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VOLTAMMETRIC BEHAVIOUR OF CARBONYL GROUP CONTAINING PESTICIDES TOPRAMEZONE, FENOMIDONE AND METHIOCARB

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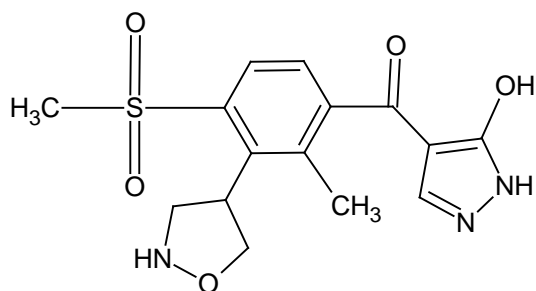
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I. INTRODUCTION

Topramezone [3-(4,5-dihydro-1,2-oxazol-3-yl)-4-methyl-*o*-tolyl](5-hydroxy-1-methylpyrazol-4-yl) methanone] is broad spectrum compound used for seed treatment and for the protection of fruits and vegetables.

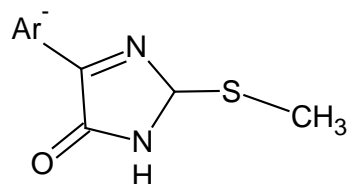


Most of the methods reported in the literature for the determination of the topramezone is based on the several techniques. Fungicides are widely used for crops that lack natural resistance to the fungal species involved. These chemicals are used to treat foliage diseases of some crops. Seeds for damping off, soil in seed beds for root and to control turf and transplant diseases. Krueva et al.[1] reported potential washing methods with LC-ESI-MS to determine pesticide residues in

oranges. Chandra mouli et al.[2] reported GC/LC-MS method for rapid screening of 250 pesticides including methiocarb in aqueous matrices.

Kateina et al.[3] evaluated the suitability of organic solvent for GC analysis of pesticides. A solid-phase micro extraction method and HPLC with diode array detection of fungicide in wine was developed by Millan et al.[4]. Gimeno et al.[5] monitored antifouling agents in water samples by on-line solid phase extraction liquid chromatography-atmospheric pressure chemical ionization mass spectrometry method. Dimitral et al.[6] determined fungicides in natural water using SPME and GC coupled with electron-capture and mass spectrometric detection. Carabias maltinez[7] developed a procedure for analysis of pesticide residue in matrices with high lipid contents by membrane separation coupled online HPLC system. HPLC-DAD [8-10] with multivariate calibration, partial least squares calibration and with spectrograms for the quantification mixtures of pesticides. Application of solid phase disc extraction,[11] dispersion extraction,[12] and partition cartridges followed by gas and liquid chromatography for the determination of fungicides in environmental water, oranges, vegetable samples.

Fenamidone((*S*)-1-anilino-4-methyl-2methylthio-4-phenylimidazolin-5-one) is imidazole fungicide. It is broad spectrum pesticide used to protect crops from fungal diseases.

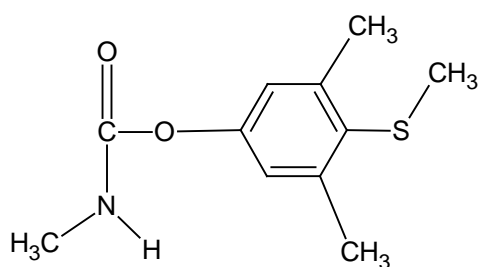


Susana et al.[13] reported GC/MS for analysis of fenamidone in grapes and wine. De mello et al.[14] reported LC with diode array

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detection (DAD) method for screening of pesticides including fenamidone in grapes and wines. Danion et al.[15] reported solid phase extractin method coupled with LC/MS for isolation of fenamidone from plants. Luigi et al.[16] analised three fungicide residues including fenamidone by applying pseudo first order kinetics and half life method in wine. Schreiber et al.[17] reported triple quadropole mass spectroscopy with liquid chromatographic (LC/MS/MS) method for analysis of fenamidone residues in food stuffs. Lutz alder et al.[18] reported GC/MS, LC/ MS/ MS, GC/ EI/ MS and LC/ ESI/ MS/MS methods for analysis of 500 high priority pesticide residues including fenamidone. Donbroun[19] reported GC/MS/MS and LC/MS/MS methods for analysis of pesticide residues in fruits and vegetables. Lambropoulou et al.[20] reported coupling of head space solid space micro extraction with ultra sonic extraction for determination of fenamidone residues in birds by using GC.

Methiocarb (4-methylthio-3,5-xyllyl methyl carba mate) is registered as acaricide for the control or kill mites in agricultural fields. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing. The traditional techniques used for such purpose are liquid chromatography and gas chromatography with electron capture detection, which is one of the most adequate due to the very low value obtainable for the detection limit.



Yang et al.[21] reported chromatographic methods ie HPLC-,GC,super critical fluid chromatography and TLC to determine methyl carbamate pesticide residues in water, soil and plant tissues. Chiron et al.[22] employed on line solid phase extraction LC/MS to investigate methiocarb residues in water samples. Alvarez et al.[23] performed the spectrophotometric determination of carbamates including methiocarb. Msahiro et al.[24] determined methyl carbamaete

pesticide residues in foods by using accelerated solvent extraction ASE and HPLC with post column fluorescence.

Parilla et al.[25] reported SPE and HPLC/DAD method to determine pesticide residues in water. Richerd[26] employed HPLC method to determine N-methyl carbamate recidues using post column hydrolysis electro chemical detection. Aulakh et al.[27] reported solid phase micro extraction HPLC for analysis of pesticides. Tomomi et al.[28] devoloped anew analytical method for determination of nine pesticide residues including methiocarb in fruits and vegetables using ESI-LC/MS/MS with direct sample injection into a short column. Davia osselton et al.[29] reported GLC, HPLC/DAD and TLC for determination of 51 common pesticides including methiocarb. Parilla et al.[30] employed SPE and HPLC photo diod array detection for determination of pesticide residues in water samples. Leejeong et al.[31] reported HPLC with UV detection method using super critical fluid extractin to determine methyl carbamates from spicked matricies. Wang et al.[32] reported SMPE/HPLC method for analysis of pesticide residues from straw berries. Feride kocl et al.[33] employed HPLC wth post column derivatisation and flurascence detectin for analysis of methiocarb in honey. Jose fernondo et al.[34] reported HPLC with chemiluminiscence detection for determination of carbamates. Moore et al.[35] reported multi residue analytical method for analysis of pesticides in water using SPE and LC/MS.

II. MATERIALS AND METHODS

a) Apparatus

The electrochemical measurements were carried outwith model Metrohm 757 VA computrace. Three electrodesystems consisting of hanging mercury electrode (HMDE) as working electrode, Ag/AgCl (salt KCl) wasused as a reference electrode and a platinum wire as an auxiliary electrode which displays negative potential range. Eli co Li-129 model glass calomel combined electrode was employed for measuring pH values.

b) Reagents

All reagents used were of analytical reagent grade. Double distilled water was used throughout the analysis. In the present investigation universal buffers of pH range 2.0 to 6.0 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, pesticide samples obtained from Rankem.

III. RESULT AND DISCUSSION

In case of methiocarb the carbonyl group is present in open chain it has the rich electronic environment because of nitrogen attached to carbonyl carbon due to this the reduction of methiocarb is some what difficult but at the same time oxygen present on carbonyl carbon suppress the electron density and facilitate to reduction when compared to the carbonyl groups present in other two compounds under observation that is fenomidone and topramezone which has one carbonyl group for each methiocarb reduces at higher negative potentials.

In topramezone the carbonyl group is present in between two rings it has the poor electronic environment because of electron withdrawing nature of aromatic rings attached to carbonyl carbon due to this the reduction of topramezone is some what easy when compared to the carbonyl group present in fenomidone. topramezone reduces at lower negative potentials.

Though there is a carbonyl group which is present in the ring fenomedone reduces at greater negative potentials than topramezone because of the electron donating nitrogen adjacent to carbonyl carbon.

a) *Differential pulse-adsorptive stripping voltammetric studies*

The DP-Adsv behaviour of topramezone, fenomidone and methiocarb ($1 \times 10^{-5} \text{M}$) was investigated over pH range 2.0 to 6.0 at the HMDE. The Faradic response exhibited is an adsorptive reduction peak (Fig. 1) which corresponded to the reduction of carbonyl group ($>\text{C} = \text{O}$) of topramezone, fenomidone and methiocarb.

b) *Effect of pH*

The position of peaks is strongly pH dependent in that it shifts to more negative potentials with increasing pH. No reduction was observed in basic medium $\text{pH} < 8.0$.

c) *Characterization of waves / peaks*

All the three compounds exhibits only one voltammetric wave / peak over the pH range 2.0 to 6.0 with all techniques. This wave / peak is attributed to the reduction of carbonyl group involving 2 electrons. Typical cyclic voltammogram

are shown in Fig. 2. No reduction peak is observed in basic medium ($8 \leq \text{pH} \leq 12$) for carbonyl groups due to the precipitation of electroactive species.

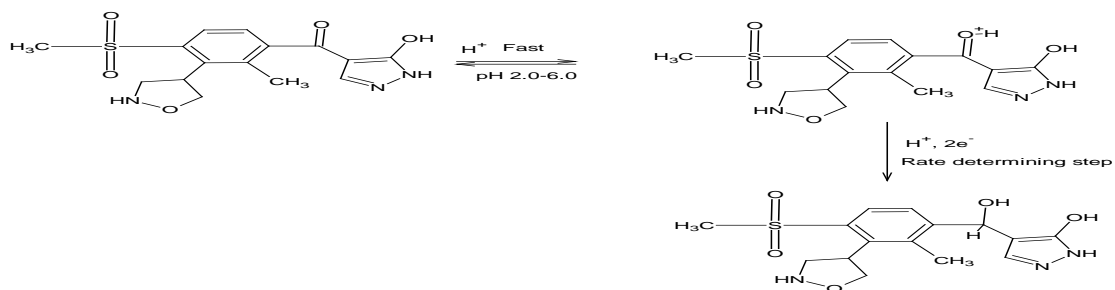
d) *Recommended analytical procedure*

A stock solution ($1.0 \times 10^{-3} \text{M}$) of samples prepared by dissolving the appropriate amount of the electro active species in dimethyl formamide. One ml of the standard solution is transferred into the voltammetric cell and made upto 9 ml with the supporting electrolyte to get the required concentration and then deoxygenated by bubbling nitrogen gas for 10 min. After recording the voltammograms, small increments of the standard solution are added and the voltammograms are recorded for each addition under similar conditions. Optimum conditions for this analysis are pH 4 concentration: $1 \times 10^{-5} \text{M}$, and scan rate : 45 mVs^{-1}

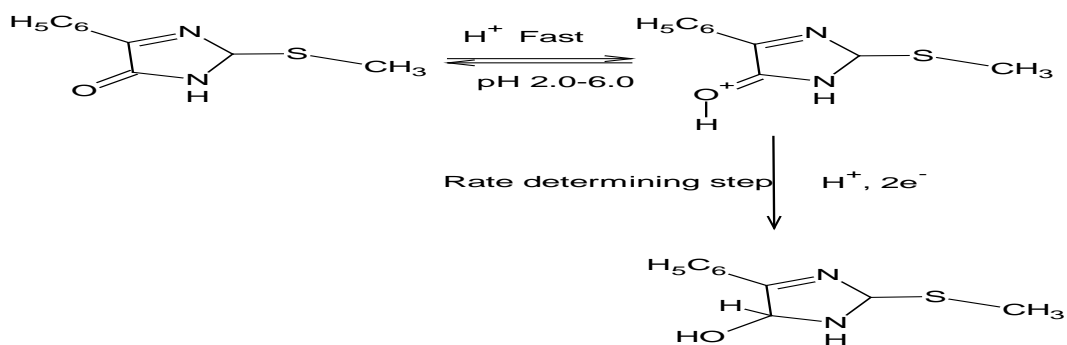
e) *Kinetic data*

The values obtained for diffusion coefficient, transfer coefficient and heterogeneous forward rate constant are given in Tables 1,2 and 3. The diffusion coefficient values evaluated from cyclic voltammetry is in good agreement indicating the diffusion controlled and adsorption at the electrode surface. The variation of diffusion current with the pH of the supporting electrolyte influences the diffusion coefficient values also to vary in the same manner. The reason for slight variation in diffusion coefficient values with increase in pH may be attributed to the decrease in the availability of protons with increase in pH of the supporting electrolyte. The rate constant values are in general found to decrease with increase in pH indicating that the electrode reaction tends to become more and more irreversible with change in pH. Based on the experimental results obtained from all the techniques employed, a possible electrochemical reduction mechanism of the three compounds under investigation has been suggested on the basis of protons and electrons involved in the reduction as shown in scheme 1,2 and 3.

Scheme 1 : Reduction mechanism of topramezone



Scheme 2 : Reduction mechanism of fenomidone



Scheme 3 : Reduction mechanism of methiocarb

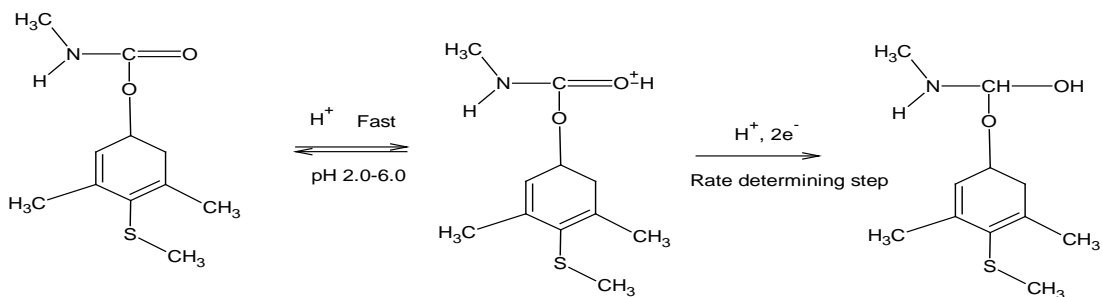


Table 1 : Typical cyclic voltammetric data of topramezone

pH	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	αn_a	$\frac{D \times 10^6}{\text{cm}^2 \text{ s}^{-1}}$	$\frac{k^0_{f,h}}{\text{cm s}^{-1}}$
2.0	0.153	7.4	0.327	7.621	3.149×10^{-3}
4.0	0.201	5.9	0.366	6.994	7.072×10^{-4}
6.0	0.301	4.9	0.318	4.971	2.542×10^{-4}

Table 2 : Typical cyclic voltammetric data of fenamidone

pH	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	αn_a	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k^0_{f,h}}{cm s^{-1}}$
2.0	0.16	9.3	0.62	2.82	8.20×10^{-2}
4.0	0.36	5.7	0.60	2.60	4.32×10^{-3}
6.0	0.38	8.2	0.61	2.30	3.89×10^{-6}

Table 3 : Typical cyclic voltammetric data of methiocarb

pH	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	αn_a	$\frac{D \times 10^6}{cm^2 s^{-1}}$	$\frac{k^0_{f,h}}{cm s^{-1}}$
2.0	0.36	5.81	0.99	5.66	2.60×10^{-6}
4.0	0.41	6.0	0.92	5.49	1.57×10^{-7}
6.0	0.61	5.55	0.88	5.22	6.47×10^{-9}

IV. CONCLUSION

In the above investigation highly potent carbonyl group containing pesticides had selected to get detailed information on the reduction behaviour of carbonyl group and electrode kinetics concerned employing cyclic voltammetry, differential pulse adsorptive stripping voltammetry, controlled potential electrolysis and millicoulometric techniques. The method shows a good reproducibility and high accuracy compared with spectrophotometric, spectrofluorimetric and chromatographic methods of analysis.

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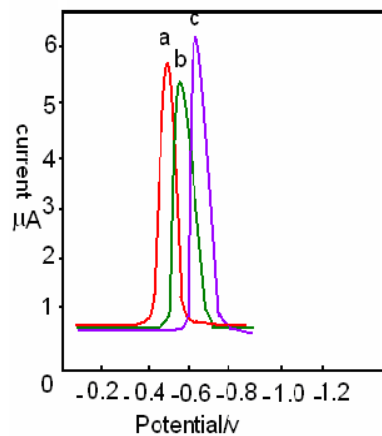


Fig 1: Stripping voltammograms at pH 4

A=Topramezone
B=Fenomidone
C=Methiocarb

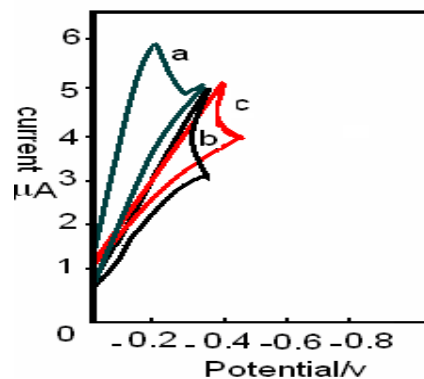


Fig 2: cyclic voltammograms at pH 4

A=Topramezone
B=Fenomidone
C=Methiocarb