Relative Recoveries of Chlorophacinone at various Working Electrodes in Voltammetry

D.Sreevani

Lecturer in chemistry,MRR Govtarts and science College,Udayagiri,Andhrapradesh,India

==

Abstract:

This paper enlightens the variance in reduction behavior of rodenticide Chlorophacinone on the surface of a variety of working electrodes that is hanging mercury drop electrode, bare carbon electrode,carbon nano tubes paste electrode by using a selective and sensitive adsorptive stripping voltammetry and reduction pattern determined by using cyclic voltammetry. Borate buffer used as supporting electrolyte which is useful to enhance the conductivity during experiment. Calculations were made by standard addition method.

Key words: Chlorophacinone ,Adsorptive Stripping Voltammetry,Hanging Mercury Drop Electrode,Bare Carbon Electrode,Carbon Nano Tubes Paste Electrode.

==

Introduction: As administration of agrochemicals is unavoidable now a days for enhancement of yields to compensate the growing population there is necessity to minimize the damage to the environment .Being agrochemicals has collateral effects[1-6] application should be selective that is based on the persistence and effect on biodiversity.Rodentinticides are a variety of pesticides which are helpful to kill rodetents usually rats in paddy fields but they kill several species and also remaining will persist a long time this disturb the soil as well as water. There is a need to identify the rodenticides easily decomposed and with little impact on biodiversity. In this connection one has to know about the amount of residual remainings and the span of persistence .For this purpose I have chosen voltammetry which is best analytical method with high sensitivity[7-10].

Experimental

a) Apparatus and Electrodes

The electrochemical measurements were carried out with Metrohm model 101 potentiostat and galvanostat. hanging mercury drop electrode,bare carbon electrode,carbon nano tubes paste electrode are used as working electrodes simultaneously.. 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, borate 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.

Result and Discussion

Chlorophacinone 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. The reduction process of Chlorophacinone 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. Millicoulometry is employed to find out the number of electrons involved in the electrode process.

Kinetic data such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constants obtained for Chlorophacinone 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 Chlorophacinone at working electrode (Fig.1.0)is attributed to reduction of Chlorophacinone.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 Chlorophacinone 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 mV/s .

Recovery Experiments

a) Analysis

Well defined and well resolved AdSV peaks of Chlorophacinone obtained at pH 4.0 is used for the quantitative estimation of chloriphacinone in water and soil samples. Both calibration and standard addition methods are used for the quantitative determination of Chlorophacinone. 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.

b) Recommended analytical procedure

The stock solution (1.0 x 10 $^{-5}$ M) of Chlorophacinone 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 chlorophacinone are pH 4.0 and scan rate 50 mVs $^{-1}$.

c) Determination of Chlorophacinone in spiked grain samples

The developed analytical procedure has been applied to the quantitative estimation Chlorophacinone in grain samples. Known amount of Chlorophacinone 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 Chlorophacinone 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 Chlorophacinone in grains by this method ranged from 84.00% ,92.00% ,98.80% which indicates the high accuracy and reproducibility of the proposed method. The results are summarized in table.1.0.

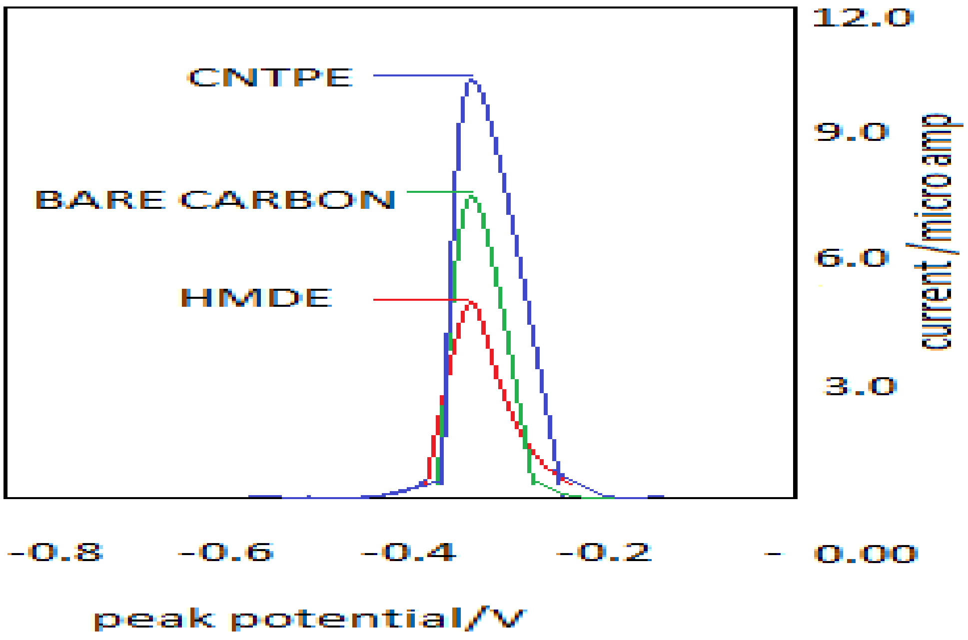

Fig 1.0.DPASV Responce at Different WE

Table 1.0: Recovery of Chlorophacinone by using various working electrodes in voltammetry.

Working Electrode	Amount added(µg)	Amount found(µg)	Recovery(%)	Standard deviation
HMDE	5.0	4.20	84.00	0.043
Bare carbon	5.0	4.60	92.00	0.056
CNTPE	5.0	4.94	98.80	0.033

Conclusion

The current part explains the detailed study of electrochemical reduction of nitro group containing pesticide Chlorophacinone 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 hanging mercury drop electrode,bare carbon electrode,carbon nano tubes paste electrode. By this approach we can say that the method employed for the determination of rodenticide Chlorophacinone differential pulse adsorptive stripping voltammetry is selective and sensitive and low consumption of sample and less tedious compare to chromatography and spectroscopy.

References:

1. Moccelini, A. C. Franzoi and I. C. Vieira,Talanta 82(1) (2010)164-170.

2. Y Wu, X Liu, F Dong, J Xu, Z Yan, X Wu, Y Zheng,Analytical Methods 5(4) (2013)1052-1057.

3. P. Parrilla; J. L. Mart nez Vidal, Analytical Letters, 30 (1997) 1719-1738.

4. Richard T. Krause, Journal of Chromatography A, 442 (1988) 333-343.

5. J. S. Aulakh; A. K. Malik; Varinder Kaur; Philippe Schmitt- Kopplin, Critical Reviews in Analytical Chemistry, 35 (2005) 71-85.

6. Tomomi Goto, Yuko Ito, Sadie Yamada Hiroshi Matsumoto, Hsiao Oka and Hisamitsu Nagase, Analytica Chimica Acta, 555 (2006) 225-232.

7. Michael David Osselton and Robert Duncan Snelling, Journal of Chromatography A , 368 (1986) 265-271.

8. S. Raja sekhar Reddy, T.Raveendranath Babu, International journal of Nano science, 12 (2013)1-5 .

9. S.Raja Sekhar Reddy, T.Raveendranath Babu, B.Sreenivasulu, International Journal of Research in Pharmacy and Life Sciences, 1 (2013) 43-47.

10. Thommandru Raveendranath babu, Sarvareddy rajasekhar reddy, Puchakayala sujana journal of electro chemical science and engeneering, 4,1 (2014) 19-26.