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A simple and sensitive differential pulse polarographic determination of dinitramine in water and agricultural samples

N.Y.Sreedhar*, S.Rajasekar Reddy, P.Reddy Prasad, C.Nageswara Reddy
Department of Chemistry, Electroanalytical Lab, S.V.University, Tirupati, A.P., (INDIA)

E-mail : sreedhar_ny@rediffmail.com

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ABSTRACT

A selective and sensitive differential pulse polarographic method for the determination of dinitramine was studied using dropping mercury electrode (DME) in universal buffer of pH range 2.0 to 12.0. The peak observed for the dinitramine 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 dinitramine concentration was linear within the concentration range of 1.0×10^{-5} to 1.0×10^{-9} 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 dinitramine in water and agricultural samples.

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KEYWORDS

Dinitramine;
Water and agricultural
samples;
Differential pulse
polarography.

INTRODUCTION

Pesticides are widely used to protect the crops from a variety of pests. The use of pesticides benefits in increasing agricultural production but the repeated and indiscriminated usage of certain pesticides have led to their accumulation in plants, animals, soils and sediments, thus effecting widespread contamination of the environment^[1]. After application, the pesticide molecules may undergo different pathways in the environment, depending on the types of interaction with the soil components^[2,3]. In soils rich in organic matter or/and clay, pesticide molecules may become immobilised by strong absorption^[4,5] that facilitates their degradation by sunlight, microorganisms or chemical reactions. In these

cases, the degradation products may be toxic or not. In mineral soils, where the interaction is commonly very weak, they may be leached by rain or irrigation waters reaching rivers, dams or under-ground waters. Under such circumstances, the risk of contamination of potable sources is quite serious.

Dinitramine (N,N-diethyl-2,6-dinitro-4-(trifluoromethyl) benzene-1,3-diamine) are selective herbicide, which act by killing weed seeds as they germinate. Due to the continuous increase in the application of such pesticide, the necessity of water analysis is always growing. The traditional techniques used for such purpose are liquid chromatography and gas chromatography with electron capture detection, which is one of the most adequate due to the very low value obtain-

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able for the detection limit. These are HPLC-UV^[6-9], GC-ECD^[10,11] square wave voltammetry (SWV)^[12-14]. However, the above techniques very expensive and demanding well equipped laboratory installations and a well-trained analysis team. On the other hand, electro analytical procedures can overcome many of such difficulties by analysing environmental samples without extractions and purification steps, thus shortening and undervaluing the pesticide analysis. DPP determinations of some nitro group containing pesticides were discussed by Benadikova et al.^[15].

The aim of this work is to study the electrochemical behavior of the herbicide dinitramine in DMF solution by differential pulse polarography and to establish the initial steps in the development of an electro analytical procedure to analyze dinitramine in spiked waters, either pure from the laboratory or polluted from local urban creeks.

EXPERIMENTAL

Apparatus

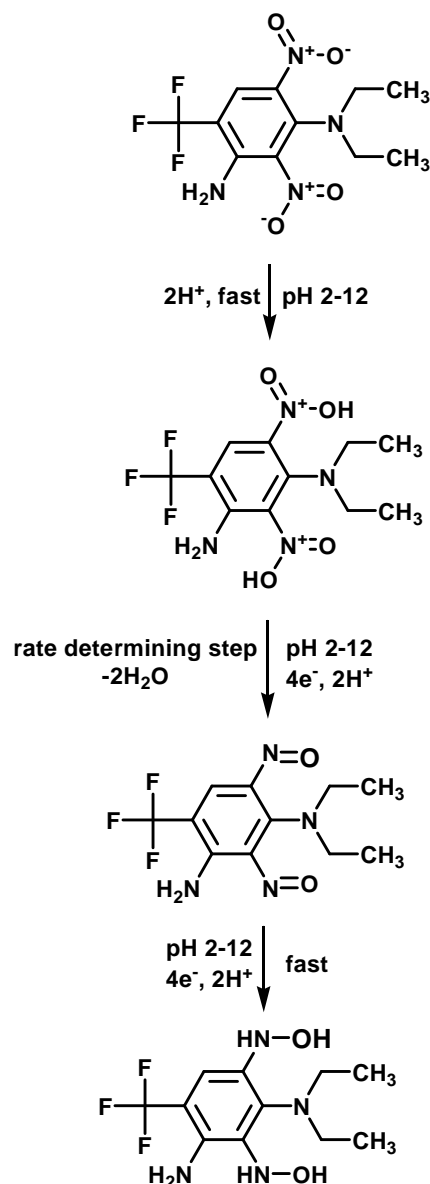
Analysis were carried out with an Elico Model CL-362, three electrode system consisting of a dropping mercury electrode (DME) as the working electrode, an Ag/AgCl reference electrode and platinum electrode as counter electrode. It was outfitted with a Model LX-300+ X-Y recorder. pH measurements were carried out with Elico digital pH meter. Dissolved air was removed from the solutions by degassing with oxygen-free nitrogen for 10 minutes. All the experiments were performed at $28 \pm 1^\circ\text{C}$.

Reagents

Dinitramine ($\text{C}_{11}\text{H}_{13}\text{F}_3\text{N}_4\text{O}_4$) was obtained from Rallis India Ltd. The purity of the compound was tested by a melting point determination. Stock solution was prepared by dissolving the required amount of compound in dimethylformamide. Universal buffers of pH range 2.0 to 12.0 was prepared using 0.2M boric acid, 0.05M citric acid and 0.1M trisodium orthophosphate^[16]. All the chemicals used were of analytical grade.

Recommended analytical procedure

Stock solution ($1.0 \times 10^{-6} \text{ mol l}^{-1}$) is prepared by



Scheme 1 : Reduction mechanism of dinitramine

dissolution of the appropriate amount of the electroactive species in dimethylformamide. 1.0ml of the standard solution is transferred into polarographic cell and made up with 9ml of the supporting electrolyte (universal buffer pH 5.0) and then deoxygenated with nitrogen gas for 10 min. After recording the polarogram, small increments of standard solution were added, and the polarograms are recorded after each addition under similar conditions. In the present study, the best precision was obtained at pH 4.0 with a drop time of 2.0 sec, pulse amplitude of 50mV, and a peak potential for dinitramine of -1.04 V respectively. The relative standard deviation and correlation coefficients were found

to be 1.22% and 0.998 for the respective compound for 5 replicants.

RESULTS AND DISCUSSION

Differential pulse polarographic behavior

The effect of the pH on the dinitramine peak potential was tested. A single, well defined polarographic peak has been observed in the pH 5.0 (Figure 1). This single peak is attributed to the facile simultaneous reduction of two nitro groups present in the title compound in eight electron reduction process to the corresponding hydroxylamine group. The electrode process for the dinitramine is found to be free from adsorption and diffusion controlled in nature which is confirmed through the linear plots of i_m versus concentration, and i_m versus $t^{2/3}$ passing through the origin^[17,18]. The slight variation of the peak potential value of the title compound was found to be pH dependent, and to shift towards more negative values along with an increase in the pH of the buffer system indicating the electrode process to be irreversible^[19].

Analysis is carried out using the currents obtained for nitro group reduction in dinitramine. It is observed that at pH 5.0, the nitro group reduction appears at the start of the potential. In alkaline solutions (pH 8.0 to 12.0), the reduction of nitro group is not easily facilitated owing to less availability of protons. In pH 6.0 the peak observed to be less due to less number of protons available. As a result protonated species concen-

tration is lowered. Hence peak current is also lowered. But in pH 5.0 the concentration of protonated species is more hence high peak current is observed. Therefore, pH 5.0 was chosen as optimum pH for further studies (Figure 2). Polarographic half wave or peak potential is characteristic property for each electro active species. Even though functional group (reducible site) present in the molecule, molecular structure, molecular weight, surrounding environment make the reduction at either less or more potentials possible, the reduction helps in their determinations in environmental samples. Before the analysis we have to prepare blank run for the samples (water and agricultural samples) which are under investigation. A definite amount of the herbicide is then added to samples and polarographic studies were carried out. If the blank gives any response based on their E_m values we can assume the other foreign substance to be present in the sample. This is the major advantage of polarography rather than other techniques. In the present investigation within the potential range (0.80V to 1.60V) no signal other than title compound is observed. This indicates that the proposed method is free from interferences. The peak heights were found to be linear over the concentration range 1.0×10^{-5} to 1.010×10^{-9} mol l⁻¹ for dinitramine respectively. The lower detection limits was found to be 1.02×10^{-7} mol l⁻¹ for the respective compound. The detection limit was calculated using the expression^[20] $dl = 3 \times Sd/m$, where Sd is standard deviation and m, the slope of the calibration plot.

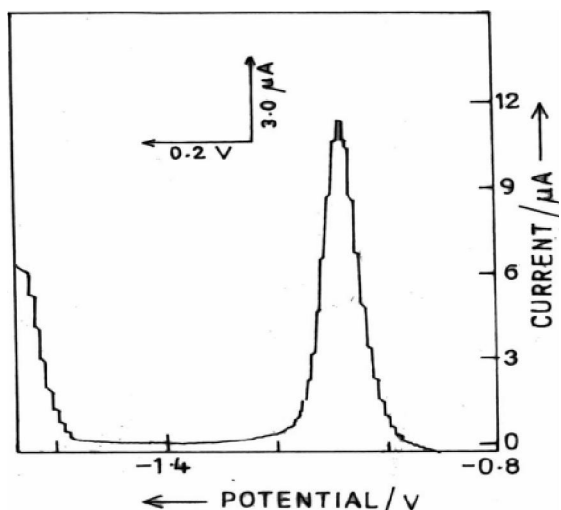


Figure 1 : Differential pulse polarogram of dinitramine at pH 5.0

Determination of dinitramine in polluted water

River water samples, which received run-off water

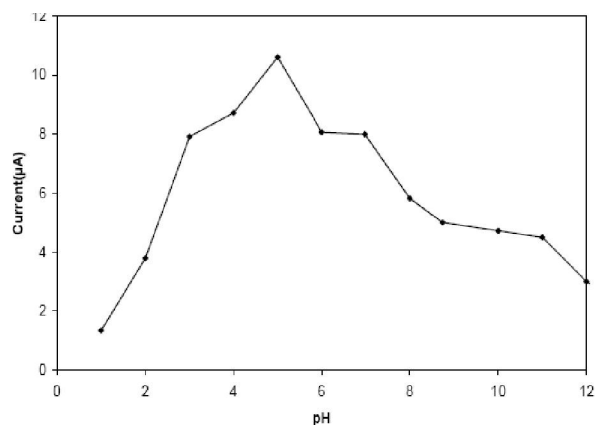


Figure 2 : Effect of pH on peak current in dinitramine

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TABLE 1 : Determination of dinitramine in water samples

Sample	Amount added (µg/ml)	Found (µg/ml)	Recovery (%) [*]	SD	RSD (%)
Tap water	0.2	0.199	99.50	0.045	0.05
	0.4	0.399	99.75	0.034	0.12
	0.6	0.597	99.50	0.024	0.03
River water (Upper water)	0.2	0.195	97.50	0.018	0.14
	0.4	0.398	99.50	0.016	0.06
	0.6	0.589	98.16	0.015	0.05
River water (lower water)	0.2	0.199	99.50	0.042	0.08
	0.4	0.400	100.0	0.011	0.01
	0.6	0.599	99.83	0.028	0.06

*Average of five determinations ± standard deviation

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. Aliquots of water samples were taken in a 25mL graduated tube, to it buffer solution was added and analyzed as described above. The recoveries of dinitramine ranged from 97.50 to 100.0% and the results are summarized in TABLE 1.

Determination of dinitramine in agricultural samples

Vegetable samples, each of 25gm, were taken, collected from agricultural field, where dinitramine had been sprayed as an herbicide. The samples were macerated with two 20mL portions of ethanol-demineralized water (1+1), filtered through a Whatman filter paper No.41 and filtrate was centrifuged at 1850g for 10min. In the filtrate was quantitatively transferred into a 50mL calibrated flask and made up to the mark with 50% ethanol. Washings were collected in a 25mL calibrated flask and aliquots were analysed as recommended procedure. The residue of dinitramine was dissolved in dimethylformamide and transferred to a 100 ml volumetric flask. Results obtained for the determination of the herbicides in vegetable samples are presented in TABLE 2. Recoveries of dinitramine ranged from 98.00 to 99.87%, which indicates the accuracy and reproducibility of the proposed differential pulse polarographic method.

Calibration graph

The calibration graph was linear in the range from 1.0×10^{-4} to 1.0×10^{-9} mol l⁻¹ and obeyed the equation

TABLE 2 : Determination of dinitramine in agricultural samples

Sample	Amount added (µg/ml)	Found (µg/ml)	Recovery (%)	SD	RSD(%)
Tamoto	1.0	0.99	99.00	0.050	0.08
	3.0	2.99	99.66	0.022	0.12
	5.0	4.98	99.60	0.028	0.04
	8.0	7.99	99.87	0.012	0.11
Brinzal	1.0	0.98	98.00	0.045	0.18
	3.0	2.98	99.33	0.032	0.02
	5.0	4.99	98.60	0.034	0.06
	8.0	7.96	99.50	0.045	0.05

*Average of five determinations ± standard deviation

$y = 0.129x + 0.162$, where y and x are the peak current (µA) and dinitramine concentration (mol l⁻¹), respectively. The detection limit, estimated from 3 times the standard deviation, was 1.02×10^{-7} . Differential pulse polarographic method can be successfully used for determinations of dinitramine in water and agricultural samples with good precision and accuracy of results.

CONCLUSIONS

The electrochemical reduction of dinitramine was successfully studied by differential pulse polarography. Several voltammetric parameters were optimised and their influence in the peak current or peak potential were adequately described by theoretical models involving electrode process, with the reagent strongly adsorbed on the surface and the transference of eight electrons per dinitramine molecule. In the analytical application, differential pulse polarography showed to be a very fast and sensitive technique that allows reaching detection limits in the range of trace analysis in natural water samples collected from Penna river belt, Nellore, A.P., India. This is one major advantages of this electroanalytical technique since it allows an economy of time and money in the environmental monitoring of pesticide contamination.

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