Polarographic Behavior and Determination of Pendimethalin in Formulations, and Environmental Samples

Mallipattu Sreedhar, Janmanchi Damodar, Nimmagadda Venkata Vijaya Jyothi, and Srinivasulu Reddy Jayarama Reddy*

Department of Chemistry, Electrochemical Research Laboratory, Sri Venkateswara University, Tirupati - 517 502, A.P, INDIA.

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A differential pulse polarographic (DPP) method for the determination of pendimethalin is described based on the reduction of a nitro group at a dropping mercury electrode in BR buffers of pH 2.0 to 12.0 using 25% acetone-water mixtures as a solvent. Also, a cyclic voltammetry (CV) technique has been used to study the behavior of pendimethalin at a hanging mercury drop electrode. The differential pulse polarographic method described here has been applied to the determination of pendimethalin in formulations, grains, soils and spiked water samples. Both standard addition and calibration methods were used for the analytical measurements. The lower detection limit was found to be 1.87×10^{-8} M (M = mol dm^{-3}).

Pendimethalin (Chart 1) is a selective herbicide which can control most annual grasses and many annual broad-leaved weeds in cereals, maize, and rice.[1] The major metabolic routes for pendimethalin involve the hydroxylation of the 4-methyl and *N*-α ethyl groups and the oxidation of these alkyl groups to carboxylic acids, nitro reduction, cyclization and conjugation.[2] In soil, the 4-methyl group on the benzene ring is oxidised to the carboxylic acid.[3] The persistence of pendimethalin, 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 crops.[4] There are several methods available for the determination of pendimethalin. Among them are electroanalytical methods, particularly voltammetric/polarographic, which has gained profound interest due to the electroactive nature of most nitro groups containing compounds, on one hand, and due to the sensitivity, accuracy and simiplicity of the technique on the other. GC-MS and GC-NPD have been used for the determination of pendimethalin in environmental samples.[5] The analysis of pendimethalin in soil has been achieved by electron-capture detection (ECD).[6] A number of herbicide residues have been determined in soil and water.[7,8] Electrochemical techniques[9—12] have been widely employed for the determination of the nitro group-containing pesticides.

This paper reports on a study of the electrode process of pendimethalin and its determination in formulations, grains, soils, and spiked-water samples employing cyclic voltammetry and differential pulse polarography.

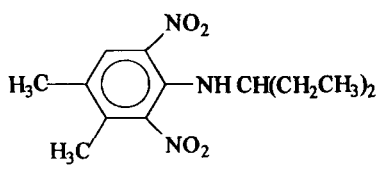


Chart 1.

Results and Discussion

The differential pulse polarographic (DPP) behavior of pendimethalin was examined in the pH range of 2.0 to 12.0. The compound was found to give two well-defined peaks in the acidic medium and one peak in the basic medium. The two peaks in the acidic medium are attributed to the simultaneous reduction of two nitro groups to hydroxylamine in an eight-electron process; the second wave/peak corresponds to a reduction of the hydroxyamino group to the amine group in a 4-electron process. The number of electrons was determined by milli coulometry. The peak-height ratios were found to be 2 : 1. As pH increased, the first wave/peak disappeared and formed as a single wave/peak with 4-electron reduction to a hydroxyamino group. In the alkaline medium, hydroxylamine is not reduced further owing to the non-availability of protons. A typical differential pulse polarogram is shown in Fig. 1.

In cyclic voltammetry (CV), a small anodic peak (a_1) was also observed in a reverse scan, as shown in Fig. 2. It is quite likely that a nitroso compound was formed, whose movement at the electrode surface may be responsible for the anodic peak. In the second scan another cathodic peak (c_2) was obtained, which may have been due to the reduction of the nitroso compound to hydroxylamine[13] formed at a_1.

The nature of the reduction process was found to be diffusion-controlled and adsorption-free in the buffer system studied, as evidenced from the linear plots of i_m vs. $t^{2/3}$ [14,15] and i_p vs. $V^{1/2}$ (where i_m is the maximum current in DPP, t is the drop time, i_p is the peak current in CV, and V is the

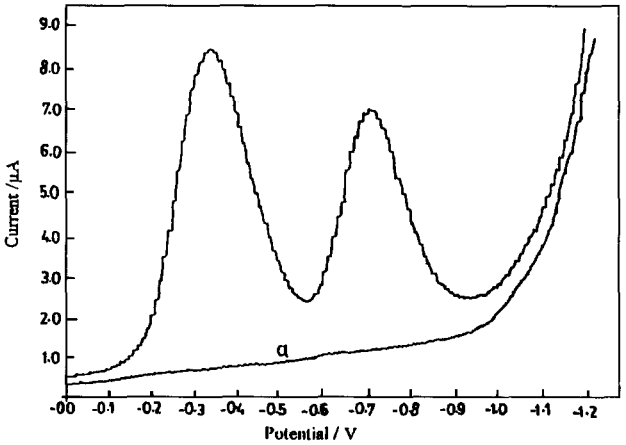


Fig. 1. Typical differential pulse polarogram of pendimethalin in pH 4.0, concentration = 1×10^{-5} M, drop time = 1.4 s, pulse amplitude = 28 mV, solvent = 25% acetone, a: blank solution of pH 4.0.

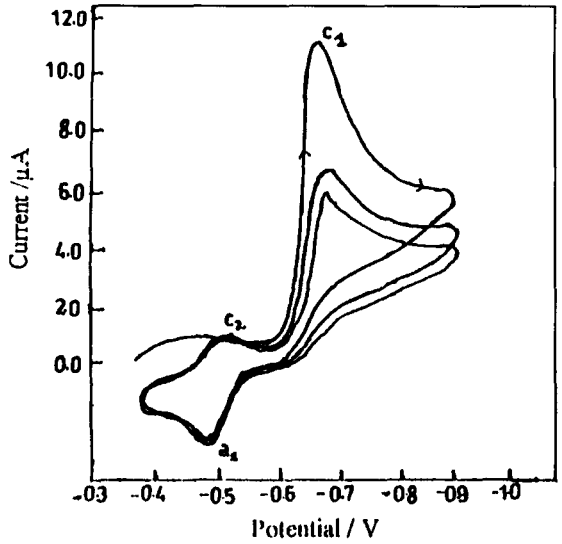


Fig. 2. Typical cyclic voltammogram of pendimethalin in pH 10.0, concentration = 1×10^{-5} M, solvent = 25% acetone, sweep rate = 45 mV s^{-1}.

scan rate) relationships. The variation of the peak potential (E_m) values of the compound was found to be pH-dependent, and shifts towards a more negative potential along with an increase in the pH of the buffer system, indicating proton involvement in the electrode process and a variation of the E_m values towards more negative potentials upon increasing the concentration of the electroactive species, indicating the irreversibility of the electrode process. From E_m vs. pH plots, the slope was found to be −72 mV, and the number of protons involved in the rate-determining step of nitro group reduction was shown to be two by using the equation

$$\Delta E_m/\Delta pH = -0.059p/\alpha n_a,$$

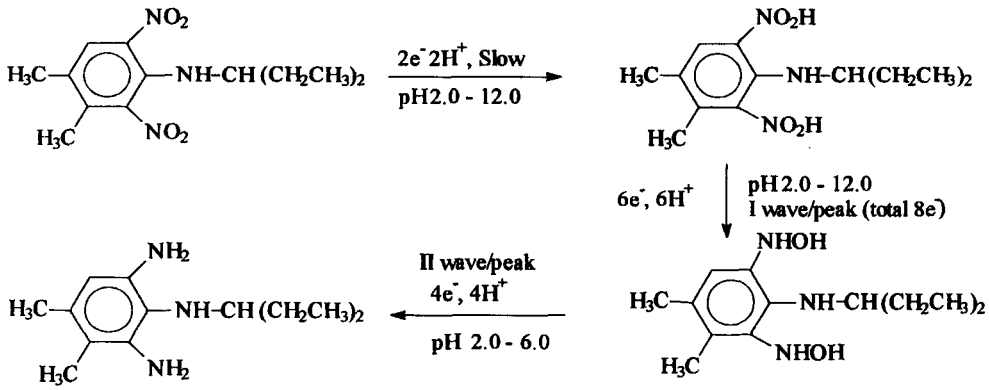
Where n_a is the number of electrons, α the transfer coefficient, and p the number of protons involved in the rate-determining step

On the basis of the results of our own investigations as well as data from the literature[16] the following mechanism may be assigned for the electrochemical reduction of pendimethalin (Scheme 1).

The number of electrons in the overall reduction process, determined by millicoulometry, was found to be twelve in the acidic medium for the reduction of two nitro groups. The first wave/peak corresponds to an eight-electron reduction (for each nitro group four electrons) and the second corresponds to a four-electron reduction process. However, it was observed to be four for each $-NO_2$ group reduction, thus making a total of eight in basic media. A controlled potential electrolysis was carried out in pH 2.0 and 12.0 at −0.578 V and −0.82 V (vs. Ag/AgCl(s), Cl^-), and the products were identified as amine and hydroxylamine, respectively, through the IR spectra (3300, 3350, 3250, and 3550 cm^{-1}).

Analysis. Because the polarographic peak that is attributed to the reduction of the nitro group at pH 8.0 is highly reproducible, it is preferred for the analysis. Both the standard addition and calibration methods were used for a quantitative estimation of the compound. The peak heights were found to be linear over the range 1.13×10^{-5} to 2.0×10^{-8} M (M = mol dm^{-3}). The detection limit was found to be 1.87×10^{-8} M. The detection limit (*D.L.*)[17] was calculated using the expression $D.L. = 3SD/m$, where SD is the Standard Deviation, and m the slope of the calibration graph.

Recommended Analytical Procedure. A standard solution (1×10^{-5} M) was prepared by the dissolution of an appropriate amount of the electroactive species in acetone.



Scheme 1.

An aliquot of the standard solution was diluted with the supporting electrolyte, and deoxygenated with oxygen-free nitrogen for 5 min. After the differential pulse polarogram was recorded, small aliquots (0.2 ml) of the standard solution were added, and polarograms were recorded after each addition under the same conditions. In the present study, the best precision was obtained at pH 8.0 with a drop time of 1.4 s, a pulse amplitude of 28 mV and an applied potential of −0.603 V (vs. Ag/AgCl(s), Cl^-). The relative standard deviation and correlation coefficients were found to be 1.34 and 0.995%.

The procedure was successfully used for the determination of this compound in their formulations, grains, soils and spiked water samples.

Analysis of Formulations. The required quantity of formulation (Herbadox, Prowl, Stomp) corresponding to a stock solution of 1×10^{-3} M was accurately measured and transferred into a 100 ml calibrated flask containing 50 ml of acetone. A solution of 1×10^{-5} M was prepared by diluting this stock solution with a buffer. The assay results in the formulations are given in Table 1. Differential pulse polarograms of various concentrations of the formulation herbicides are given in Fig. 3.

Analysis of Herbicide in Grains and Soils. Grain (rice or wheat) samples (50 g) or soil samples (20 g) were sprayed with a known amount of pendimethalin and left for 2—4 h. The samples were extracted with ethyl acetate (2×100 ml) by shaking in a flask for 10 min. The organic phase was filtered under suction through Whatmann No. 1 filter paper. The solvent was removed through evaporation. The residue of pendimethalin was dissolved in acetone and transferred into a 50 ml volumetric flask.

The results obtained for the determination of herbicide in grains and soils are presented in Table 2.

Determination of Pendimethalin in Spiked-Water Samples. A 100 ml sample of tap water was spiked with herbicide at different concentration levels (each concentration 3 times), taken into a 2 L seperatory funnel, and shaken for few minutes. The solution was passed through a Whatmann Nylon® membrane filter (0.45 μm size). The elution was carried out with 3×50 ml of dichloromethane. The organic solvent was filtered through anhydrous sodium sulfate and

Table 1. Determination of Pendimethalin in Formulations

Compound	pH of supporting electrolyte	Labelled amount mg	Average[a] amount ±*SD*	Average recovery (%)
Herbadox	8.0	3.0	2.94 ± 0.026	98.00
	8.0	5.0	4.92 ± 0.031	98.40
Prowl	8.0	3.0	2.91 ± 0.017	97.00
	8.0	5.0	4.93 ± 0.025	98.60
Stomp	8.0	3.0	2.89 ± 0.021	96.33
	8.0	5.0	4.90 ± 0.030	98.00

a) Each value is an average of three determinations.

Table 2. Recoveries of Pendimethalin Added to Grains and Soils

Compound	Amount Added	Average amount found/mg		Average Recovery[a]/%	
		Rice	Soil	Rice	Soil
Pendimethalin	5.0	4.898	4.903	97.96	98.06
	10.0	9.909	9.881	99.09	98.81
	15.0	14.887	14.832	99.25	98.88
	20.0	19.761	19.649	98.80	98.24

a) Each value is an average of three determinations.

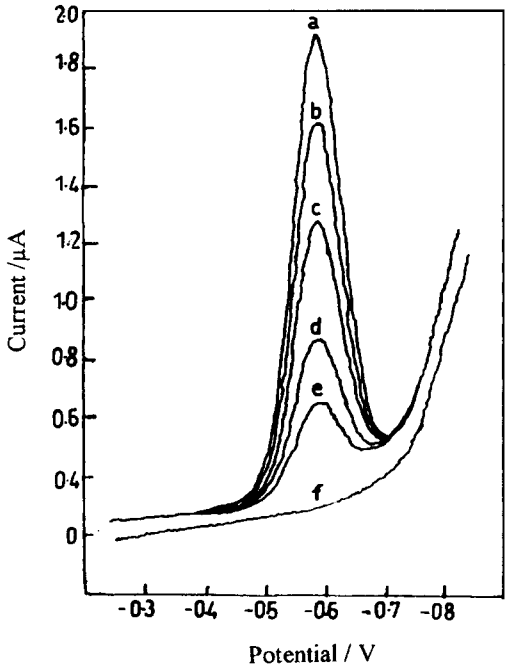


Fig. 3. Typical differential pulse polarograms of formulation, Herbadox in pH 8.0, drop time = 1.4 s, pulse amplitude = 28 mV, a: 1.13×10^{-5} M, b: 5×10^{-6} M, c: 1×10^{-6} M, d: 1×10^{-7} M, e: 2×10^{-8} M, f: blank.

Table 3. Recoveries of Pendimethalin in Spiked Water Samples

Compound	Amount added	Average amount found	Average recovery[a] ±*SD*
	M	M	%
Pendimethalin	2×10^{-7}	1.91×10^{-7}	95.5 ± 0.017
	4×10^{-7}	3.90×10^{-7}	97.5 ± 0.015
	6×10^{-7}	5.95×10^{-7}	99.16 ± 0.045
	8×10^{-7}	7.91×10^{-7}	98.8 ± 0.032

a) Each value is an average of three determinations.

evaporated to dryness. Small volumes of hexane were added to remove dichloromethane completely. The residue was dissolved in acetone and then transferred to a 50 ml volumetric flask. Table 3 gives recoveries of pendimethalin in spiked water samples.

Experimental

Differential pulse polarographic and cylic voltammetric studies were performed using a Metrohm E-506 polarecorder equipped with a Metrohm 663VA stand and a 612 VA scanner coupled to a digital-2000 X-Y/t recorder. A dropping mercury electrode (of area 0.0232 cm^2) and a hanging mercury drop electrode (of area 0.2324 cm^2) were used as working electrodes for DPP and CV, respectively. The reference electrode was an Ag/AgCl(s), Cl^- electrode and the counter electrode was a platinum electrode. A metrohm-632 pH meter was useful to measure the pH. All experiments were carried out at 28±1 °C.

A Britton-Robinson (BR) buffer solution was prepared containing 0.04 M of acetic acid (99%), 0.04 M of orthophosphoric acid (85%), and 0.04 M of boric acid. The pH range, from 2.0 to 12.0, was adjusted using 0.2 M of sodium hydroxide. All of the chemicals were of analytical reagent grade. Pendimethalin was kindly provided by Cyanamid India Ltd., Bombay.

Interference Studies. S-triazine herbicides, atrazine, prometryn, simiazine, terbutryn and methoprotryne are usually used along with analyte, pendimethalin in the field. Terbutryn, methoprotryne which gave signals at more negative potentials than pendimethalin (−0.98V, −0.91 V) were found not to interfere with the analyte signal. Atrazine, prometryn, simazine decreased the signal of the analyte by only 8% when a 30-fold excess of these are added. Humic acid, as one of the most important water-soluble soil organic components when analyzing water samples, did not produce any change in the recovery of pendimethalin under the same conditions, even when a 50-fold excess was added.

Conclusion

The data incorporated in Tables 1, 2, and 3 suggest that in addition to pendimethalin, other constituents present in formulations, grains and soils did not interfere in the above method. The principal advantage of the proposed polarographic method over the other ones is that the excipients do not interfere and a separation procedure is not necessary. Consequently, the method can be employed in routine analysis. The proposed procedure assures a good precision and accuracy of pendimethalin determination in formulation, grains, soils and spiked-water samples, although no rigorous protocol is required compared with other methods.

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