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Polarographic behavior and analysis of Flumetralin in formulations and environmental samples

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Abstract

A differential pulse polarographic (DPP) method for the determination of Flumetralin is described based on the reduction of a nitro group at a dropping mercury electrode (DME) in Briton-Robinson buffers of pH 2.0 to 12.0 using 25% acetone-water mixture as a solvent. Also a cyclic voltammetric (CV) technique has been used to study the behaviour of Flumetralin at a hanging mercury drop electrode (HMDE). The DPP method described here has been applied to the analysis of Flumetralin in formulations, grains, soils and spiked water samples. Both standard addtion and calibration methods were used for the analytical measurements. The lower detection limit was found to be 1.87×10^{-8} M.

Key Words: Flumetralin, Polarographic behaviour, Analysis, Formulations, Environmental samples.

Introduction

Pesticides containing nitro substituents are extensively used in agriculture throughout the world. Flumetralin is one of the dinitroaniline pesticide families and is an economically important class of agricultural compound used to prevent the growth of grasses and weeds in cultivated crops. The volatility persistence of Flumetralin, together with the variability under environmental

conditions among different areas, results in a residual amount of herbicide in soil that can be phytotoxic to sensitive corps [1], in soil [2,3] plants [4,5] and in air [6]. There are several methods available for the determination of Flumetralin; mostly chromatographic methods are reported to be used for the determination of the dinitroaniline herbicide in various matrices. This includes HPLC [7], GC with mass selective detection [8] and with electron capture detection [9,10] and LC with fluorescence detection [11].

Among the electroalalytical methods, DPP and CV plays an important role because of their rapidity and selectivity in the analysis of pesticide residues.. The electrochemistry of aromatic nitro compounds such as pesticides and drugs has been thoroughly investigated and reported over the years [12-17]. The nitro group containing systems are polarographically reduced at the dropping mercury electrode [18] and are successfully applied for the analysis of pesticides and herbicides [19, 20]. D.C.polarographic behaviour of some of the dinitroaniline herbicides have been studied [21]. The behavior and analysis of dinitroanlliline herbicides such as pendimethalin, benfluralin and trifluralin have been reported by Jayarama Reddy et al [22-23].

In the present investigation, agriculturally important nitro group containing Flumetralin has been chosen to get more information on the electrode kinetics as well as reduction behaviour of nitro group concerned by employing modern electrochemical techniques such as d.c and a.c polarography, cylic voltammetry, diffential pulse polarography, millicoulometry and controlled potential electrolysis. Differential pulse polarographic method has also been used for the determination of the title compound in various environmental matrices.

Materials and Methods

We performed dc polarographic measurements using Model 364 polarographic analyzer coupled with a BD8 Kipp and Zonen recorder. Metrohm unit E 506 polarecord coupled with E 612 VA-scanner, E 648 VA – controller and a digital electronics X – Y/t recorder were used for cyclic voltammertric and differential pulse polarographic measuremtns. A three–electrode combination was used with the dropping mercury electrode as working electrode in dc polarography and DPP, and with a hanging mercury drop electrode in CV. Saturated calomel electrode (SCE) was used as the reference electrode in dc polarography and Ag/AgCl (s), Cl^- electrode in CV and DPP. Platinum wire was employed as an auxiliary electrode in all the techniques to complete the electrolytic circuit. All experiments were carried out at 28 ± 1^0C.

A Britton-Robison (BR) buffer solution was prepared containing 0.04M of acetic acid (99%), 0.04M of orthophosphoric acid (85%), and 0.04M of boric acid. The pH range, from 2.0 to 12.0, was adjusted using 0.2M of sodium hydroxide. All of the chemicals were of Analar grade. Flumetralin was obtained from Ciba-Geigy pvt. Ltd., Mumbai, and was used without further purification.

Results and Discussion

Characterization of wave/peak

The electrochemical behaviour of Flumetralin has been studied over the pH range 2.0 to 12.0. A single well defined wave/peak is observed throughout the pH range for Flumetralin in all the

techniques. This single wave/peak is attributed to the simultaneous reduction of two nitro gropus in the eight electron process to the corresponding hydroxylamine groups. Typical voltammograms are shown in Figs.1 to 4.

In cyclic voltammetric experiments, a small anodic peak (a_1) has been observed in the reverse scan at higher pH values (pH≥10) for Flumetralin (Fig.2). 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 again. A maximum is observed for the reduction of nitro group at pH 2.0 to 6.0. Triton X-100 (0.002%) solution is used to obtain well defined waves.

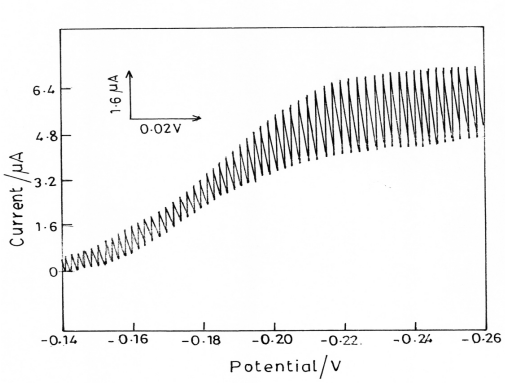


Fig.1.Typical d.c. polarogram of Flumetralin in pH 4.0 Con: 0.5 mM Drop time: 3s

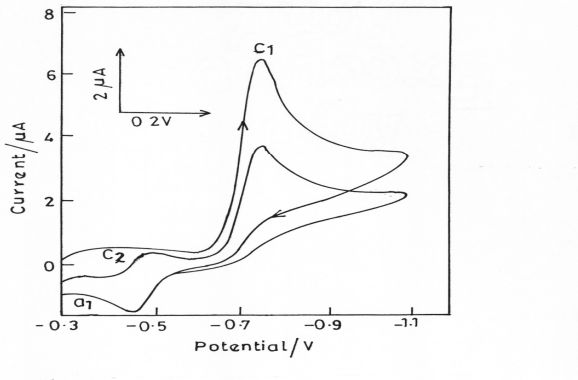


Fig.2. Typical Cyclic Voltammogram of Flumetralin in pH 12.0 Con: 0.5 mM Scan rate: 40 mV s^{-1}

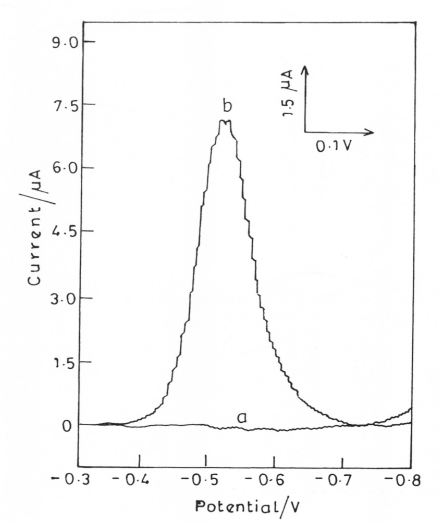


Fig..3. Typical a.c. Polarogram of Flumetralin in pH 8.0 Con.0.5 mM Drop time.2s a:base line b: a.c.peak

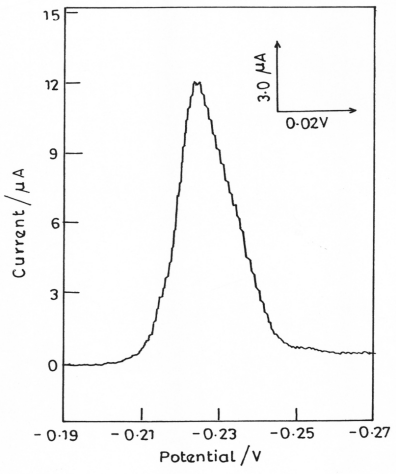


Fig.4. Typical Differential pulse polarogram in of Flumetralin in pH 4.0 con.0.5 mM Drop time.2s Pulse amplitude.50mV

Nature of the electrode process

The nature of the wave/peak is found to be diffusion controlled and adsorption free in the buffer systems taken, as shown by the linear plot of i_d vs. $h^{1/2}$ (Fig.5), i_p vs. $v^{1/2}$ (Fig.6) and i_m vs.$t^{2/3}$ (Fig.7) which is found to pass through origin. The irreversibility of the electrode process is confirmed by the log-plot analysis of the wave. The slope of E_{dc} vs.{log(i/id-i)-0.506 logt} plot exceeds appreciably 54.2/n mV. The variation of peak potential with scan rate also indicates the irreversible nature of the electrode process. Further, $E_{1/2}$, E_p and E_m values are observed to have shifted towards more negative values with increasing concentration of the depolarizer. The $E_{1/2}$ and E_p values of Flumetralin is found to be dependent on pH and shift towards more negative values with the increase in the pH of the buffer solutions, indicating proton involvement in the electrode process. The number of protons involved in the rate determining step is found to be two as evidenced from the linear plots of $E_{1/2}$ vs. pH (Fig.8).

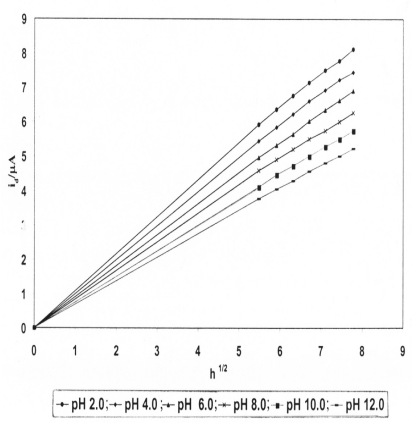


Fig.5. i_d vs $h^{1/2}$ plots of Flumetralin Con.0 0.5 mM

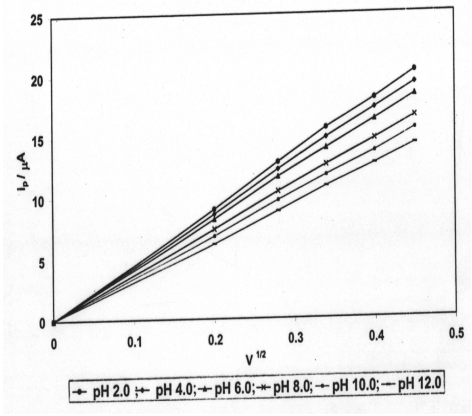


Fig.6. I_p vs $v^{1/2}$ plots of Flumetralin Con.0 0.5 mM

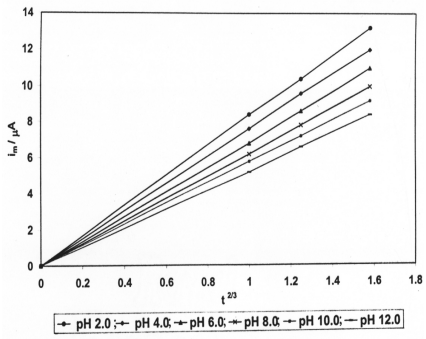


Fig.7. I_m vs $t^{2/3}$ plots of Flumetralin Con.0.5 mM, Drop time:3s

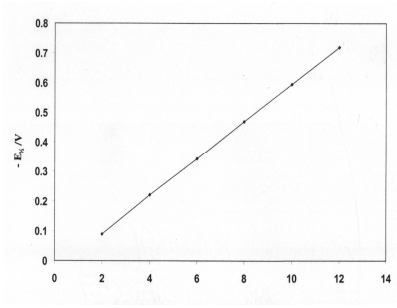


Fig.8. $E_{1/2}$ vs pH plots of Flumetralin Con.0.5mV

Identification of the product

Millicoulometry is employed to find out the number of electrons involved in the electrode process. It is found to be eight (for each nitro group four electrons) for the reduction of two nitro groups in Flumetralin at acidic (pH 2.0) and basic (pH 12.0) medium.

Controlled potential electrolysis (CPE) has been carried out in a modified cell with mercury pool cathode, saturated calomel electrode and platinum wire as anode. This experiment is carried out in pH 4.0 at applied potentials of -0.21V for Flumetralin. After electrolysis, the reduced product is extracted with ether. The ethereal layer is evaporated on water bath and the product is identified as the corresponding hydroxylamine. The isolation product is confirmed as hydroxylamine by I.R. spectral data (N-H stretch: 3420 cm^{-1}, O-H stretch: 3060-3000 cm^{-1} and N-H bend: 1575 cm^{-1} as shown in Fig.9.

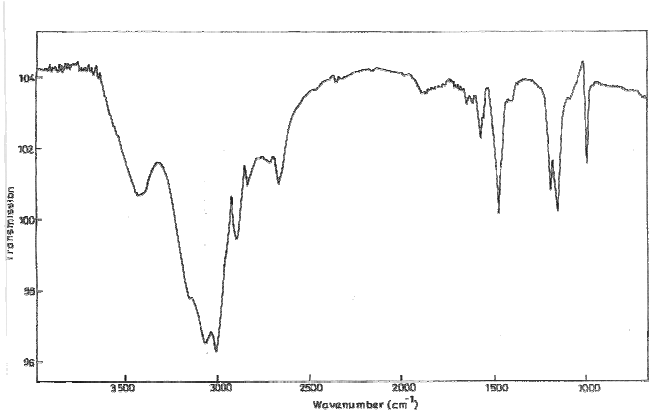


Fig .9. I.R.Spectrum of the reduction product of Flumetralin

Kinetic data

The values obtained for transfer coefficient (α), diffusion coefficient (D) and heterogeneous forward rate constant ($k^{o}_{f.h}$), at various pH values in different techniques, are given in tables 1 to 4. The diffusion coefficient values evaluated form all the techniques are in good agreement. This is evident particularly where no adsorption complication is involved in the electrode process. The reason for slight decrease in diffusion coefficient values with increase in pH may be due to the less availability of protons with increase in pH of the buffer solution.

Table 1. Typical d.c. polarographic data of Flumetralin
Concentration: 0.5mM, Drop time:3s

pH	-Ep/V	Ip/μA	άn_a	D$x10^6$/ cm^2 s^{-1}	$K^0_{f.h}$/ cm s^{-1}
2.0	0.10	9.0	1.64	7.05	$5.44x10^{-6}$
4.0	0.24	8.6	1.60	6.81	$4.92x10^{-6}$
6.0	0.40	8.2	1.54	6.72	$3.41x10^{-7}$
8.0	0.55	7.4	1.50	6.64	$7.17x10^{-8}$
10.0	0.69	6.8	1.46	6.51	$4.28x10^{-10}$
12.0	0.76	6.4	1.42	6.42	$4.11x10^{-13}$

The heterogeneous forward rate constant values calculated are, in general, found to decrease with increase in the pH of the solution. This trend shows that the electrode reaction tends to become more and more irreversible with increase in pH. The rate constant values obtained for the reduction of nitro group is high in acidic medium in all the techniques, indicating that the rate of reaction is fast in acidic solution due to high proton involvement which makes the reduction process easier. But, in basic media, the reduction process does not easily occur owing to the less

availability of protons. Consequently, lower values are obtained for the rate constants in basic medium in contrast to acidic medium.

Table.2. Typical Cyclic voltmmetric data of Flumetralin
Concentration:0.5 mM, Scan rate:40 mVms^{-1}

pH	-E_m/V	I_m/µA	άn_a	Dx10^6/ cm^2 s^{-1}	$K^0_{f,h}$/ cm s^{-1}
2.0	0.07	13.2	1.58	7.03	3.29x10^{-6}
4.0	0.22	12.0	1.62	6.27	2.12x10^{-7}
6.0	0.39	10.8	1.53	6.12	4.61x10^{-8}
8.0	0.53	10.0	1.68	5.90	1.70x10^{-10}
10.0	0.64	9.2	1.52	5.76	3.64x10^{-11}
12.0	0.80	8.4	1.58	5.62	2.44x10^{-12}

Table .3. Typical a.c. Polarographic data of Flumetralin
Concentration: 0.5mM, Drop time:3s

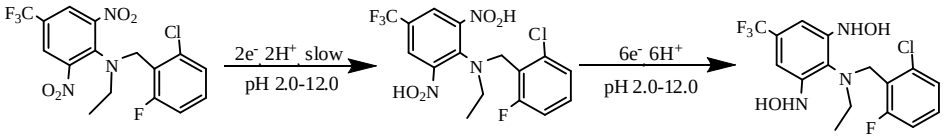
pH	-$E_{1/2}$/V	I_d/µA	άn_a	Dx10^6/ cm^2 s^{-1}	$K^0_{f,h}$/ cm s^{-1}
2.0	0.06	7.1	1.67	7.14	5.02x10^{-6}
4.0	0.19	6.5	1.63	6.85	4.42x10^{-7}
6.0	0.34	6.0	1.68	6.78	2.38x10^{-8}
8.0	0.46	5.5	1.59	6.66	6.74x10^{-10}
10.0	0.58	5.0	1.60	6.61	3.45x10^{-12}
12.0	0.72	4.6	1.53	6.54	2.44x10^{-14}

Table. 4. Typical Differential pulse polarographic data of Flumetralin
Concentration: 0.5mM, Drop time:3s, Pulse amplitude:50 mV

pH	-Es/V	Is/µA	ά	Dx10^6/ cm^2 s^{-1}	Ks/ cm s^{-1}
2.0	0.08	9.6	0.85	7.11	4.59x10^{-5}
4.0	0.23	8.5	0.83	6.24	3.42x10^{-6}
6.0	0.39	8.2	0.80	6.08	5.81x10^{-7}
8.0	0.54	7.4	0.85	5.95	2.92x10^{-9}
10.0	0.65	6.6	0.81	5.88	4.86x10^{-10}
12.0	0.77	6.3	0.84	5.74	3.61x10^{-11}

Electrode mechanism

Based on the results obtained form different techniques, the reduction mechanism of the nitro group present in flumetralin can be proposed as follows:



Analysis

In the present study differential pulse polography (DPP) has been employed for the quantitative determination of Flumetralin in grain, soil and spiked water samples. Flumetralin is found to exhibit sharp and well resolved peak in pH 4.0 and this peak is chosen for quantitative studies. Both standard addition and calibration methods are used. The peak heights are found to be linear over the concentration range 1.2×10^{-5} M to 2.8×10^{-8} M with lower detection limits of 1.2×10^{-8} M. The correlation coefficients and relative standard deviation values are found to be 0.988 and 1.28% for 10 replicants.

Recommended analytical procedure

Standard stock solution (1×10^{-3} M) of the Flumetralin is prepared by dissolving an appropriate amount of electroactive species in ethanol.1ml of the standard solution is transferred into a polarographic cell, made up with 9 ml of the supporting electrolyte and then deoxygenated with nitrogen gas for 10 minutes. The polarogram is recorded. Later small increments (0.2ml) of standard solution are added and the polarograms are recorded after each addition under the identical conditions. In the present study the best precision is obtained at pH 4.0 with a drop time of 2 sec, a pulse amplitude of 50 mV and applied potential of -0.22 V. This method is successfully employed for the determination of the compound in agricultural formulations, grains, soil and water samples.

In the present analysis, flumetralin formulation namely Prime is chosen. The required quantity of formulation corresponding to a stock solution of concentration 1×10^{-3} M is accurately measured and transferred into a 100 ml calibrated flask containing 50 ml of ethanol. A solution of 1×10^{-5} M is prepared by diluting this stock solution with the buffer solution and the above described procedure is employed. Assay results for the selected formulation is given in Table.5.

Grain (rice) samples (50 g) and soil samples (25g) are sparyed with known amounts of the Flumetralin and left for 2-4 hrs. The samples are extracted with acetone (2×50 ml) by shaking the flask for 5 min. The organic phase is filtered under suction through Whatmann No.1 filter paper. The solvent is removed through evaporation and the residues of the compounds are dissolved in ethanol and transferred into a 50 ml volumetric flask. The results obtained for the determination of Flumetralin in grains and soils are presented in Table.6.

Table.5. Determination of Flumetralin in agricultural formulations
Pulse amplitude: 50 mV, Drop time: 2s

Compound	Labelled amount (mg)	Average amount found (mg) ±SD	Average recovery (%)
Prime (Flumetralin formaulation)	5.0	4.91 ± 0.081	98.90
	10.0	9.91 ± 0.080	99.10
	15.0	14.89 ± 0.047	99.26

A 1000 ml samples of tap water is spiked with the pesticide at different concertration levels (each concentration 3 times) taken into a 2 L separatory funnel and shaken for a few minutes.

The solution is passed through whatmann Nylon® memebrane filter (0.45 μm size). The elution is carried out with 3×50 ml dichloromethane. The organic solvent is filtered through anhydrous sodium sulfate and evaporated to dryness. Small volumes of hexane are added to remove dichloromethane completely. The residue is dissolved in ethanol and then transferred to a 50 ml volumetric flask. Table.6 gives the recovery of Flumetralin in spiked water samples.

Table .6. Recoveries of Flumetralin added to grains, soils and spiked tap water samples(Pulse amplitude: 50 mV, Drop time: 2s)

Sample	Amount added (mg)	Average amount found (mg) ±SD	Average recovery (%)
Rice	10.0	9.83±0.08	98.30
	20.0	19.76±0.035	98.80
Soil	10.0	9.79±0.040	97.9
	20.0	19.69±0.070	98.45
Spiked tap water	2	1.96±0.034	98.00
	4	3.95±0.021	98.75
	6	5.86±0.060	78.66

Conclusion

The work describes the electrochemical behaviour of Flumetralin based on the reduction of the nitro group at DME and HMDE. The recovery results show that DPP is a simple, reliable and inexpensive method for the determination of Flumetralin in formulation and environmental samples. The main advantage of the proposed method over the other ones is that the excipients do not interfere and a separation procedure is not necessary.

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