ISSN : 0974 - 7540 Volume 3 Issue 3

Trade Science Inc.

Research & Reviews On Electrochemistry

Full Paper

RREC, 3(3), 2012 [105-108]

Differential pulse polarographic determination of bromethalin in water and vegitables

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Received: 2^{nd} July, 2011 ; Accepted: 2^{nd} August, 2011

ABSTRACT

A selective and sensitive differential pulse polarographic method for the determination of bromethalin was studied using dropping mercury electrode (DME) in universal buffer of pH range 2.0 to 12.0. The peak observed for the bromethalin are attributed to the reduction of nitro groups and showed to be pH 5.0. A systematic study of various experimental conditions, such as pH, scan rate and pulse amplitude were studied. The relationship between peak current and bromethalin concentration was linear within the concentration range of 1.0 x 10^{-9} to 1.0 x 10^{-5} mol l^{-1}. The standard deviation and relative standard deviation were found to be±0.05 and 1.22% respectively. The method is simple, sensitive and free from interferences of other pesticides and diverse ions. The method has been satisfactorily applied to the determination of bromethalin in water and agricultural samples.

KEYWORDS

Bromethalin;
DPP;
Water and vegetable samples.

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, solid-phase extraction (SPE)[1]1or supercritical fluid extraction (SCFE) and solid phase micro extraction (SPME)[2]. 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[3, 4, 5]. reported high performance liquid chromatography with UV-VIS spectrometric and HPLC negative-ion Atmospheric pressure chemical ionization (APCI)-Mass spectrometric approches which commonly used for detection and confirmation of bromethalin[6], reported TLC extended by GC/MS to determine bromethalin in environmental samples[7], employed GC-MS method for determination of bromethalin in dimethilated form.

APPARATUS AND REAGENTS

The electrochemical measurements were carried out with Elico-362 polarographic analyser. Three ectrode systems consisting of dropping mercury electrode (DME) as working electrode, Ag/AgCl (saltKCl) was used as a reference electrode and a platinum wire as an auxiliary displays negative potential electrode which range. Elico Li-129 model glass calomel combined electrode was employed for measuring pH values. All reagents used were of analytical reagent grade. Double distilled water was used throughout the experiment. In the present investigation universal buffers of pH range 2.0 to 12.0 are used as supporting electrolytes and are prepared by using 0.2M boric acid, 0.05M citricacid and 0.1M trisodiumorthophosphate solutions. bromethalin obtained from Rallis India Ltd., Bangalore, India. The purity of the pesticide sample was tested by thin layer chromatography and also melting point determinations.

DIFFERENTIAL PULSE POLAROGRAPHIC BEHAVIOUR

At DME bromethalin (1x10^{-5}M) exhibits a well defined differential pulse polarogram (Figure 1). The systematic studies of the various experimental and instrumental parameters that affect the polarogram response is carried out in order to establish the optimum conditions.

EFFECT OF PH

The pH of a solution is critical factor affecting both the rate and equilibrium state of the reduction process and the rate of the electrode reaction. The influence of the pH on the DPP response was studied at dropping mercury electrode of the 1x10^{-5} M for bromethalin between the pH ranges 2.0 to 12.0. It can be observed from Figure 2, the maximum peak currents are obtained with pH 6.0. When the pH was increased from 8.0 to 12.0, the peak potentials shifted towards more negative values.

EFFECT OF SCAN RATE

Polarograms obtained for increasing values of the scan rate showed the existence of a linear dependence of the peak current intensity on the scan rate between 40 to 60 mVs^{-1}. The peak currents were directly proportional to the scan rate indicating that the system was adsorption controlled.

CHARACTERISATION OF WAVES /PEAKS

The electrochemical behaviour of bromethalin was examined over the pH range from 2.0 to 12.0. A single well defined peak is observed throughout the pH range in all above techniques. This single peak is attributed to the reduction of two nitro group in bromethalin involve in 8 electron process to the corresponding hydroxylamine group. The typical cyclic voltammograms of these two compounds are shown in Figure 3.

In cyclic voltammetric experiments, a small anodic peak (a_1) has been observed in the reverse scan at higher pH values (pH >10.0) for bromethalin. In the second scan, another small cathodic peak (c_2) at more positive potentials than (c_1) is noticed. The anodic peak (a_1) may be due to the oxidation of hydroxylamine formed at (c_1) to nitroso derivative and the cathodic peak (c_2) may be attributed to the reduction of the nitroso derivative to the hydroxylamine group again.

IDENTIFICATION OF THE PRODUCT

In acidic medium hydroxylamine is the final product and number of electrons involved in the reduction process is eight in universalbuffer with pH 6.0 it is evidenced by the results obtained in millicoulometric technique.

KINETIC DATA

The values for transfer coefficient (α), diffusion coefficient (D) and heterogeneous forward rate constant ($k^o_{f,h}$) at various pH values in cyclic voltammetry technique were given in TABLE 1.

The forward rate constant ($k^0_{f,h}$) values for bromethalin is found to decrease with increase in pH. This trend shows that the electrode process becomes more irreversible with increase in pH of the solution.

ANALYSIS

Differential pulse polarography has been used for quantitative estimation of bromethalin using both calibration and standard addition methods. The polarographic peak is attributed to the reduction of two nitro groups and is preferred for the analysis of agriculture and water samples. The optimum pH for obtaining well resolved peak for quantitative determination of bromethalin is found to be 6.

Investigated compound is found to exhibit well resolved peak at pH 6.0, and the sharp well resolved peak was chosen for quantitative studies. Peak currents were linear over the bromethalin concentration range of 1.0 x 10^{-9} M to 1.0 x10^{-5} M with lower detection limits of 1.09 x 10^{-8} M. The relative standard deviation and correlation coefficients are found to be 1.25%, 0.996 respectively for 10 replicates.

DETERMINATION OF BROMETHALIN IN SPIKED WATER SAMPLES

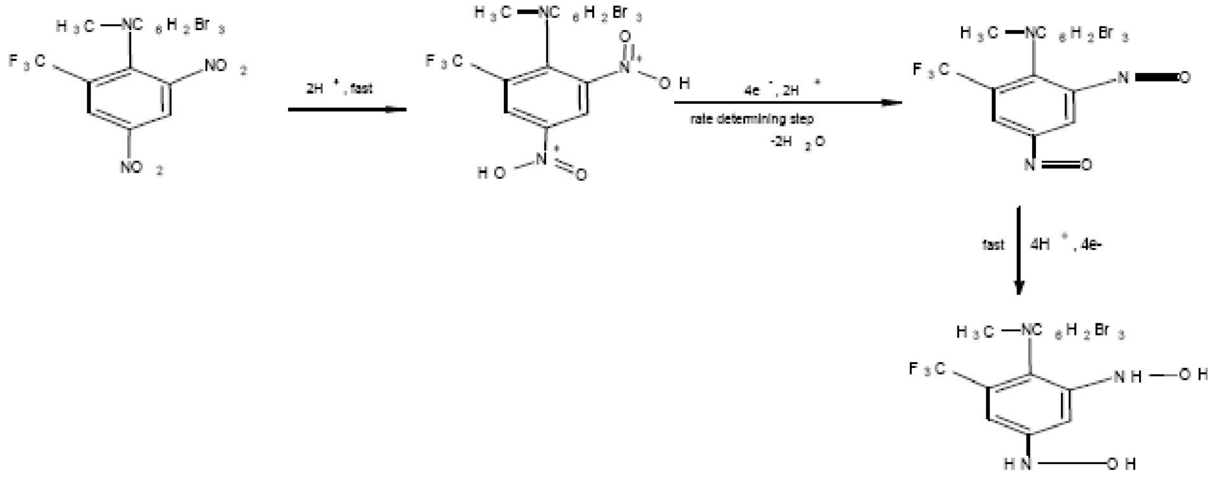
River water samples, which received run-off water from agricultural field, were collected from penna river belt, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper and spiked with known amount of bromethalin. Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analysed as described above. The average recoveries obtained for bromethalin in above two samples ranged from 98.33 to 99.80% and the results were summarized in TABLE 2.

DETERMINATION OF BROMETHALIN IN AGRICULTURAL SAMPLES

Vegetable samples (peas & spinach) collected from agricultural fields and each of 25gm were taken. The samples were socked with two 20ml portions of ethanol- demineralized water(1+1), filtered through a Whatman filter paper No.41 and the filtrate were added with known amount of bromethalin and centrifuged at 1850g for 10 min. The filtrate was quantitatively transferred into a 50mL calibrated flask and made upto the mark with 50% ethanol. Washings were collected in a 25mL calibrated flask and aliquots were analysed by DPP procedure described above. The residue of bromethalin was dissolved in dimethyl formamide and transferred to a 100 mL volumetric flask. Results obtained for the determination of the bromethalin in vegetables samples presented in TABLE 3. The mean recoveries obtained for bromethalin in two vegetable samples ranged from 98.50 to 99.83%, which indicates the accuracy and reproducibility of the proposed differential pulse polarographic method.

TABLE 1 : Typical cyclic voltammetric data of bromethalin concentration: 0.5 mM, scan rate: 40 mVs^{-1}

pH of the supporting electrolyte	$-E_p$ / V	i_p / μA	α n_a	$D \times 10^6$ / $cm^2\,s^{-1}$	$k^0 f,h$ / $cm\,s^{-1}$
2.0	0.72	9.4	0.72	4.03	6.94 x 10^{-13}
4.0	0.85	9.6	0.83	3.62	2.30 x 10^{-13}
6.0	0.73	6.8	0.93	2.68	9.23 x 10^{-14}
8.0	1.14	9.0	1.37	2.45	2.62 x 10^{-15}
10.0	1.30	8.8	1.45	2.23	4.28 x 10^{-17}
12.0	1.44	7.0	1.54	2.10	3.23 x 10^{-18}



Scheme 1 : Electrode mechanism of bromethalin

TABLE 2 : Recoveries of bromethalin in spiked water samples

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (%)	Standard deviation
Tap water	0.3	0.299	99.66	0.055
	0.5	0.499	99.80	0.024
	0.7	0.697	99.57	0.014
River water	0.3	0.295	98.33	0.028
	0.5	0.498	99.60	0.026
	0.7	0.689	98.42	0.035

TABLE 3 : Recoveries of bromethalin in spiked agricultural samples

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (%)	Standard deviation
peas	2.0	1.96	98.00	0.040
	4.0	3.95	98.75	0.032
	6.0	5.99	99.83	0.038
	8.0	7.88	98.50	0.012
spinach	2.0	1.98	99.00	0.035
	4.0	3.98	99.33	0.022
	6.0	5.95	99.16	0.014
	8.0	7.96	99.50	0.045

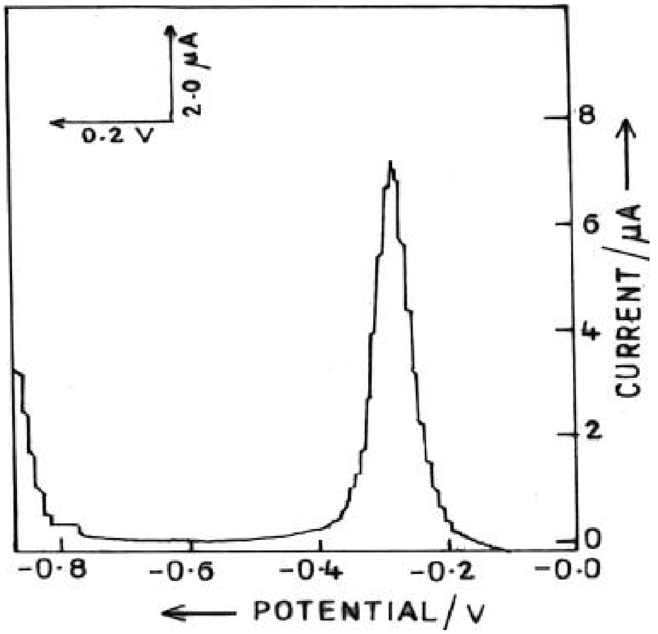


Figure 1 : Differential pulse polarogram of bromethalin at pH 6.0 concentration: 1x10^{-5} M; pulse amplitude: 50mV ; drop time : 2sec.

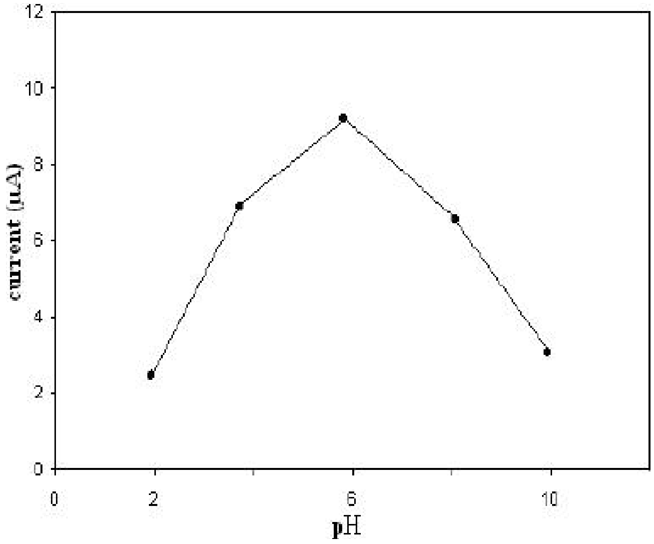


Figure 2 : Effect of pH on peak current in bromethalin

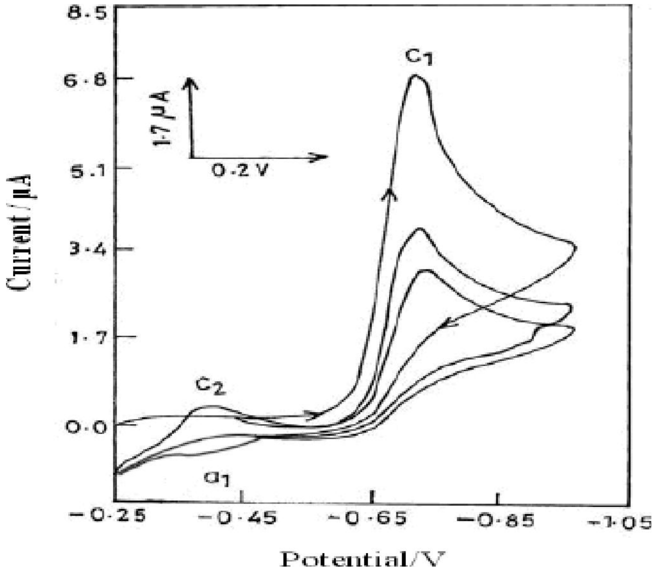


Figure 3 : Typical cyclic voltammogram of bromethalin for an accumulation time of 80 sec at HMDE; accumulation potential: -0.5V; rest time:10 sec; stirring rate: 1500 rpm; scan rate: 40 mVs^{-1}; concentration: 1x10^{-5} M; pH:6.0.

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