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## Electrochemical behaviour of the herbicide oxabetrinil and its determination in soil and water samples

N.Y.Sreedhar, S.Rajasekar Reddy\*, P.Reddy Prasad, K.Chandra Mohan

Electroanalytical Lab, Department of Chemistry, Sri Venkateswara University, Tirupati, (INDIA)

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### ABSTRACT

A sensitive differential pulse adsorptive stripping voltammetric method for the determination of oxabetrinil with universal buffer solution was described. The method was based on the adsorptive accumulation of oxabetrinil at Hanging Mercury Drop Electrode (HMDE). The cyclic voltammograms demonstrate the adsorption of this compound at the mercury electrode. A systematic study of various operational parameters that affect the stripping response was carried out by DP-AdSV with accumulation potential of -1.0V and accumulation time 60 sec. From the calibration method, it is observed that the peak current shows a trend found to be linear over the concentration range  $1.0 \times 10^{-8}$ M to  $1.0 \times 10^{-5}$  for with lower detection limit  $0.99 \times 10^{-7}$ M. Relative standard deviation and correlation coefficient were found to be 0.97% and 0.996 for oxabetrinil. © 2011 Trade Science Inc. - INDIA

### KEYWORDS

Adsorptive stripping  
voltammetry (AdSV);  
Oxabetrinil;  
Soil;  
Water samples.

### INTRODUCTION

Oxabetrinil [(Z)-1, 3-dioxolan-2-ylmethoxyimino (phenyl) acetonitrile] have long persistence which leads to accumulation in soil and crops that have been treated directly. Prevention of negative effects of herbicides requires a systemic control of their remains in agricultural products, food, soil and water.

Parilla et al.<sup>[1]</sup> employed SPE and HPLC photo diode array detection for determination of pesticide residues in water samples. Moore et al.<sup>[2]</sup> reported multi residue analytical method for analysis of pesticides in water using SPE and LC-MS. Bosschere et al.<sup>[3]</sup> applied daphnia magna bio assay for rapid screening of insecticide residues in dogs and cats. Reddy et al.<sup>[4-6]</sup> extensively studied electrochemical behaviour of azomethine group containing pesticides.

### MATERIALS AND METHODS

The electrochemical measurements were carried out with model Metrohm 757 VA computer. Three electrode systems consisting of hanging mercury electrode (HMDE) as working electrode, Ag/AgCl (salt KCl) was used as a reference electrode and a platinum wire as an auxiliary electrode which displays negative potential range. Elico Li-129 model glasscalomel combined electrode was employed for measuring pH values. All reagents used were of analytical reagent grade. Double distilled water was used throughout the. In the present investigation universal buffers of pH range 2.0 to 12.0 are used as supporting electrolytes and are prepared by using 0.2 M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate solutions. Oxabetrinil obtained from Meghamani Organics Ltd., Paldi,

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Ahmedabad, India. The purity of the pesticide sample was tested by thin layer chromatography and also melting point determinations.

### Differential pulse-adsorptive stripping voltammetric studies

By using DP-AdSV oxabetrinil yielded single peak at HMDE (Figure 1). This peak was follow to establish the optimum conditions. The standard addition and calibration methods have been employed to estimate oxabetrinil in environmental matrices.

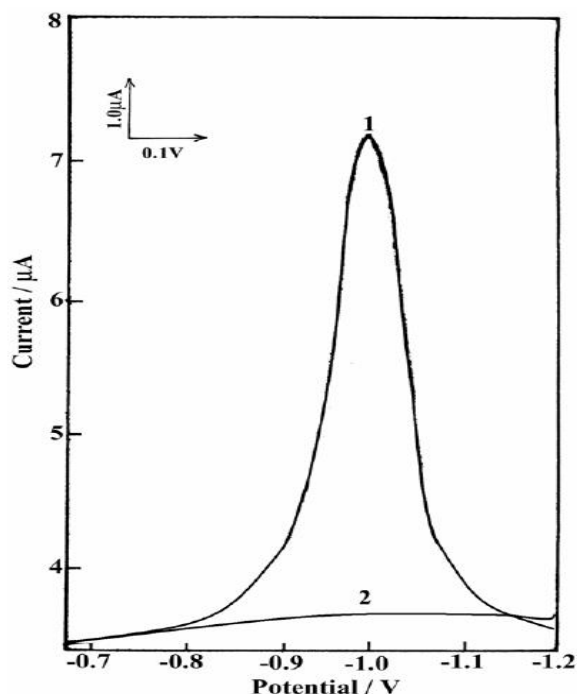


Figure 1 : Typical differential pulse adsorptive stripping voltammogram of oxabetrinil at HMDE (pH 4.0): (1) accumulation time: 60 sec., accumulation potential: -1.0 V; rest time: 10 sec. (1) concentration  $1.0 \times 10^{-5} \text{M}$ , (2) blank

### Effect of pH

The pH of a solution is a critical factor affecting both the rate and equilibrium state of the accumulation process and rate of the electrode reaction. The influence of the pH on the DP-AdSV response was studied at HMDE at  $1.0 \times 10^{-5} \text{M}$  with accumulation times 60 sec. respective electrode between pH 2.0 to 6.0 it can be observed from Figure 2 that the maximum peak potentials were obtained with pH 4.0. The shift of the peak potentials towards more negative values indicating proton participation in the reduction process.

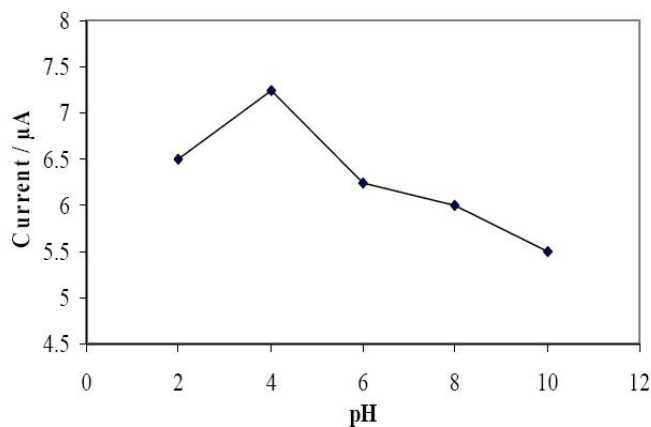


Figure 2: Effect of pH on oxabetrinil solution at HMDE; accumulation time: 60 sec.; accumulation potential: -1.0V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate:  $40 \text{ mVs}^{-1}$ ; pulse amplitude: 25 mV

### Effect of accumulation potential

The influence of the accumulation potential on the AdSV signal was studied with accumulation time of 60 sec. at HMDE for  $1.0 \times 10^{-5} \text{M}$  oxabetrinil solution. From the Figure 3 it was observed that  $i_p$  value for -1.0V at pH 4.0 because of an increase accumulation rate, due to the more favourable alignment of molecules by the electric field at the electrode solution interface.

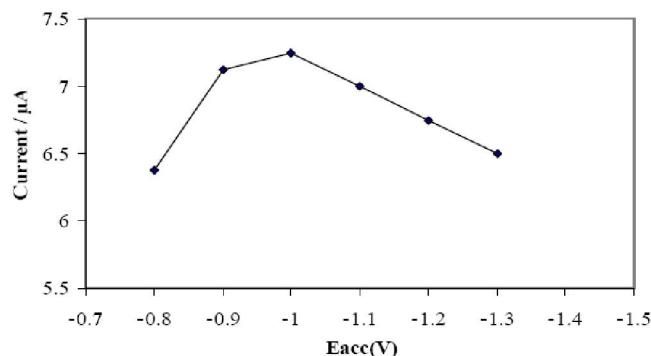
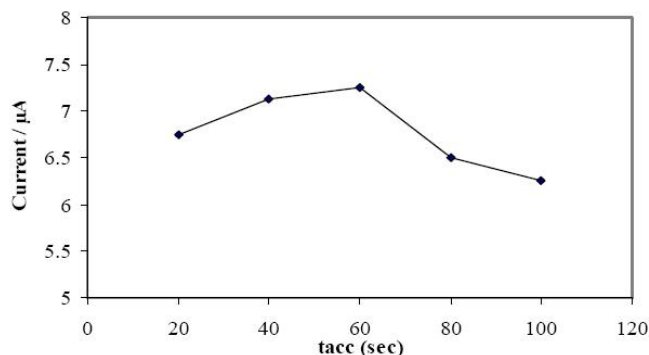


Figure 3 : Effect of accumulation potential on the DP-AdSV response of oxabetrinil at HMDE; accumulation time: 60 sec; rest time: 10 sec., stirring rate: 2000 rpm; scan rate:  $40 \text{ mVs}^{-1}$ ; pulse amplitude: 25 mV

### Effect of accumulation time

Figure 4 shows plot of cathodic peak current for adsorptive stripping voltammetry against accumulation time ( $t_{acc}$ ) for different concentrations of oxabetrinil. At first, peak current increased linearly with  $t_{acc}$  indicating that before adsorptive equilibrium reached, the longer the pre-concentration time, the more the oxabetrinil were adsorbed and larger the peak current. However,

after 60 sec., the peak current tended to level off, illustrating that adsorptive equilibrium of oxabetrinil on the mercury electrode surface was achieved.



**Figure 4 :** Effect of accumulation time on the DP-AdSV response of oxabetrinil at HMDE; accumulation potential: -1.0 V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 40 mVs<sup>-1</sup>; pulse amplitude: 25 mV

### Effect of scan rate

The effects of varying the potential scan rate on the reduction peak current of oxabetrinil were examined. The reduction peak current increases linearly with scan rate over the range from 25 mVs<sup>-1</sup> to 60 mVs<sup>-1</sup> as expected for the reduction of oxabetrinil being adsorbed. Best sensitivity was achieved at a scan rate of 40 mVs<sup>-1</sup> for oxabetrinil.

### Characterisation of peak / wave

Oxabetrinil were found to give a single well defined peak in acidic solutions (2 < pH < 6). Increase of pH from 4.0 leads to decrease of the peak current. In the acidic medium the peak of the compound is due to the reduction of >C = N group in two electron process. Typical cyclic voltammogram of oxabetrinil are shown in Figure 5.

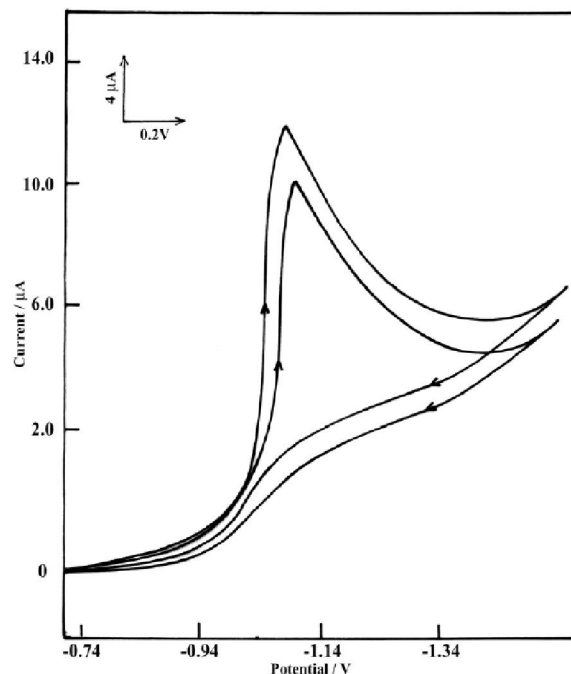
## ELECTRODE MECHANISM

Based on the above results and from the literature, the following reduction mechanism may be proposed for oxabetrinil in entire pH range is shown in Scheme 1.

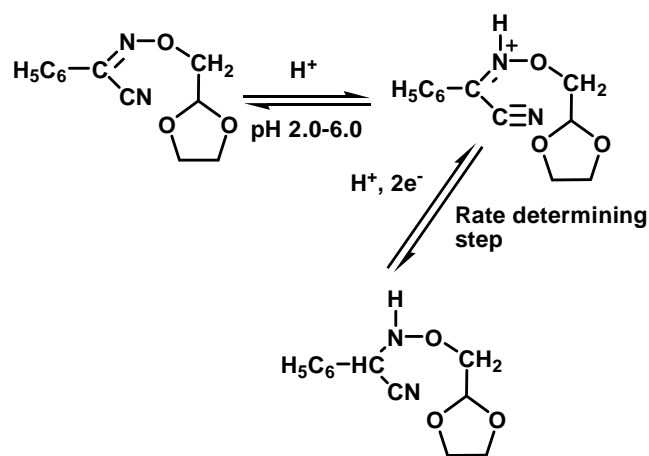
### Kinetic data

Kinetic parameters such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constants for oxabetrinil are given in TABLE 1. The diffusion coefficient values were noticed to be in good agreement from cyclic voltammetry. The heterogeneous forward rate con-

stants were decreasing with an increase in pH of the supporting electrolyte, which may account for the shift of reduction potentials towards more negative values with increase in pH. This trend is particularly evident where the proton transfer is involved in the electrode process.



**Figure 5 :** Typical cyclic voltammogram of oxabetrinil at pH 4.0 concentration: 0.5 mM; scan rate: 50 mVs<sup>-1</sup>



**Scheme 1 :** Reduction mechanism of oxabetrinil

**TABLE 1 :** Typical cyclic voltammetric data of oxabetrinil concentration: 0.5mM scan rate: 50 mVs<sup>-1</sup>

pH of the supporting electrolyte	$-E_p$ V	$i_p$ $\mu A$	$\alpha n_a$	$D \times 10^6$ $cm^2 s^{-1}$	$k^0_{th}$ $cm s^{-1}$
2.0	0.99	13.0	0.38	2.32	$6.12 \times 10^{-9}$
4.0	1.05	12.0	0.30	2.13	$8.12 \times 10^{-10}$
6.0	1.13	10.8	0.23	1.79	$3.21 \times 10^{-11}$

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### Analysis

Well defined and well resolved wave / peak of oxabetrinil obtained at pH 4.0 was used for the quantitative determination of oxabetrinil in environmental samples. Both calibration and standard addition methods are used for the quantitative determination of the oxabetrinil. From the calibration method, it is observed that the peak current shows a trend found to be linear over the concentration range  $1.0 \times 10^{-8} \text{M}$  to  $1.0 \times 10^{-5}$  for with lower detection limit  $0.99 \times 10^{-7} \text{M}$  for oxabetrinil. For 5 replicates, relative standard deviation and correlation coefficient were found to be 0.97% and 0.996 for oxabetrinil.

### Recommended analytical procedure

The stock solution ( $1.0 \times 10^{-3} \text{M}$ ) of oxabetrinil are prepared by dissolving the required quantity of the electroactive species in methanol. Standard solutions are prepared by dilution of stock solution with suitable amount of methanol. 1 mL of the standard solution is transferred into voltammetric cell and is made with 9 mL of the supporting electrolyte and then deoxygenated by bubbling oxygen free nitrogen gas for 10 min. After recording the voltammogram, small increments of standard solutions (0.2 mL) are added and then voltammograms are recorded for each addition under similar experimental conditions. The optimum conditions for the analytical determination of oxabetrinil at pH 4.0 are found to be drop time of 2 sec., pulse amplitude of 25 mV and applied potential of -1.0 V for oxabetrinil.

### Determination of oxabetrinil in water samples

River water samples, which received run-off water from agricultural field, were collected from swarnamukhi river belt, Vakadu, Nellore district, A.P.,

**TABLE 2 : Recoveries of oxabetrinil in spiked water samples**

Sample	Amount added ( $\mu\text{g/mL}$ )	Amount found ( $\mu\text{g/mL}$ )	Recovery (%)	Standard deviation
Water (Creak)	4.0	3.81	95.25	0.021
	8.0	7.81	97.62	0.007
	12.0	11.5	96.50	0.016
Water (River)	4.0	3.96	99.00	0.009
	8.0	7.91	98.77	0.010
	12.0	11.80	98.33	0.018

India. These samples were filtered through a Whatman No.41 filter paper and added with known amount of oxabetrinil were added. Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analysed as described above. The recoveries of oxabetrinil in two samples ranged from 98.0% to 99.3% and the results are summarized in TABLE 2.

### Determination of oxabetrinil in soil samples

The same procedure has been applied for the determination of oxabetrinil in soil samples collected from Pennar delta, Nellore, Swarnamukhi delta Vakadu, Nellore Dt, AP, India. Collected soil sample were dried and allowed to pass through a 2.8 nm sieve and subsequently homogenised in ball mill. Aliquots (50 g) of soil sample were added with known amounts of both solutions and kept contact for 24 hours. After this period, the mixture was extracted with 20 ml of methanol three times. The solvent evaporated and the residue was dissolved in methanol and subjected to voltammetry. By means of standard addition method, the quantity of herbicide was estimated. The recoveries in two samples ranged from 95.00% to 99.00% and are given in TABLE 3.

**TABLE 3 : Recoveries of oxabetrinil in spiked soil samples**

Sample	Amount added ( $\mu\text{g/mL}$ )	Amount found ( $\mu\text{g/mL}$ )	Recovery (%)	Standard deviation
Soil (Swarnamukhi delta)	4.0	3.80	95.00	0.031
	8.0	7.82	97.75	0.017
	12.0	11.56	96.33	0.026
Soil (Pennadelta)	4.0	3.96	99.00	0.019
	8.0	7.90	98.75	0.010
	12.0	11.82	98.50	0.018

## CONCLUSION

In conclusion, the proposed work a simple and economical low consumption differential pulse adsorptive stripping voltammetric method can be used satisfactorily for determination of oxabetrinil in soil and water samples. The proposed method using AdSV not only is one of the most sensitive methods for the determination of oxabetrinil but also excellent in terms of selectivity and simplicity.

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