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Polarographic and Voltammetric Determination of Dithianon in Environmental Samples

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ABSTRACT

The electrochemical reduction behaviour of Dithianon has been studied by cyclic voltammetry (CV) and differential pulse polarography (DPP) in methanolic Britton-Robinson buffer of pH 2.0-12.0. The nature of electrode process was studied, the number of electrons was evaluated and the reduction mechanism was proposed. Quantitive determination was carried out in the concentration range 1.5×10^{-5} M to 2.5×10^{-8} M using a DPP method with a lower detection limit of 2.0×10^{-8} M. The proposed method was successfully applied in the determination of Dithianon in grains, soils and water samples.

Key words*: Dithianon; Reduction behaviour; Mechanism; Analysis; Environmental samples*

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INTRODUCTION

Dithianon,(5,10-dihydro-5,10-dioxonaphtho(2,3-b)-1,4-dithi-in-2,3-dicarbonitrile) (Figure 1) is a quinone group containing pesticide and is a class of aromatic diketones, in which the carbonyl groups form part of the ring system. Several quinone pesticides are commonly used to treat foliage diseases of some crops.
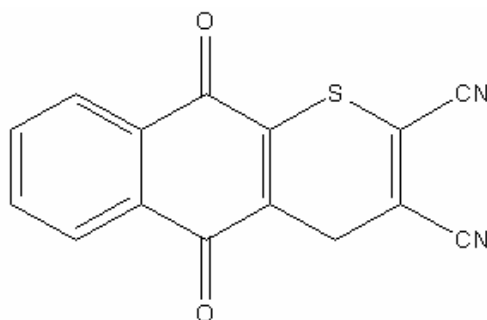

Figure 1: Structure of Dithianon

The electrochemical behaviour of quinones in aprotic media has been studied extensively. But most of the studies are devoted to understand the fundamental electrode processes [1]. Polarography has been used as an analytical method for quinone- hydroquinone system [2]. The applications are summarized and compiled periodically in Analytical Chemistry Annual Reviews [3]. Adkins and Cox [4] reported reduction potential of anthraquinone and phenanthraquinone in unbuffered tetramethy ammonium hydroxide solutions [5]. Wawzonek et al [6] reported half-wave potentials for anthraquinones in buffered media. Edward et al [7] studied the polarographic behaviour of a large number of hydroxyl substituted benzoquinones, naphthaquinones and anthraquinones.

The present investigation deals with electrochemical reduction behaviour and analysis of Dithianon by using cyclic voltammetry and differential pulse polarography at both dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE).

MATERIALS AND METHODS

Apparatus
A Metrohm unit: E 506 polarecord coupled with E 612 VA-scanner, E 648 VA-combistand, E 608 VA-controller, and a digital electronics 2000 X-Y/t recorder are used for cyclic voltammetric and differential pulse polarographic measurements. All the electrochemical measurements are carried out with three-electrode design at 25 ± 0.1^0C. The DME (area: 0.0223 cm^2, flow rate of Hg: 2.73 mg/sec, and mercury column height: 35 cm) and HMDE (with an area of 0.0328 cm^2) are used as working electrodes. Ag/AgCl (s), Cl$^-$ electrode is used as reference electrode for cyclic voltammetry and differential pulse polarography. Platinum electrode is used as counter electrode for both the techniques. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode, and spot galvanometer, was used for controlled potential electrolysis.

Reagents and solution
Dithianon was obtained from Cyanamid (India) Ltd., Bombay. The purity of the sample was tested by melting point determination and TLC analysis. Britton-Robinson buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid, and 0.1 M trisodium orthophosphate. All the chemicals used are of pure analar grade. Stock solution of Dithianon was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. Before running the voltammograms the test solution was purged with purified nitrogen for 10 min. A 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima.

Experimental Procedure
A standard stock solution of Dithianon (1×10^{-3} M) was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. 1ml of the standard solution is transferred into a polarographic cell and made up with 9 ml of the supporting electrolyte by 10 times dilution sensitivity is decreased and the solution is deoxygenated with oxygen-free nitrogen gas for 10 min. After recording the polarograms, small increments (0.2ml standard solution) are added and the polarograms are recorded after each addition under similar conditions. The optimum conditions for the analytical determination of Dithianon in pH 4.0 were found to be drop time 1.4s, pulse amplitude 50mv and applied potential of -0.49 v. The related standard deviations and correlation co-efficient for 10 replicates are found to be 1.23% and 0.996 for Dithianon.

RESULTS AND DISCUSSION

Characterisation of wave/peak

The electrochemical behaviour of Dithianon has been examined over the pH range 2.0 to 12.0. It exhibits a single well defined wave/peak in the entire pH range. The wave/peak is attributed to the reduction of the quinone group to the corresponding hydroquinone in a two electron process. In cyclic voltammetry, an anodic peak (a) is observed in the reverse scan. This anodic peak may be ascribed to the oxidation of the formed hydroquinone to the corresponding quinone. Typical voltammograms are shown in Figure 2 and Figure 3.
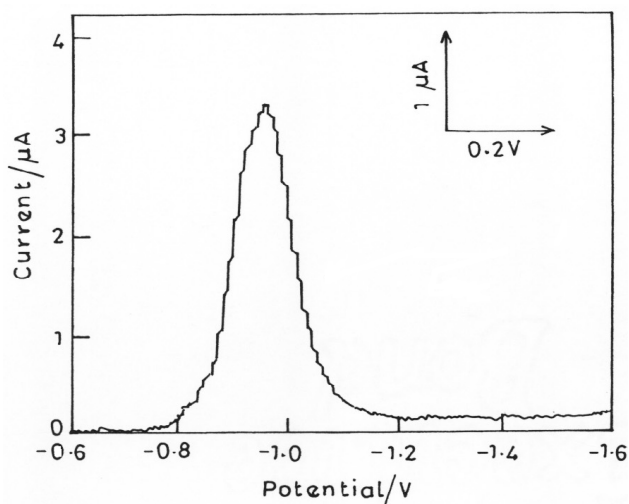

Figure 2: Typical differential pulse polarogram of Dithianonin pH 12.0, Concentration : 0.5 mM Drop time : 2s Pulse amplitude : 50 mv
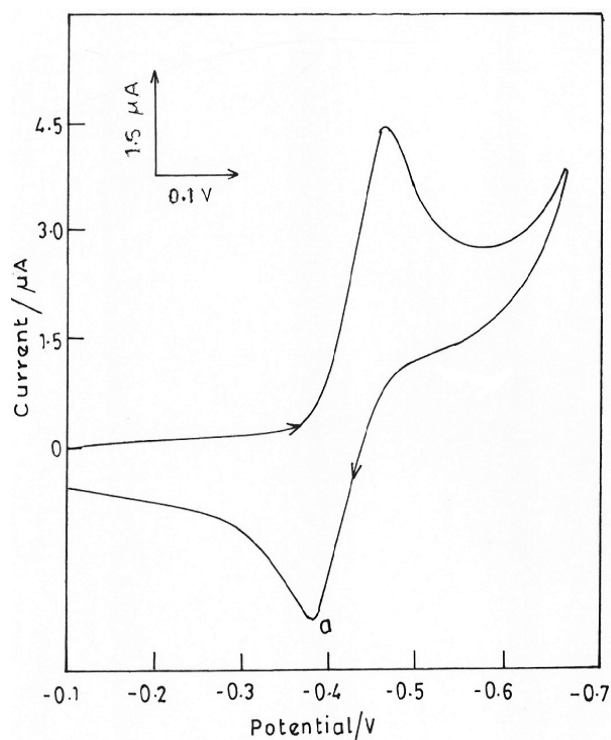

Figure 3: Typical cyclic voltammogram of Dithianon in pH 4.0 Concentration: 0.5mM Scan rate : 40 mV s^{-1}

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Nature of the Electrode Process
The diffusion controlled adsorption free nature of the electrode process is evidenced from the linear plots of i_p vs $v^{1/2}$ (Figure 4) and i_m vs $t^{2/3}$ (Figure 5) passing through origin in all supporting electrolytes ranging from pH 2.0 to 12.0. The experimental constancy $i_p/v^{1/2}$ with scan rate (V) in cyclic voltammetry indicates that the electrode processes is diffusion controlled.
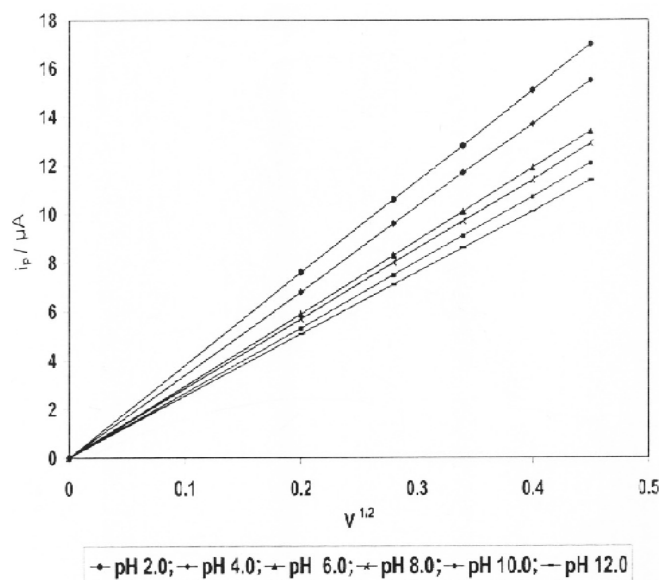

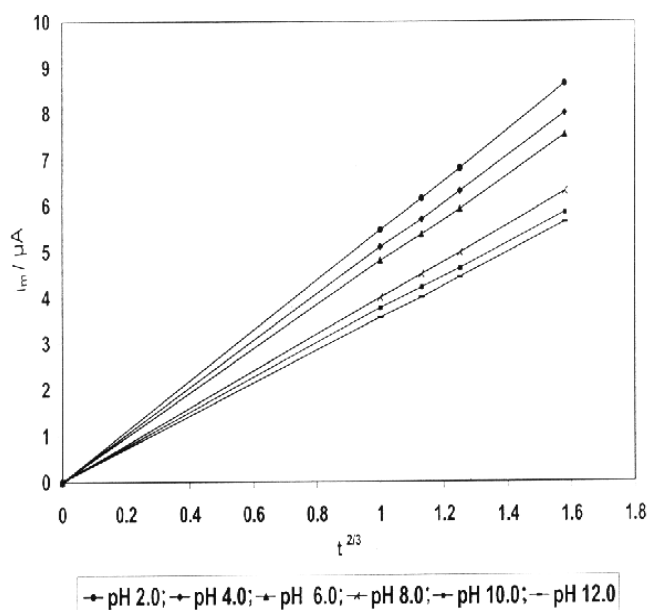**Figure 4: i_p vs $V^{1/2}$ plots of Dithianon**

Figure 5: i_m vs $t^{2/3}$ plots of Dithianon

The $E_{1/2}$ and E_p values of the reduction wave/peak are found to be independent of the concentration of the electroactive species indicating the electrode processes is to be reversible in Dithianon. The reversibility of the electrode process is also verified by the logarithmic analysis of polarographic curves. The solve of the E vs log (i / i_d-i) plot and the numerical values of $E_{1/4}$-$E_{3/4}$ are found to be almost equal to 59/n mv of Dithianon. The linearity in the plots of i_m vs 1-σ /

1+ σ in DPP and the presence of anodic peak in CV reverse scan also confirm that the reduction processes are reversible.

The half – wave and peak potential are shifted towards more negative potentials with increasing in pH of the buffer solution indicating the participation of proton in the reduction process. The number of protons involved in rate determining step is calculated from $E_{1/2}$ vs pH plot and is found to be one for the reduction process. Two electrons are given in the scheme.

Identification of the product
Millicoulometry is employed to find out the number of electrons involved in the electrode process. It is found to be two in 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 as reference electrode and platinum wire electrode as counter electrode. About 50 mg of the electroactive species under investigation is dissolved in a minimum amount of methanol and added to the cell containing supporting electrolyte (pH 4.0) the applied potential was fixed at -0.50 V. The electrolysis is carried out approximately for 4 hours, the product formed after controlled potential electrolysis is identified as the corresponding hydroquinone by IR spectral studies (The characteristic peaks for hydroxyl group O-H stretch broad peak 3500 – 3200 cm^{-1}, O-H bend: 1410 cm^{-1} and C-O stretch: 1230 cm^{-1}).

Kinetic data
Diffusion coefficient values calculated at various pH values in DPP and CV are shown in Table 1 and Table 2. The adsorption free nature of the electrode process is clearly evidenced from the nearly equal diffusion coefficient values obtained from DPP and CV for Dithianon. The diffusion coefficient values are seen to decrease gradually, which account for the decrease in diffusion current with increase in pH due to less availability of protons.

Table 1: Typical differential pulse polarogrpahic data of Dithianon Concentration: 0.5mM, Drop time: 1.4s, Pulse amplitude: 50 mV

pH of the supporting electrolyte	$-E_m/V$	$i_m/\mu A$	$Dx10^6/cm^2\ s^{-1}$
2.0	0.36	5.1	4.44
4.0	0.49	4.7	3.66
6.0	0.55	4.2	3.31
8.0	0.63	3.9	3.23
10.0	0.73	3.7	3.11
12.0	0.96	3.3	2.84

Table 2: Typical cyclic voltammetric data of Dithianon, Concentration : 0.5 mM, Scan rate : 40 mV s^{-1}

pH of the supporting electrolyte	$-E_p/V$	$i_p/\mu A$	$Dx10^6/cm^2\ s^{-1}$
2.0	0.35	4.9	4.59
4.0	0.47	4.4	3.68
6.0	0.55	4.2	3.20
8.0	0.71	3.9	3.11
10.0	0.82	3.7	3.02
12.0	0.94	3.4	2.49

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Electrode mechanism.

Based on the above results and observation obtained in the present investigation, as well as from the literature [8] the following reduction mechanism may be proposed to the compound in the entire pH range (Scheme):
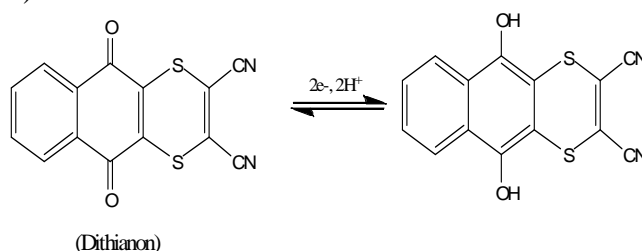

(Dithianon)

Figure 6: Scheme for Electrode Mechanism of Dithianon

Analysis

In the present investigation diferential pulse polarography has been employed to work out analytical procedures for the estimation of Dithianon in grains, soil and water samples using both calibration and standard addition methods. Investigated compound is found to exhibit well resolved peak in pH 4.0 which was chosen for quantitative studies. The peak currents are found to vary linearly with the concentration of the depolarizer over the concentration range 1.5×10^{-5} M to 3.0×10^{-8} M for Dithianon. The detection limit is found to be 2.0×10^{-8} M, which are calculated from the expression $dl = 3Sd/m$

where 'dl' is the lower detection limit

'Sd' is the standard deviation and

 'm' is the slope of the calibration plot.

 Analysis of Dithianon in grains

Sample is piked with known amount of standard grain (rice, 50g), which are previously made in the form of loose powder and left for 2-4 hrs. The samples were extracted with dichloromethane twice each time with 30ml. Then the mixture was transferred into Buchner funnel and filtered under suction. The extract was taken into a separating funnel to which 30 ml of water, 10 ml of saturated sodium chloride and 30 ml of dichloromethane are added and thoroughly shaken for 2 min. The combined extracts are filtered over 50 g of anhydrous sodium sulphate and the solvent is evaporated through rotatory evaporator. The residues are dissolved in methanol and transferred into 50 ml volumetric flask. A recovery of Dithianon in grain samples are incorporated in Table 3.

 Analysis of Dithianon in soil

 Soil samples were dried in a filter paper at laboratory temperature, allowed to pass through a 2.8 m sieve and homogenized in a ball mill. An aliquot (10g) of soil sample was spiked with known amounts of Dithianon solution and left for 2-4 hrs. These are extracted with hexane three times. Each time 50ml of hexane was used. The combined extracts were dried over anhydrous sodium sulphate and the solvent was removed through evaporation .The residue was dissolved in methanol and transferred into 50 ml standard flask. Recoveries of Dithianon in soil samples are presented in Table 3.

 Analysis of Dithianon in water sample

 A 1000 ml of water samples (Tap and well water) was spiked with the known amounts of the Dithianon left for 1hr. An aliquot of the solution was passed through a Whatmann Nylon membrane filter (0.45 pore size) and the filtrates were passed through a Sep-Pak C18 cartridge previously activated with 10 ml of acetonitrite and 5ml of deionised water. Elutions were carried

out with 10 ml of acetonitrite and filtered through anhydrous sodium sulphate. The organic phase was evaporated to dryness in rotatory vacuum evaporator. The residues are dissolved in methanol and added to cell containing buffer solution. The results obtained from the water samples are shown in Table 4.

Table 3: Recoveries of Dithianon added to grains and soils, Pulse amplitude : 50mV, Drop time : 1.4 s

Amount added (mg)	Average amount found* (mg) ± SD		Average recovery (%)	
	Rice	Soil	Rice	Soil
4.0	3.98±0.098	4.02±0.021	99.50	100.50
8.0	7.96±0.017	7.85±0.037	99.50	98.12
12.0	11.98±0.023	11.98±0.012	99.67	99.83
16.0	15.95±0.017	15.97±0.045	99.69	99.81

*Each value is an average of four determinations

Table 4: Recoveries of Dithianon added to water samples, Pulse amplitude : 50mV, Drop time : 1.4 s

Sample type	Amount added (M)	Average amount found* (M)	Average recovery (%)
Tap water	2×10^{-6}	1.96×10^{-6}	98.00
	4×10^{-6}	3.93×10^{-6}	98.25
Well water	6×10^{-6}	5.96×10^{-6}	99.33
	8×10^{-6}	7.9×10^{-6}	98.87

*Each value is an average of four determinations

CONCLUSION

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

Acknowledgment

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