedipham in the presence of metamitron at high concentrations.

Anilide herbicides are encouraging weed control agricultural chemicals for a wide variety of crops, including potatoes, cotton, rice and corn. p-Acetanisidide (methacetin) is a member of the family of acetanilide compounds and its sensitive voltammetric determination was carried out from the peak at +1060 mV in pH 2.4 B–R buffer solution.[41] Although p-acetanisidide gave a peak at +1120 mV in the presence of the phenmedipham compound, there was no significant interference effect. Phenmedipham herbicide at a concentration of 1 mg/L could be determined with +1.3%, –1.3%, and –7.7% relative error in the presence of p-acetanisidide (methacetin) at 1 mg/L, 5 mg/L, and 10 mg/L, respectively. Accordingly, determination of the phenmedipham herbicide in the presence of p-acetanisidide (methacetin) is possible in an acceptable range of error.

In conclusion, when carbendazim, benomyl, aclonifen, ethofumesate, metamitron, and p-acetanisidide (methacetin) pesticides were examined at the same concentration with phenmedipham, the interference effect was below the 10% tolerance limit. If the amount of carbendazim, aclonifen, and ethofumesate is increased 5-fold, they can still be determined at the 5% tolerance limit. Percent recoveries for phenmedipham in the presence of carbendazim, benomyl, aclonifen, ethofumesate, metamitron, and methacetin are summarized in Table 2. From these evaluations, it can be said that the method's selectivity, accuracy, and applicability are quite good.

2.6. Analytical determination of carbendazim and p-acetanisidide (methacetin) in the presence of phenmedipham

It was examined whether accurate and reproducible determinations of other important pesticides were possible besides the target compound, since pesticides could be found together with others instead of alone in the areas where they are applied. For this purpose, the amounts of phenmedipham and carbendazim were kept in equal amounts (both 1.0 mg/L) and square wave voltammograms were recorded for carbendazim determination. Under the experimental and instrumental optimization conditions stated, 5 and 10 mg/L standard carbendazim concentrations were added to a voltammetric cell containing phenmedipham and carbendazim at a concentration of 1.0 mg/L. The carbendazim peaks at +1100 mV produced equivalent current increases with standard carbendazim additions, and no change was observed in peaks at +1320 mV as expected. From the carbendazim peak increments of +1150 mV for 1.0 mg/L carbendazim could be determined with –1% relative error in the presence of 1.0 mg/L phenmedipham (Figure 4a). A similar study was conducted for p-acetanisidide

Table 2. Percent recoveries for the phenmedipham in the presence of carbendazim, benomyl, aclonifen, ethofumesate, metamitron, and methacetin.

	% Recovery		
Pesticides tested for interference effect	1:1*	1:5*	1:10*
Carbendazim (benzimidazolylcarbamate fungicides)	103.5 ± 0.7	101.7 ± 1.3	93.8 ±1.7
Benomyl (benzimidazolylcarbamate fungicides)	94.5 ± 2.8	115.5 ± 2.9	150.9 ± 3.2
Aclonifen (nitrophenyl ether herbicides)	104.3 ± 1.8	102.9± 0.7	96.2 ± 1.4
Ethofumesate (benzofuranyl alkylsulfonate herbicides)	101.9 ± 3.1	99.9 ± 2.2	99.1 ± 0.4
Metamitron (triazinone herbicides)	93.8 ± 1.7	64.10 ± 0.9	42.5 ± 1.2
p-Acetanisidide (methacetin) (Anilide herbicides)	101.3 ± 1.8	98.7± 1.5	92.3 ± 0.5

*: Phenmedipham and pesticide mass ratio (m/m): 1 mg/L phenmedipham and 1 mg/L pesticide; 1 mg/L phenmedipham and 5 mg/L pesticide; 1 mg/L phenmedipham and 10 mg/L pesticide (n = 3).

and analytical determinations were made for p-acetanisidide from the peak increments occurring at +1120 mV. p-Acetanisidide could be determined with 3.0% relative error in the presence of 1.0 mg/L phenmedipham (Figure 4b). Fortunately, when all three species were present together in the same medium, phenmedipham could be easily detected. As a result, carbendazim and p-acetanisidide assays have been successfully performed in the presence of phenmedipham due to the selectivity, reproducibility, and accuracy of the developed voltammetric method (Table 3).

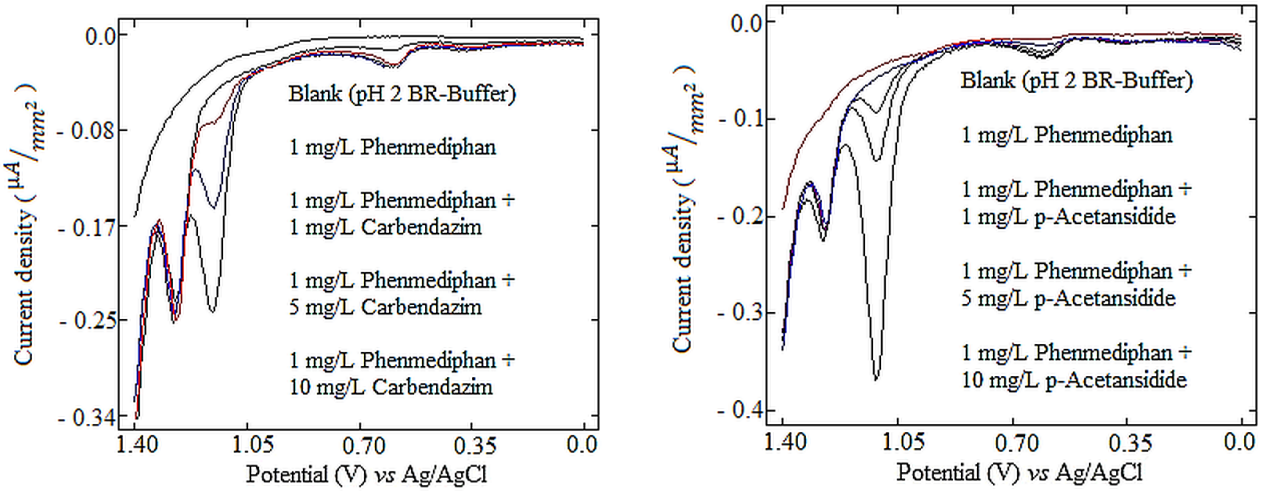


Figure 4. a. Determination of 1.0 mg/L carbendazim in the presence of 1.0 mg/L phenmedipham (pH 2 B–R buffer solution; ΔE_s = 6 mV; f = 60 Hz; ΔE = 10 mV; t_{acc} = 60 s; E_{acc} = +200 mV). b. Determination of 1.0 mg/L p-acetanisidide in the presence of 1.0 mg/L phenmedipham (pH 2.0 B–R buffer solution; ΔE_s = 6 mV; f = 60 Hz; ΔE = 10 mV; t_{acc} = 60 s; E_{acc} = +200 mV).

Table 3. Determination of p-acetanisidide and carbendazim in the presence of 1.0 mg/L phenmedipham.

	p-Acetanisidide	Carbendazim
Added	1.00 mg/L	1.00 mg/L
Found	1.03 ± 0.01 mg/L	0.99 ± 0.01 mg/L
Relative error (%)	3.0%	–1.0%
RSD (%)	0.97%	1.01%

n = 3.

2.7. Analytical application

Since phenmedipham is used for the control of weeds and broad-leaved harmful plants in sugar beet production, the method was applied to the phenmedipham assay in saturated tea sugar prepared as a spiked natural sample. A saturated sugar solution was prepared by adding an excess amount of tea sugar purchased from a local market to 50 mL of purified water at 80 °C. The solution was then cooled to room temperature and the precipitate was filtered through the aid of a filter paper. Ten milliliters of this filtrate was taken and the phenmedipham solution was prepared in a saturated tea sugar solution. After 0.1 mL of sample from this aliquot was completed to 10.0 mL with a pH 2.0 B–R buffer solution in the voltammetric cell, the voltammograms were recorded under optimizing conditions for the 1.0 mg/L phenmedipham assay. Using the MWCNTPE, a voltammetric assay of 1.0 mg/L phenmedipham in saturated tea sugar was successfully performed and the results are summarized in Table 4. Accordingly, 1.0 g/L phenmedipham in the sugar solution was successfully determined with a relative error of –4.7% and a relative standard deviation of 3.15%. Evaluating these results, it can be said that the accuracy, precision, and applicability of the method are quite good.

Table 4. Determination of phenmedipham in saturated tea sugar.

Phenmedipham	
Added (mg)	1.00
Found (mg ± mg)	0.95 ± 0.03
Average recovery (%)	95.0
RSD (%)	3.16
Relative error	–5.0

n = 3.

2.8. Conclusion

In this study, a novel voltammetric report was published for the first time using MWCNTPEs to determine the herbicide phenmedipham. When the performances of two electrodes were compared within pH 2.0 B–R buffer for the phenmedipham assay, the MWCNTPE provided much more sensitive and well-defined peaks compared to the GCE. The phenmedipham compound gave an oxidation peak at +1320 mV versus Ag/AgCl on the MWCNTPE and this peak was used to examine the applicability and selectivity of the square wave voltammetric method in the presence of other fungicides. The interference effect of carbendazim, benomyl, aclonifen, ethofumesate, metamitron, and p-acetanisidide (methacetin) pesticides tested at the same concentration as that of phenmedipham was found to be below the 10% tolerance limit. Phenmedipham in the sugar solution was also successfully determined with a relative error of –4.7% and a relative standard deviation of 3.15%.

Evaluating these results, it can be said that the accuracy, precision, and applicability of the method are quite good.

3. Experimental

3.1. Apparatus

Electrochemical studies with SWV and CV were performed with a Bioanalytical Systems (BAS) voltammetric analyzer, the Epsilon potentiostat/galvanostat (BAS, West Lafayette, IN, USA). The voltammetric analyzer was connected to a BAS C3 solid electrode cell stand. The working electrode was a MWCNTPE with a diameter of $\varphi = 3$ mm. A platinum wire was used as the auxiliary electrode. The third electrode was the reference Ag/AgCl (3 M NaCl, BAS) electrode.

3.2. Reagents

Phenmedipham was purchased from Sigma-Aldrich. MWCNT powder (mesh size, –270, <53 mm) was provided by Merck. Sulfuric acid was used for pH 1 and 2 solutions. Acetic, orthophosphoric, and boric acids (0.04 M) were used to prepare B–R buffer solutions from pH 2.0 to 6.0 by adding the required amount of 2 M NaOH to this triple acid mixture and monitoring with a pH meter. To prepare the phenmedipham stock solution, 0.0050 g of phenmedipham powder was precisely weighed and dissolved in 10 mL of acetone by ultrasonic stirring. The stock and dilute solutions were prepared daily and stored in the dark in a refrigerator when not in use.

To prepare MWCNTPEs, the multiwalled carbon nanotube powder (MER Corporation, mesh size <53 μm) was mixed with water-immiscible mineral oil at a mass ratio of 70% and 30%, respectively.[42] This mixture, made homogeneous in a mortar, was plugged into the hollow part of the BAS MF 2010 electrode attached to the BAS C3 stand, then polished with a polishing cloth. It was then washed with distilled water and dried. Carbon nanotubes are highly attractive for creating voltammetric sensors because they have unique properties in terms of electrical conductivity, mechanical strength, and a wide range of applicable potentials. They also provide high sensitivity, rapid response, and improved electron transfer with small dimensions and relatively large surface areas.

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