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Determination of carbonyl group containing pesticide monalide in vegetable samples by using deferential pulse polarographic method

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ABSTRACT

In this investigation electrochemical behavior of monalide is studied and its residues in vegetable samples is determined by using deferential pulse polarographic method. In this investigation dropping mercury electrode is used as working electrode and universal buffer with pH range 4.0-6.0 is used as supporting electrolyte. Investigated compound was found to exhibit well resolved peak at pH 4.0. Peak currents were linear over the concentration range of 1.0×10^{-5} M to 1.0×10^{-10} M with lower detection limit of 1.09×10^{-9} M. The relative standard deviation and correlation coefficients were found to be 1.25%, 0.996 respectively for 10 replicates.

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KEYWORDS

Deferential pulse polarography;
Monalide;
Universal buffer;
Dropping mercury electrode;
Vegetable samples.

INTRODUCTION

Carbonyl group containing pesticides are playing vital role in the agriculture field. These pesticides are widely used as pre and post emergent weed control agents (herbicides) for a wide variety of crops, namely corn, sorghum, wheat, rice, sugar cane and for fruits, vegetables and wine yards, consequently, they are found in river water^[1-5].

Monalide (4'-chloro-2,2-dimethylvalerianilide) ($C_{13}H_{18}ClNO$) is herbicide Several analytical methods were used for the determination of traces of monalide in different matrices that is in biological and environmental. William C. steen and Timothy w. collette determined Microbial Degradation of Seven Amides by Suspended Bacterial Populations by using chromatographic techniques^[6]. Khizar hayat I et al. Determined pesticide residues in blood samples of villagers involved in pesticide application at District Vehari (Punjab), Pakistan

by using gas chromatography^[7]. Guo-Fang Pang, determined 405 pesticide residues in grain by accelerated solvent extraction then gas chromatography-mass spectrometry or liquid chromatography-tandem mass spectrometry^[8]. But there is no polarographic method in literature cited above so in the present paper a selective and sensitive DPP method were reported.

EXPERIMENTAL

Apparatus and electrodes

Polarographic assays were performed using a model 364 polarographic analyzer supplied by Princeton applied research corporation, (Princeton, NJ USA) coupled with a kipp and zonen BD8x-t recorder. A dropping mercury electrode (DME) was used as working electrode and a saturated calomel electrode (SCE) as the reference electrode. Differential pulse polarograms were recorded with a unit supplied by metrohm

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(herisau,Switzerland)coupled with E 506 polarocard and E 612 VA scanner. Cyclic voltamograms obtained by adigital electronics model 2000x-y/t recorder (Mumbai,India) in cnection with the above unit. The DME used had an area of 0.223cm^2 at adrop time of 2s. A hanging mercury drop electrode (HMDE) used had an area of 0.223cm^2 in cyclic voltammetry. In all the above experiments platinum wire was used as auxillary electrodeallthe experiments were performed at 25°C . pH measurements were carried out with elico digital pH meter(Hyderabad,India). The millicoulometric apparatus used was supplied by radelkis (Budapest,hungary) cotrolled potential ektrolysis was carried out using a techno potentiostat(tech.ini electronics, luknow,India) in amidified cell with a mercury pool cathode saturarted colomel reference electrode.

Reagents and solutions

Pure samples obtained from RANKEM india lim-ited. The purity of sample was tested with tin layer chromatography and melting point determinations. Stock solution of pesticide under investigation were prepared in dimethylformamide. Universal buffer cotaining 0.2Mboric acid,0.05Mcitric acid and 0.1M trisodium orthophosphate were used as supporting electrolyte.

RESULT AND DISCUSSION

Differential pulse polarographic behaviour

Figure 1 exhibits differential pulse polarogram for $1 \times 10^{-5}\text{M}$ monalide with DME. The systematic studies of the various experimental and instrumental parameters that affect the polarographic response were carried out in order to establish the optimum conditions.

Effect of pH

The pH of a solution is critical factor affecting both the rate and equilibrium state of the reduction process and the rate of the electrode reaction. The influence of the pH on the DPP response was studied at DME of the $1 \times 10^{-5}\text{M}$ monalide with, between the pH ranges 2.0 to 6.0. It can be observed from Figure 2 that the maximum peak currents are obtained with pH 4.0.

Effect of scan rate

Differential pulse polarogram obtained for increas-

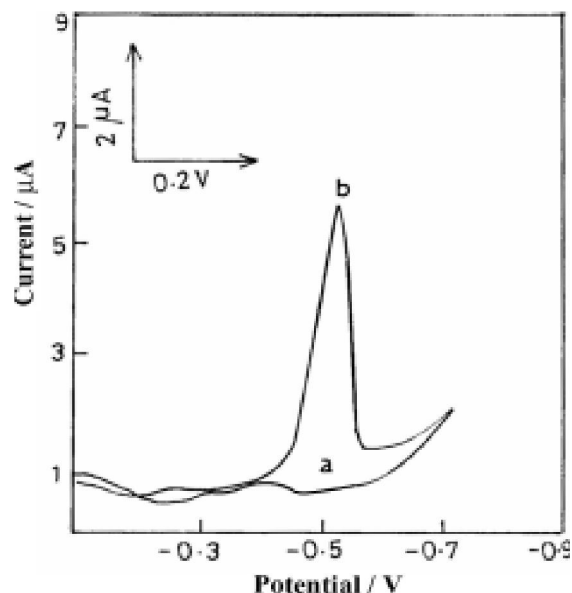


Figure 1 : Differential pulse polarogram of monalide at pH 4.0 concentration: $1.0 \times 10^{-5}\text{M}$; pulse amplitude: 50 mV droptime: 2sec.

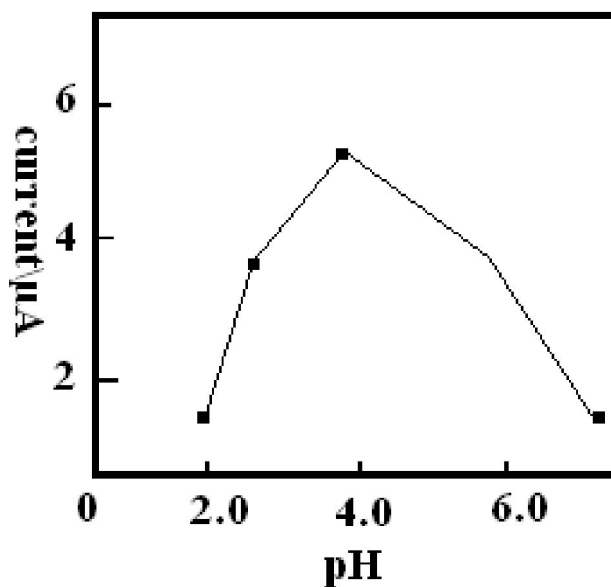


Figure 2 : Effect of pH on peak current in monalide

ing values of the scan rate showed the existence of a linear dependence of the peak current intensity on the scan rate between 10 to 60mVs^{-1} . The peak currents were directly proportional to the scan rate indicating that the system was adsorption controlled.

Characterization of waves/ peaks

Voltammetric behaviour of monalide has been studied over the pH range from 2.0 to 6.0. A single well resolved peak is observed throughout the pH range and this single peak is due to the reduction of carbo-

nyl group in 2 electron process to the corresponding hydroxyl group. Typical cyclic voltammogram is shown in Figure 3.

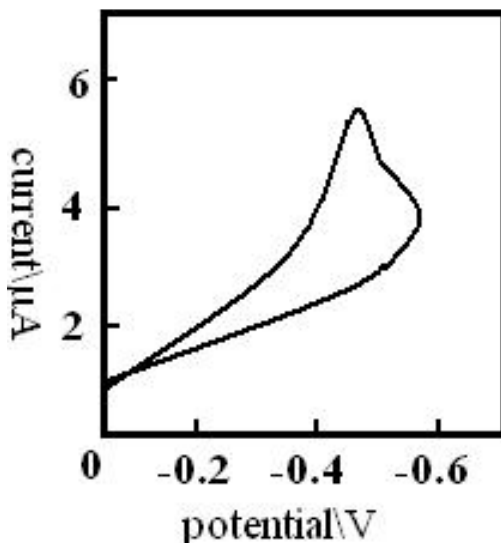


Figure 3 : Typical cyclic voltammogram of monalide for an accumulation time of 80 sec at HMDE, accumulation potential: -0.6V; Rest time: 10 sec; stirring rate: 1500 rpm; scan rate: 45 mV s⁻¹; concentration: 1.0x10⁻⁵M; pH:4.0.

Nature of electrode process

The reduction process are found to be diffusion controlled and adsorption on the electrode surface in the buffer systems studied as evidenced from the linear plots of i_p vs $v^{1/2}$ which found to pass through origin. The irreversible nature of the peaks are seen from log plot analysis. Further, E_p values were observed to be shifted towards more negative values with increasing concentration of depolarizer. The current function ($i_p / Cv^{1/2}$) in the above compound is found to be fairly constant with the scan rate (v) and the electrode process was purely diffusion controlled and adsorption on the electrode surface without any kinetic complications.

Identification of the product

Number of electrons involved in the electrode process determined by employing millicoulometric technique and it is found to be 2 in pH 4.0 for monalide, which indicates the final product to be hydroxyl compound.

Kinetic data

The values obtained for transfer coefficient, diffusion coefficient and heterogeneous forward rate constant for monalide are given in TABLE 1. The diffusion

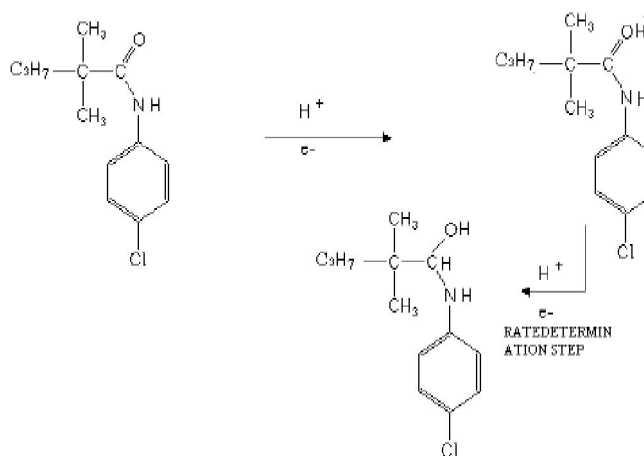
TABLE 1 : Cyclic voltammetric data of monalide, Concentration: 1.0x10⁻⁵M; Scan rate: 45mVs⁻¹

pH	$-E_p$ V	i_p μA	αn_a	$D \times 10^6$ cm ² s ⁻¹	$k^0_{t,h}$ cm s ⁻¹
2.0	0.36	5.81	0.99	5.66	2.60x10 ⁻⁶
4.0	0.43	5.73	0.92	5.49	1.57x10 ⁻⁷
6.0	0.61	5.55	0.88	5.22	6.47x10 ⁻⁹

coefficient values evaluated from cyclic voltammetric technique were found to be in good agreement indicating the diffusion controlled. The diffusion coefficient values are decreasing with an increase in pH values. The reason may be due to the decrease in availability of protons with an increase in pH of the supporting electrolyte. The rate constant values in general found to decrease with an increase in pH indicating that the electrode reaction tends to become more and more irreversible with change in pH.

Electrodemechanism

Based on the result obtained the Electrodemechanism proposed is as in Scheme 1.



Scheme 1 : Reduction mechanism of monalide at pH 4.0

Analysis

The polarographic peak is due to the reduction of carbonyl group and therefore preferred for the analysis of agriculture and water samples. The optimum pH for obtaining well resolve peak for quantitative determination of monalide are found to be 4.0.

Investigated compound was found to exhibit well resolved peak at pH 4.0, and the sharp well resolved peak was chosen for quantitative studies. Peak currents were linear over the monalide concentration range of 1.0x 10⁻⁵ M to 1.0x10⁻¹⁰ M with lower detection

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limits of 1.09×10^{-9} M. The relative standard deviation and correlation coefficients were found to be 1.25%, 0.996 respectively for 10 replicates.

Recommended analytical procedure

A standard solution of monalide (1.0×10^{-5} M) prepared in DMF. 1 mL of standard solution were transferred into a polarographic cell and made up with 9 mL of supporting electrolyte (pH 4.0) and de oxygenated with nitrogen gas for 10 min, subjected to polarography. After obtaining the polarogram, a small increment of standard solution of monalide is added to polarographic cell and deoxygenated for 10 min and polarogram were recorded under similar conditions and validity of method was checked. In the same manner 10 polarograms are recorded for 10 standard additions. The optimum conditions for analytical determination were found to be at pH.4.0 with drop time of 2 sec, a pulse amplitude of 60 mV.

Determination of monalide in spiked vegetable samples

25g of samples were digested and macerated with two 20mL portions of ethanol-demineralized water (1+1), filtered through a Whatman filter paper No.41 and filtrate was centrifuged at 1850g for 10 min The filtrate was quantitatively transferred into a 50mL calibrated flask and made up to the mark with 50% ethanol and were added with known amounts of monalide.

Aliquots transferred into polarographic cell and analyzed by following recommended analytical procedure. Results obtained for the determination of the herbicide in vegetables samples are presented in TABLE V.2. Mean recoveries obtained for monalide ranged from 98.00 to 99.85%.

TABLE 2 : Recoveries of monalide in spiked vegetable samples

Sample	Amount added $\mu\text{g/ml}$	Amount found $\mu\text{g/mL}$	recovery(%)	Standard Deviation
	1.0	0.99	99.00	0.050
potato	3.0	2.99	99.66	0.022
	5.0	4.98	99.60	0.028

CONCLUSION

Electroanalytical procedures have been identified as powerful methods for the analysis of different pesticides down to 10^{-9} M level with reproducible results. The described electroanalytical method have conveniently been applied and which has been routinely adopted for the determination of pesticides in food grains, vegetables and other environmental samples.

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