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Electrochemical determination of propiconazole residues in environmental samples by voltammetry at HMDE

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ABSTRACT

In this study the residues of propiconazole in environmental samples such as grains and water samples based on its voltammetric behavior at hanging mercury drop electrode(HMDE). The reduction product is identified by using cyclic voltammetry and the universal buffer with pH range 2.0-6.0 is used as supporting electrolyte. The best curve and highest peak current are obtained in universal buffer at pH 4.0. Accumulation potential(-0.60V),Accumulationtime(70 sec)and Scanrate (50mVs.$^{-1}$) are optimized. Calculations made of by standard addition method. The peak heights are in linear trend over the concentration range of 1.0 x 10-8 to 1.0 x 10-5 M. The relative standard deviation and correlation coefficient for propinacazole was 0.97% and 0.998 respectively. The lower detection limit for propiconazole compound was 0.92 x 10-7 M.

KEYWORDS

Propiconazole;
HMDE;
DP-ASV;
Cyclic voltammetry;
Universal buffer;
Grains;
Water samples.

INTRODUCTION

Propiconazole(2*RS*,4*RS*;2*RS*,4*SR*)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1*H*-1,2,4-triazole) ($C_{15}H_{17}Cl_2N_3O_2$) is broad spectrum fungicide (conazole fungicides). Defferent methods are employed for determination of propiconazole residues in environmental samples. Lopez et al.[1] determined fungicides carbendazim, metalaxyl, folpet, and propiconazole in must and wine by using HPLC method. Karina et al.[2] Determined Propiconazole Residue in Boronia Extract by using gass chromatography/mass spectroscopy. But there is no literature fond for the determination of propiconazole residues in environmental samples by using electro chemical methods such as polarography,voltammetry. Rasekhar reddy et al.[3] employed voltametry for the determination of oxabetrinil residues in environ mental samples. In this work deferential pulse adsorptive stripping voltammetry employed for the determination of propiconazole residues in vegetables.

DIFFERENTIAL PULSE-ADSORPTIVE STRIPPING VOLTAMMETRIC STUDIES

Propiconazole exhibits a single well-defined peak in the pH range 2.0 to 6.0, when potential was scanned from -1.05 V and so on at HMDE (Figure 1) which is due to the reduction of the azomethine group. The experimental parameters that affect the AdSV signal car-

ried out by considering stripping peak in order to establish the optimum conditions. Both standard addition and calibration methods are employed for the determination of propiconazole in grains and water.

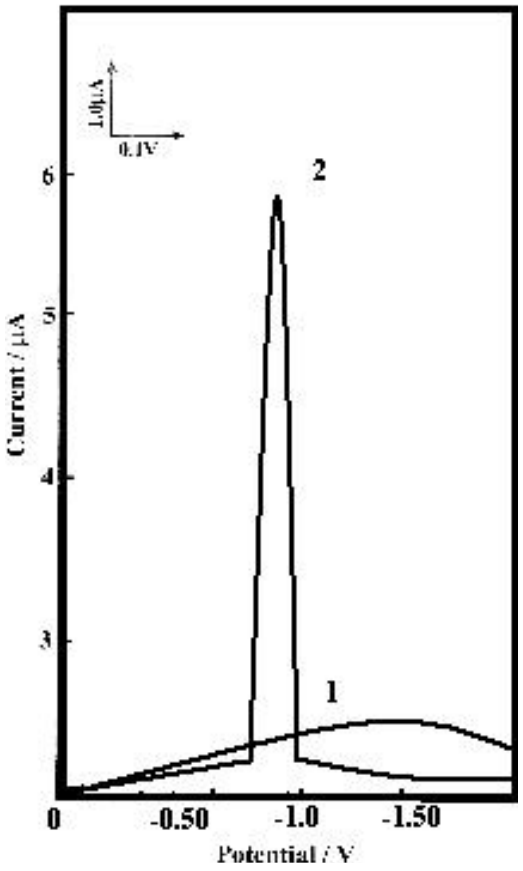


Figure 1 : Typical differential pulse adsorptive stripping voltammogram of propiconazole at pH (4.0), accumulation Potential : -0.8 V; rest time: 10 sec., accumulation time : 60 sec; scan rate: 50 mVs^{-1}; (2)sample $1.0x10^{-5}$ mM.(1) blank.

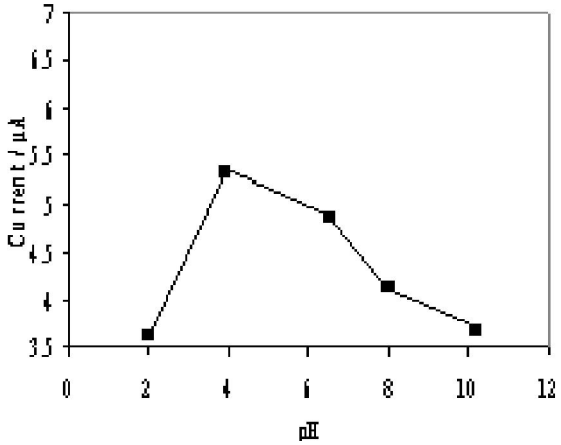


Figure 2 : Effect of pH on propiconazole solution at HMDE; accumulation time: 60 sec.; accumulation potential: -0.7V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 50 mVs^{-1}; pulse amplitude: 50 mV.

EFFECT OF PH

The peak current i_p, increased gradually with the increase of pH of the solution till it reaches the maximum value at pH 4.0 (Figure 2). A shift of the peak potential towards more negative value with increase in pH indicates the existence of a protonation reaction coupled with the propiconazole reduction process. The best curve and highest peak current are obtained in universal buffer at pH 4.

EFFECT OF ACCUMULATION POTENTIAL

The influence of accumulation potential from -0.5 V to -1.0 V on the peak height for $1.0x10^{-5}$ propiconazole was tested using AdSV technique in the presence of universal buffer (pH 4.0) an enhanced adsorption peak at potential -0.60V obtained as shown in Figure 3.

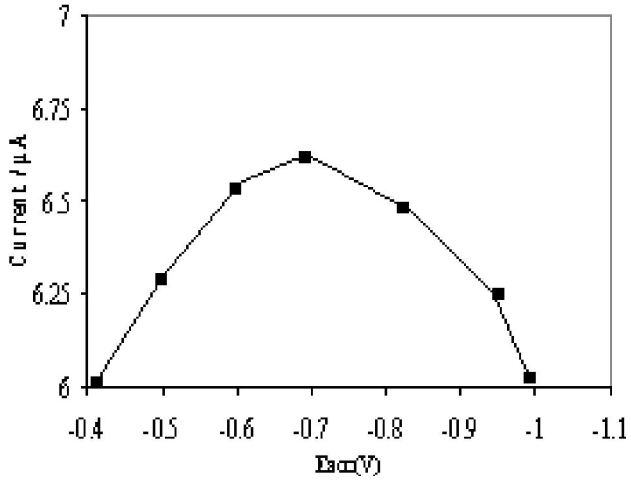


Figure 3 : Effect of accumulation potential on the DP-AdSV response of propiconazole at HMDE; accumulation time: 60 sec.; rest time: 10 sec., stirring rate: 2000 rpm; scan rate :50 mVs^{-1}; pulse amplitude: 50 mV.

EFFECT OF ACCUMULATION TIME

The adsorption behaviour of propiconazole has a particular importance to enhance the sensitivity of voltammetry. At first, peak current increased linearly with t_{acc} which indicates that before adsorptive equilibrium is reached, the longer the accumulation time, the more the propiconazole becomes adsorbed and larger is the peak current. However, after 60 sec. accumula-

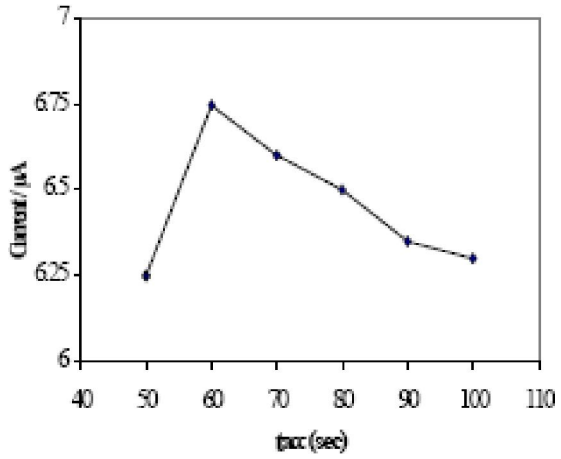


Figure 4 : Effect of accumulation time on the DP-AdSV response of propiconazole at HMDE; accumulation potential: -0.7V; rest time: 10 sec., stirring rate: 2000 rpm; scan rate: 50 mVs^{-1}; pulse amplitude: 50 mV.

tion time, the peak current tended to level off, illustrating that adsorptive equilibrium of propiconazole on the mercury electrode surface is achieved. Figure 4 shows the effect of accumulation time on peak currents for 1.0x10^{-5}M of propiconazole. The accumulation time of 70 sec. is used for further studies.

EFFECT OF SCAN RATE

The effects of varying the potential scan rate on the reduction peak current of propiconazole was examined. The reduction peak current increased linearly with the scan rate over the range from 25 mVs^{-1} to 75 mVs.$^{-1}$ Better sensitivity was observed at 50mVs.$^{-1}$

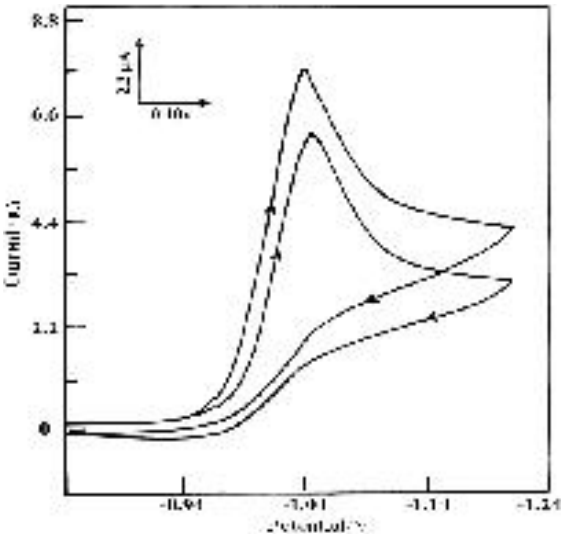


Figure 5 : Typical cyclic voltammogram of propiconazole at pH 4.0 concentration: 1.0x10^{-5} mM; scan rate : 50 mVs^{-1}.

CHARACTERIZATION OF WAVES / PEAKS

The effect of pH on the voltammograms has been investigated by recording the current voltage curves for propiconazole at a concentration of 0.5 mM in universal buffer systems over the pH range of 2.0 to 6.0. propinacazole exhibits a single well-defined wave / peak obtained in pH 2.0 to 6.0 in all the techniques, corresponding to the reduction of two azomethine groups in 4 electron process. Typical cyclic voltammogram are shown in Figure 5.

NATURE OF THE ELECTRODE PROCESS

Based on the linear plots i_p vs $v^{1/2}$ passing through origin the reduction process is found to be diffusion controlled and adsorption free. The shift of peak potential (E_p) towards more negative values with increase in concentration of depolariser, indicates 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 process. The dependence of i_p / pH curves shows a behaviour in accordance with a process in which a proton transfer provides the electrochemical reduction of the acid form to form an electroactive species. The number of protons involved in the rate determining step is found to be 4.

IDENTIFICATION OF REDUCTION PRODUCTS

Number of electrons involved in the overall reduction process of propiconazole is found to be 4 and it is evidenced by millicoulometric technique. Controlled potential electrolysis conducted at -1.0V vs SCE at pH 4.0 and the corresponding decay noted by using the galvanometer. The electrolysis is allowed to proceed virtually to completion.

KINETIC DATA

Kinetic parameters such as diffusion coefficient, transfer coefficient and heterogeneous forward rate constant values evaluated and reported in TABLE 1. The diffusion

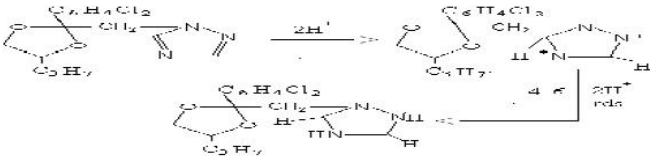
TABLE 1 : Typical cyclic voltammetric data of propiconazole concentration: $1.0x10^{-5}$M, scan rate: 50 mVs^{-1}

pH of the supporting electrolyte	$-E_p$ V	i_p μA	αn_a	D x 10^6 cm^2 s^{-1}	$k^0_{f,h}$ cm s^{-1}
2.0	0.90	8.2	0.43	1.50	4.10 x 10^{-9}
4.0	0.98	7.5	0.32	1.48	8.92 x 10^{-10}
6.0	1.04	7.1	0.24	1.28	6.23 x 10^{-12}

coefficient values were 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 account for the shift of reduction potentials towards more negative values with increase in pH. This trend was particularly evident where proton transfer was involved in the electrode process.

Electrode mechanism

Based on the results obtained from all the techniques, the electro-chemical reduction mechanism is as follows.



ANALYSIS

Adsorptive stripping voltammetry is a suitable technique for the analysis of propiconazole due to its high sensitivity and resolution. The well resolved stripping voltammetric peak for the analytical purpose was obtained at pH 2.0 to 6.0, because in the buffer solution of higher alkalinity (pH < 8) the reduction of azomethine group is not easily facilitated owing to the less availability of protons. The peak heights are in linear trend over the concentration range of 1.0×10^{-8} to 1.0×10^{-5} M. The relative standard deviation and correlation coefficient for propiconazole was 0.97% and 0.998 respectively. The lower detection limit for propiconazole compound was 0.92×10^{-7} M.

RECOMMENDED ANALYTICAL PROCEDURE

Analytical procedure for the voltammetric determination of propiconazole is as follows. A standard solution of propiconazole ($1.0x10^{-5}$M) is prepared in methanol.1 mL of standard solution is transferred in to cell and made up with 9 mL of supporting electrolyte and then purged with oxygen free N_2 gas for 10 min. prior to each run. After obtaining the voltammogram, small addition of standard solutions are added and voltammogram recorded after each addition under similar experimental parameters. The optimum conditions for the determination of propiconazole in pH 4.0 with a drop time of 2 sec., pulse amplitude of 50 mV and applied potential of -0.98 V vs. SCE.

DETERMINATION OF PROPICONAZOLE IN SPIKED GRAIN SAMPLES

The developed analytical procedure has been applied to the quantitative estimation of propiconazole in grain samples. Known amounts of propiconazole were sprayed on grain (wheat, rice) samples (25 g) and left for 1-2 hours. Then the samples are weighed, crushed and homogenized. The extracts were prepared by treatment of the above sample with two 50 mL portions of acetone and evaporated to dryness. The residue of propiconazole dissolved in methanol and transferred to a 100 mL volumetric flask. Results obtained for the determination of propiconazole. The results are summarized in TABLE 2.

TABLE 2 : Recoveries of propiconazole in spiked grain samples

Sample	Amount added (μg/mL)	Amount found (μg/mL)	Recovery (%)	Standard deviation
Wheat	2.0	1.96	98.00	0.0212
	6.0	5.95	99.16	0.0252
Rice	3.0	2.96	98.66	0.007
	5.0	4.92	98.40	0.021

DETERMINATION OF PROPICONAZOLE IN SPIKED WATER SAMPLES

River water samples, which received run-off water from agricultural field, were collected form swarnamukhi river belt, Vakadu, Nellore district, A.P., India. These samples were filtered through a Whatman No.41 filter paper and added with known amount of

propiconazole. Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analyzed as described above. The results are furnished in TABLE 3.

TABLE 3 : Recoveries of propiconazole in spiked water samples

Sample	Amount added (µg/mL)	Amount found (µg/mL)	Recovery (%)	Standard deviation
Water-1	2.0	1.97	98.50	0.0312
(Tank)	6.0	5.96	99.33	0.0152
Water-2	3.0	2.95	98.33	0.007
(Irrigation)	5.0	4.90	98.00	0.031

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