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Voltammetric Determination of Bromethalin by using Polymer Coated Ion Selective Bare Carbon Electrode

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I. Introduction

Bromethalin [α,α,α-trifluoro-N-methyl-4,6-dinitro-N-(2,4,6-tribromophenyl)-o-toluidine] is a new commercial dinitroaniline rodenticide for the control of comensal rodents. Current methods for the analysis of pesticides containing nitro group compounds involve either liquid –liquid extraction [1] solid-phase extraction (SPE)[2] supercritical fluid extraction (SCFE) and solid phase micro extraction (SPME) [3].The main disadvantages of these methods were use of large quantities are often toxic and not eco-friendly solvents, the elaborate cleaning up time-consuming procedures and the need for concentration of analytes before analysis [4]. Mesmer and Fluler [5] reported high performance liquid chromatography with UV-VIS spectrometric and HPLC negative-ion. Braselten and Jonson [6] reported TLC extended by GC/MS to determine bromethalin in environmental samples. Melissa et al [7] developed a new type of all-solid-state ion-selective electrode based on a transuding layer of a network of single-walled carbon nanotubes. The extraordinary capacity of carbon nanotubes to promote electron transfer between heterogeneous phases made the presence of electroactive polymers or any other ion-to-electron-transfer promoter. Javad Zolgharnein et al. [8] reported simultaneous determination of propanil and monalide by modified glassy carbon electrode with nickel oxide nanoparticles, using partial least squares modified by orthogonal signal correction and wavelet packet transform.Though metal and non metal electrodes used for electro analysis [9-10] better reproducibility achieved in this approach.

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II. Experimental

a) Apparatus and Electrodes

The electrochemical measurements were carried out with Metrohm model 101 potentiostat and galvanostat. The three-electrode system consisted of polymer coated ion selective bare carbon electrode prepared by using poly vinyl chloride (PVC) solvent membrane and tetra phenyl borate(TPB) as ion pairing agent used as working electrode. Ag/AgCl reference electrode and a platinum wire used as auxiliary electrode. The electrodes joined the cell through holes in its Teflon cover. All of the potentials given in this work were measured with respect to this reference system. Electrochemical experiments were carried out in a voltametric cell at room temperature. A magnetic stirrer was used during the accumulation step. The Eli co Li-129 model glass calomel combined electrode was employed for measuring pH values.

b) Reagents and solutions

All reagents used were of analytical reagent grade. Double distilled water is used throughout the analysis. In the present investigation, universal buffers in the pH range 2.0 to 6.0 are used as supporting electrolytes and prepared using 0.2 M boric acid, 0.05 M citric acid and 0.1 M tri sodium orthophosphate solutions. Pesticide samples are obtained from Bayer crop, India, Ltd.

III. Result and Discussion

Bromethalin is found to a 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 2 nitro groups in 4 electron process. Typical cyclic voltammogram shown in Fig.1.

The reduction process of bromethalin is found to be diffusion controlled and adsorption on the electrode surface in the buffer systems studied as evidenced from linear plot $i_p$vs $v^{1/2}$ passing through origin. The shift of peak potential (E_p) towards more negative values with increase in concentration of depolarizer, shows that the electrode process is irreversible. This is further confirmed by log-plot analysis. The variation of peak potentials with scan rates and absence of anodic peak in the reverse scan in cyclic voltammetry indicates the irreversible nature of the electrode processes. The dependence of i_p/pH curves shows a behavior in accordance with a process in which a proton transfer provides the reduction of the acid form to form an electro active species. The number of protons taking part in the rate determining step is 4.

Millicoulometry is employed to find out the number of electrons involved in the electrode process. The results obtained from millicoulometry have shown that the number of electrons is 4 for bromethalin. The number of protons involved in the rate determining step (scheme I) of the electrode process is 4. Controlled potential electrolysis experiments are carried out at -0.8 V at saturated colomel electrode at pH 4.0.to collect reduction product.

Kinetic data such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constants obtained for bromethalin is summarized in table 1.0.The diffusion coefficient values are noticed to be in good agreement from cyclic voltammetry. The heterogeneous forward rate constants were decreasing with an increase in pH of the supporting electrolyte, which may responsible 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.

a) Dp-ASV studies and optimum conditions

Peak of bromethalin at working electrode (Fig.2.0) is attributed to reduction of bromethalin.This peak followed to establish the optimum conditions. The standard addition and calibration methods have been employed to estimate the compound in grain samples. Maximum peak potentials are obtained with pH 4.0.The shift of the peak potentials towards more negative values indicating proton participation in the reduction process.

The effects of varying the potential scan rate on the reduction peak current of bromethalin is examined. The reduction peak current increases linearly with scan rate over the range from 20 mVs^{-1} to 60 mVs^{-1} as expected for the reduction of being observed. Best sensitivity achieved at a scan rate of 50 mVs^{-1}.

IV. Recovery Experiments

a) Analysis

Well defined and well resolved AdSV peaks of bromethalin obtained at pH 4.0 is used for the quantitative estimation of bromethalin in water and soil samples. Both calibration and standard addition methods are used for the quantitative determination of bromethalin. From the calibration method, it is observed that the peak current shows a trend found to be linear over the concentration range Peak currents were linear over the concentration range of 1.4x 10^{-8} M to 1.3×10^{-9} M with lower detection limit of 10^{-10} M. The relative standard deviation and correlation coefficients are found to be 1.15%, 0.985 respectively for 10 replicates. Calculations made by standard addition method.

b) Recommended analytical procedure

The stock solution (1.0 x 10^{-5} M) of bromethalin is 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 added 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) added and then voltammograms recorded for each addition under similar experimental conditions. The optimum conditions for the analytical determination of bromethalin are pH 4.0 and scan rate 50 mVs^{-1}.

c) Determination of bromethalin in spiked grain samples

The developed analytical procedure has been applied to the quantitative estimation bromethalin in grain samples. Known amount of bromethalin is sprayed on grain samples (25 g) and left for 1-2 hours. Then the samples are weighed, crushed and homogenized and treated with 50mL acetone and evaporated to dryness. The residue of bromethalin dissolved in methanol and transferred to a 100 mL volumetric flask. 1 mL of the standard solution is transferred into voltammetric cell and added 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) were added and then voltammograms recorded for each addition under similar experimental conditions. Results obtained for the determination of bromethalin in grains by this method ranged from 98.66 to 99.50% which indicates

the high accuracy and reproducibility of the proposed method. The results are summarized in table.2.0

V. Conclusion

The present part describes the detailed study of electrochemical reduction of nitro group containing pesticide bromethalin from the results obtained from cyclic voltammetry, differential pulse adsorptive stripping voltammetry, millicoulometry and controlled potential electrolysis in methanol as solvent in the supporting electrolytes of pH ranging 2.0 to 6.0. To overcome partial load over current density and for improved electrode kinetics polymer coated ion selective bare carbon electrode prepared by using poly vinyl chloride (PVC) solvent membrane and tetra phenyl borate (TPB) as ion pairing agent used as working electrode to avoid the environmental pollution arises due to metal electrodes.

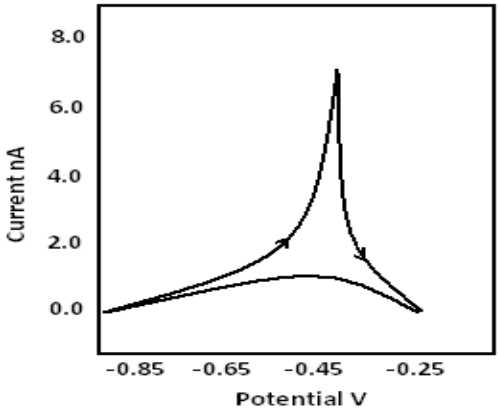


Fig.1.0: Typical cyclic voltammogram of bromethalin at polymer membrane electrode, pH 4.0 concentration: 0.5 mM; scan rate: 50 mVs^{-1}

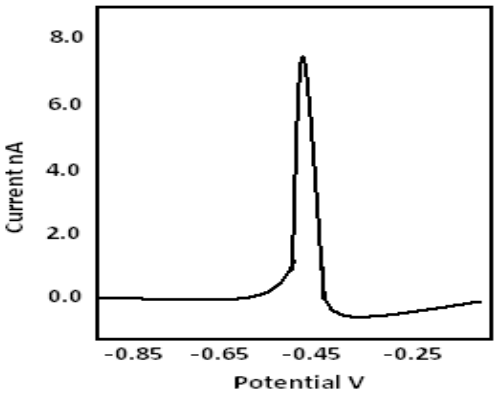
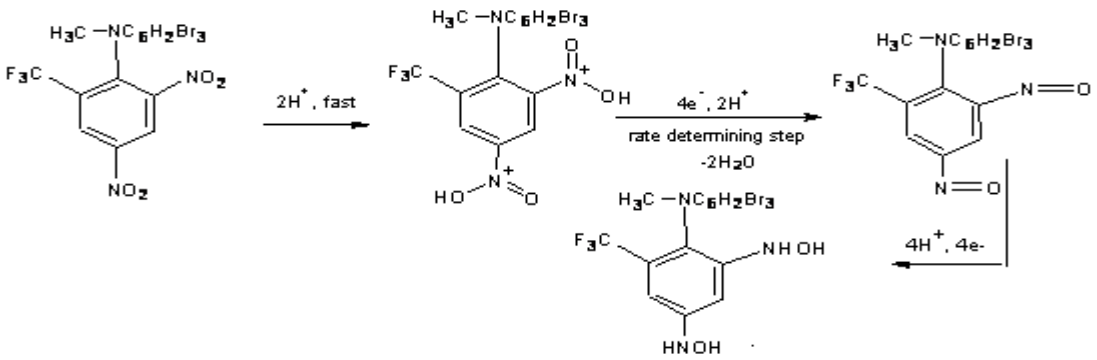


Fig. 2.0: Typical differential pulse adsorptive stripping voltammogram of bromethalin at polymer membrane electrode, pH4.0, scan rate: 50mVs^{-1}



Scheme I: Reduction mechanism of bromethalin at polymer membrane electrode: pH 4.0.

Table 1: Typical cyclic voltammetric data of of bromethalin:concentration: 0.5 mM, scan rate: 50mVs^{-1}

pH	Ep/V	Ip/nA	$\alpha\, n_a$	$\frac{D \times 10^6}{cm^2\ s^{-1}}$	$\frac{k^0_{f,h}}{cm\ s^{-1}}$
4.0	0.45	6.5	0.42	1.28	1.02 x 10^{-10}

Table 2: Recoveries of of bromethalin in spiked grain samples

Grains	Amount added (ng/mL)	Amount found (ng/mL)	Recovery (%)	Standard deviation
Black gram	2.0	1.99	99.50	0.021
Rice	3.0	2.96	98.66	0.007

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