ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Differential pulse polarographic determination of chlomethoxyfen in environmental samples

K.Balaji[1], C.Sridevi[2] and C.Suresh Reddy[1]*

[1]Department of Chemistry, S.V.University, Tirupati-2, Andhra Pradesh, India.
[2]Department of Chemistry, S.P.W. Degree and PG College, Tirupati-2, Andhra Pradesh, India.

ABSTRACT

The differential pulse polarographic (DPP) behaviour of chlomethoxyfen has been studied in the universal buffers ranging from pH 2.0 to 12.0. A simple, rapid, DPP method has been developed for the quantitative determination of chlomethoxyfen in environmental samples. The substance is extracted from the sample with water, the appropriate buffer of selected pH is added to an aliquot and the solution then polarographed at a dropping mercury electrode. The resultant single reduction peak is well developed and permits a precise quantitative determination. Both standard addition and calibration methods are used.

Key words: Differntial pulse polarography, Chlomethoxyfen, Analysis, Environmental samples.

Corresponding author
Email: csrsvu@gmail.com

ISSN: 0975-8585

INTRODUCTION

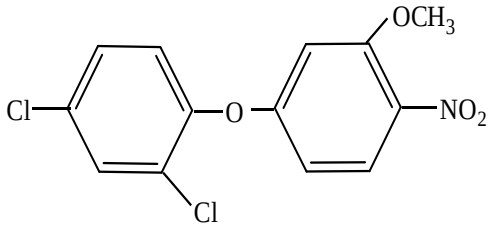

Fig. 1: Chemical structure of Chlomethoxyfen

Chlomethoxyfen [5-(2, 4-dichlorophenoxy)-2-nitroanisole] is a potent herbicide (**Fig. 1**), which is effective against many annual weeds and some perennials [1, 2]. There are increasing kinds of chemical substances in the environment that cause large social problems. Pesticides runoff from agricultural lands impacts the water environment [3, 5] and some of the pesticides are endocrine disputing compounds [6, 7]. Therefore, it is necessary to limit the chemical substances discharged into the environment as much as possible, and also to remove them as completely as possible. To remove pesticides from water in the environment, photochemical decomposition by ultraviolet irradiation [8], ozonation [9] or alkaline hydrolysis [10, 11] have usually been used.

A review of the literature reveals that very little attention has been paid to the polarographic behaviour of chlomethoxyfen. The purpose of this work is to establish the experimental conditions that permit the study of the electrochemical reduction behaviour of chlomethoxyfen and its determination in water samples and grains by differential pulse polarography (DPP).

EXPERIMENTAL

Apparatus

The differential pulse polarograms were obtained with a Metrohm E 506 polarecord connected to E 648 VA – combistand and E 608 VA-controller. A three electrode combination was employed consisting of a dropping mercury electrode (area: 0.0223 cm^2) Ag/AgCl (s), Cl^- electrode and a platinum electrode as an auxillary electrode. Model LI 120 Elco digital pH meter was used for pH measurements. All the experiments were performed at 298 ± 0.1K.

Reagents and solutions

Universal buffers of pH 2 to 12 were prepared by using 0.2 M boric acid, 0.05 M citric acid and 0.1 M trisodium orthophosphate. All the chemicals used were of AnalaR grade.

Pure chlomethoxyfen was obtained from Hindustan Ciba-Geigy Ltd., Bombay and was used without further purification. A stock solution (1x 10^{-2} M) of the title compound was prepared in double distilled water.

ISSN: 0975-8585

General procedure for studying polarograhic behavior

A 0.5 ml volume of the stock solution of chlomethoxyfen was placed in the polarographic cell and 9.5 ml of the appropriate buffer was added and the solution purged with oxygen-free nitrogen for 10 min prior to each run.

Preparation of calibration graph

A stock solution of chlomwthoxyfen ($1x10^{-3}$ m) was prepared in distilled water and solutions containing various concentrations in the range 10^{-4} M to 10^{-7} M were prepared by the dilution of the stock solution with the appropriate buffer of selected pH. The polarograms of the final sample solutions were obtained after deacration for 10 min. A graph of measured current was plotted against chlomethoxyfen concentration. The lower detection limit (d) was calculated using the following equation [12].

dl = 3 sd/m where sd = standard deviation and m = slope of the calibration plot.

Analysis of environmental samples (water and grains)

A standard stock solution ($1x10^{-5}$ M) is prepared by dissolution of the appropriate amount of electroactive species in acetone. 1 ml of standard solution is transferred into a polarographic cell containing 9 ml of the supporting electrolyte. Then the solution is purged with oxygen free nitrogen gs for 10 min prior to each run. After recording the polarogram, small increments (0.2 ml) of standard solutions are added and the polarograms are recorded after each addition under similar conditions. In the present study the best precision is obtained in pH 8.0, drop time 1.4s, pulse amplitude 50 mV and applied potential of -0.61 V vs. Ag/AgCl (s), Cl^-.

RESULTS AND DISCUSSION

Chlomethoxyfen is found to give two well defined peaks in the pH range 2.0 to 6.0. The first peak is found to be due to the reduction of the nitro group to hydroxylamine in a four electron process and the second to the reduction of the hydroxylamine to amine in a two electron process (**Fig. 2**). The peak height ratios are found to be 2:1. However, in alkaline solutions pH 8.0 to 12.0) the title compound exhibits only a four electron peak which corresponds to the reduction of the nitro group to hydroxylamine. In the alkaline medium, hydroxylamine is not reduced further to amine owing to the non-availability of protons.

The diffusion controlled and adsorption free nature [13] of the electrode process is evidenced from the linear plots of i_m vs $t^{2/3}$ passing through origin (where i_m is the maximum peak current in DPP). The reduction potential (E_p) value of chlomethoxyfen peak is found to depend on pH and shift towards more negative value with increase in the pH of the buffer solutions. Results are shown in **table-1.**

Differntial pulse polarography is used for the quantitative estimation of chlomethoxyfen in environmental samples using both calibration and standard addition methods. Analysis is carried out using the current obtained for the nitro group reduction in chlomethoxyfen. It is observed that at pH 8.0 the nitro group reduction appears at the start of the potential. In alkaline solutions the reduction of nitro group is not easily facilitated owing to the less availability of protons. The optimum pH range for obtaining will resolved peaks for the quantitative determination of the title compound is found to be pH 6 to 8. Peak currents are linear over the chlomethoxyfen concentration range $1.25x10^{-5}$ M to $2.1x10^{-9}$ M with lower detection limit of $1.96x10^{-9}$ M

Standard addition method is successfully utilized for the analysis of chlomethoxyfen in environmental samples without any prior separation. The optimum conditions for the analytical determination are found to be a drop time of 1.4 sec and pulse amplitude of 50 mV. In the present study the best precision is obtained in pH 8.0. The recovery of 97 to 99.45% obtained with the proposed differential pulse polarogrpahic method indicated its accuracy and reproductivity.

The relative standard deviation and correlation coefficients for 10 replicants are found to be 1.32% and 0.993 respectively. The above described procedure is successfully applied for the determination of the herbicide in water and grain samples.

Water samples are collected and shaken for a few seconds. In order to remove particulate material, samples are passed through 0.45 µm filter (Millipore). Aliquot of (50 ml) samples are spiked with the herbicide stock aolution. After shaking, the solution is passed through a sep-Pak plus C_{18} cartidge previously activated with 5 ml of ethanol and 1 ml of deionised water. The analytes are then eluted with 10 ml of dichloromethane and evaporated to dryness. The residue is dissolved in acetone and transferred into the 50 ml volumetric flask. Recoveries are given in **table-2.**

10 ml of the known amounts of analyte solution are added to grain (rice, 20 g) samples and kept in contact for 2-4 hrs. After this period, the samples are extracted with acetone (3x50 ml) by shaking the flask for 10 min. Then the organic phase is filtered through Whatmann No.1 filter paper. After the evaporation of the solvent, the residues are dissolved in acetone and transferred into a 50 ml volumetric flask. The recoveries of the herbicide in grain samples are given in **table-3**.

ISSN: 0975-8585

Table 1. Typical Differential pulse polarographic characteristics of chlomethoxyfen Concentration 0.5mM, Drop time: 1.4 s, pulse amplitude: 50 mV

pH of the supporting electrolyte	$-E_P$ V	$-i_m$ µA
2.0	a) 0.08	12.4
	b) 0.21	5.6
4.0	a) 0.22	10.8
	b) 0.48	5.1
6.0	a) 0.42	8.8
	b) 0.69	3.1
8.0	0.61	8.2
10.0	0.74	7.8
12.0	0.87	7.5

Figure 2. Typical differential pulse polarography of chlomethoxyfen in pH4.0 Concertration: 0.5 mM Drop time: 1.4s Pulse amplitude: 50 mV

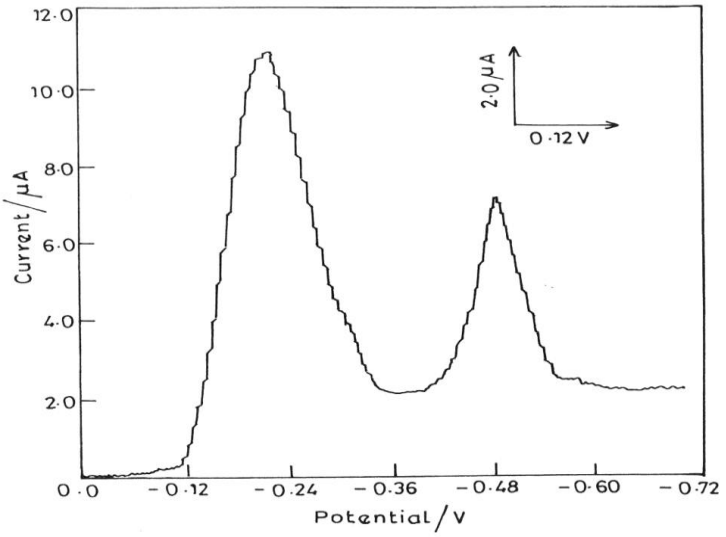

Table 2. Recoveries of chlomethoxyfen added to water samples Pulse amplitude: 50 mV, Drop time: 1.4 s

Labeled amount (mg)		Average amount found (mg) ± SD		Average recovery (%)	
Well water	Tap water	Well water	Tap water	Well water	Tap water
5.0	5.0	4.94 ± 0.030	4.91 ± 0.028	98.90	98.20
10.0	10.0	9.79 ± 0.062	9.85 ± 0.055	97.90	98.50
20.0	20.0	19.78 ± 0.071	19.89 ± 0.058	98.90	99.45

ISSN: 0975-8585

Table 3. Recoveries of chlomethoxyfen added to grain samples Pulse amplitude: 50 mV, Drop time: 1.4 s

Labeled amount (mg)	Average amount found (mg) ± SD	Average recovery (%)
2	1.95 ± 0.018	97.50
4	3.92 ± 0.050	98.00
6	5.90 ± 0.038	98.33
8	7.89 ± 0.059	98.62
10	9.88 ± 0.068	98.80

CONCLUSION

The results indicate that the above proposed methods were simple, rapid and sensitive with reasonable precision and accuracy which makes it as choice for routine quality control analysis. There was no interference of excipients present in environmental samples through out the experimental process that reflects the accuracy and precision of method.

ACKNOWLEDGEMENT

The author (KB) thanks for UGC [No.F.31 – 24 (SC) 2007 (SA – III)], New Delhi for providing Post Doctoral Fellowship.

REFERENCES

[1] Jocobs J.M, JacobsN.J, ShermanT.D and Duke S.O. Plant physiol 1991; 97:197-203.
[2] Hikiwa M. Pest management Science 2006; 15:562-570.
[3] Schulz R, Peall SKC. Environ Sci Technol 2001; 35:422-426.
[4] Shipitalo M. J Owens LB. Environ Sci Technol 2003; 37:944-950.
[5]Lerch RN, Blanchard PE. Environ Sci Technol 2003; 37:5518-5527.
[6] Kluwe WM. J Agric Food Chem 1981; 59:71-83.
[7] Kluwe WM. J Agric Food Chem 1981; 59:84-95.
[8] Hirahara Y, Sayato Y and Nakamuro KJ. Jpn J Toxicol Environ Health 1998; 44:45-461.
[9] Okumura T. Jpn J Soci Water Environ 1992; 15:62-69.
[10] Greenhalgh R, Dhanan KL and WeinbergerP. J Agric Food Chem 1980; 28:102-105.
[11] Drossman H, Johnson H and Mill T. Chemosphere 1988; 17:1509-1530.
[12] Smyth MR and Osteryoung JG. Anal Chem 1978; 50:1632.
[13] Smyth MR and Osteryoung JG. Anal Chem. Acta 1978; 96:335.