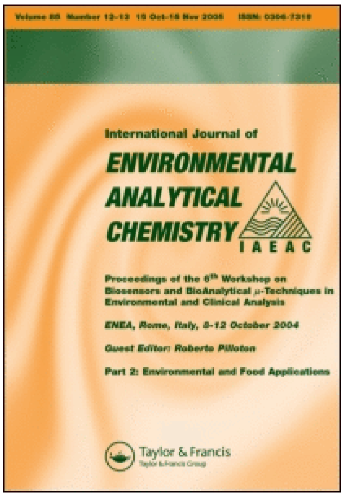

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Differential Pulse Polarographic Determination of Benfluralin and Trifluralin in Formulations Soils and Grains

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DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF BENFLURALIN AND TRIFLURALIN IN FORMULATIONS SOILS AND GRAINS

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The electrochemical behavior of the herbicides benfluralin and trifluralin was studied using differential pulse polarography in universal buffers of pH range 2.0 to 12.0. The cathodic peak observed for the herbicides are attributed to the reduction of nitro groups and showed to be pH dependent. Differential pulse polarography at dropping mercury electrode was used to establish an electroanalytical procedure for the determination of the herbicides benfluralin and trifluralin in formulations, soils and grains. Quantitative measurements were successful in the concentration range of $1.25X10^{-5}$ to $2.85X10^{-9}$ M, the lower concentration representing the detection limit by differential pulse polarography.

Keywords: Benfluralin; trifluralin; formulations; grains; soils; differential pulse polarography

INTRODUCTION

Benfluralin (N-butyl-N-ethyl-α,α,α-trifluoro-2,6 -dinitro-p-toluidine) and trifluralin(α,α,α-trifluoro-2,6-dinitro-N-N-dipropyl-p-toluidine) are selective herbicides, which act by killing weed seeds as they germinate. They are used for the control of many annual grasses and broad-leaved weeds in brassicas, ornamentals, cereals and vegetables[1,2]. They absorbed by the soil, and are extremely resistant to leaching. Hence, reliable analytical methods are neccessary for their determination. Trifluralin has been determined in soils and leaves by zero-order and derivative spectrometry[3], and in soils by gas chromatography with mass selective[4] and electron capture[5] detectors. Nash has described a gas-liquid

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chromatographic method for the determination of benfluralin[6]. Differential pulse polarography (DPP) is one of the several voltammetric methods possessing the intrinsic sensitivity and functional group specificity required for its use in the determination of herbicides in environmental samples. In comparison with spectrometry and chromatographic techniques, DPP technique employed in this study is cheaper, fast and easier to carry out[7]. Moreover, direct polarographic analysis can be carried out on samples for which direct use of spectrophotometry is not possible and the use of optical and chromatographic methods would involve preliminary separations and tedious sample handling. Substituted dinitroanilines were determined by polarography conducted in aqueous EtOH[8]. Treflan was extracted from soil with MeOH-water and determined by polarography[9]. DPP determination of some nitro group containing pesticides were discussed by Benadikova etal.[10]. Reviewing the literature revealed that, upto the present time nothing has been published concerning their determination in soils, grains and formulations using differential pulse polarography.

This short communication explores the reduction behavior of the herbicides benfluralin and trifluralin and describes a highly sensitive differential pulse polarographic method for measuring trace levels of these herbicides in formulations, soils and grains.

EXPERIMENTAL

Apparatus

Differential pulse polarography was performed with Metrohm E 506 polarecord connected to E 616 VA-Scanner. The electrode assembly consisted of a dropping mercury electrode of area 0.0223 cm^2 as the working electrode; a saturated Ag/AgCl(s), cl^- as the reference electrode, and a platinum wire as the auxiliary electrode were used. 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 ± 1°C.

Chemicals

Benfluralin and trifluralin was obtained from Promochem, Germany. The purity of the compounds was tested by a melting point determination. Stock solutions were prepared by dissolving the required amounts of compounds in dimethylformamide. Universal buffers of pH range 2.0 to 12.0 were prepared using 0.2 M boric acid, 0.05 M citric acid and 0.1M trisodium orthophosphate[11]. All the chemicals used were of analytical grade.

RESULTS AND DISCUSSION

Differential pulse polarographic behaviour

A single, well-defined polarographic peak has been observed over the entire pH range studied. This single peak is attributed to the facile simultaneous reduction of two nitro groups present in the title compounds in eight electron reduction process to the corresponding hydroxylamine group. Typical differential pulse polarogram for benfluralin and trifluralin are shown in Figure 1. The electrode process for the two herbicides are 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[12, 13]. The slight variation of the peak potential values of the title compounds were 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[14].

Analysis

Analysis is carried out using the currents obtained for nitro group reduction in benfluralin and trifluralin. It is observed that at pH 2.0, 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 concentration is lowered. Hence peak current is also lowered. But in pH 4.0 the concentration of protonated species is more hence high peak current is observed. Therefore, pH 4.0 was chosen as optimum pH for furhter studies. Polarographic half wave or peak potential is characteristic property for each electroactive species. Eventhough 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 (grains or soils) 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

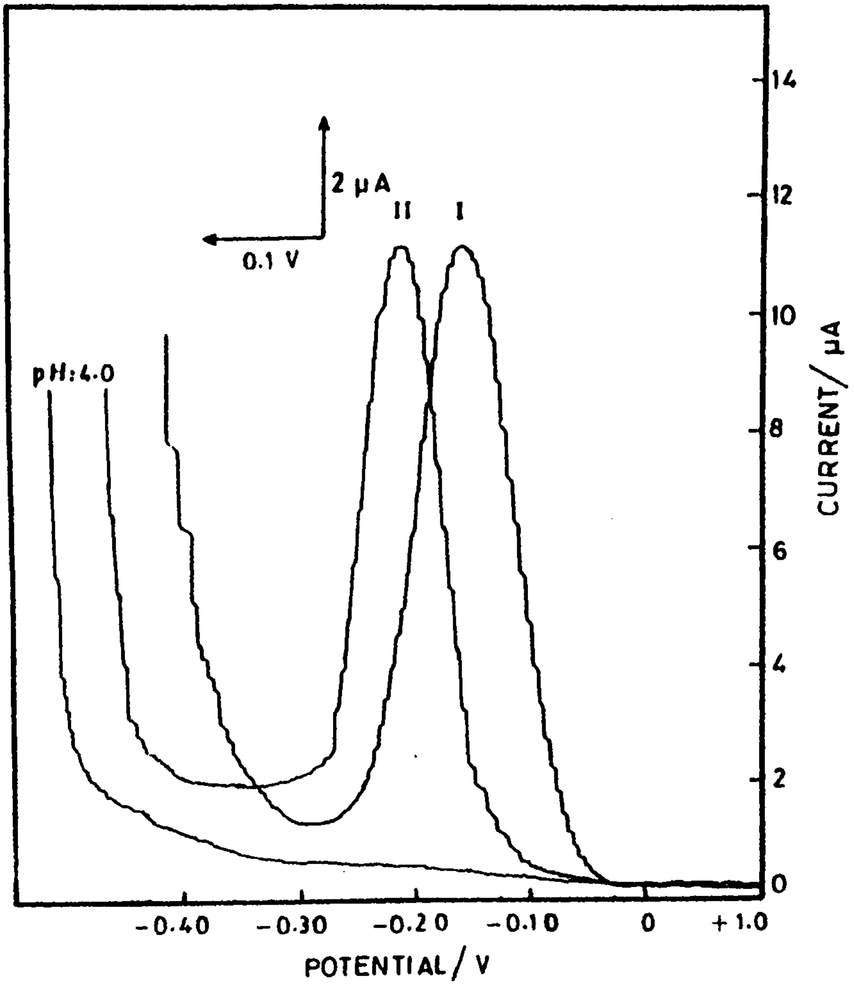

FIGURE 1 Typical differential pulse polarogram of benfluralin (I) and trifluralin (II) at pH 4.0. Concentration = 1.0X10^{-5} M Pulse amplitude = 50 mV Drop time = 2 sec

sample. This is the major advantage of polarography rather than other techniques. In the present investigation within the potential range (0.0V to –0.40V) 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 1.25 × $10^{-5}$to 2.0 × 10^{-9}M and 1.4X10^{-5} to 2.85 × 10^{-9}M for benfluralin and trifluralin respectively. The lower detection limits were found to be 1.02 × 10^{-9} M and 1.05 × 10^{-9} M for the respective compounds. The detection limit was calculated using the expression[15] dl = 3 × Sd/m, where Sd is standard deviation and m, the slope of the calibration plot.

Recommended analytical procedure

A stock solution (1X10^{-5} M) is prepared by dissolution of the appropriate amount of the electroactive species in dimethylformamide. 1 ml of the standard solution is transferred into polarographic cell and made up with 9 ml of the supporting electrolyte and then deoxygenated with nitrogen gas for 10 min. After recording the polarogram, small increments (0.5 ml) 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 sec, a pulse amplitude of 50 mV, and an applied potential (peak potential) of −0.16 V and −0.21 V for benfluralin and trifluralin respectively. The relative standard deviation and correlation coefficients were found to be 1.22% and 0.99 and 1.28% and 0.99 for the respective compounds for 10 replicants.

Analysis of formulations

The title compounds are available in different formulations. But both the compounds are not available in single formulation. Though these compounds having same activity, the acting upon the pest is varied. In India the title compounds are used individually for the same purpose. So it is the possibility for the presence of two compounds in a single real sample though they are not present in a single formulation. Hence the simultaneous method is applicable for their estimation of spiked as well as real samples. In general, the usual concentrations of real sample is found to be in microgram level. The developed analytical method is useful even in the order of nanogram level. Hence it is very easy to estimate these herbicides in real samples.

The required quantity of formulations corresponding to a stock solution of concentration of 10^{-3} M was accurately measured and transferred into a 100 ml calibrated flask containing 50 ml of dimethylformamide. A solution of approximately 10^{-5} M was prepared by dilution of this stock solution with appropriate universal buffer. Assay results for benfluralin (Benefex, Balan) and trifluralin (Treflan, Elancolan) in formulations at pH 4.0 are given in Table I. Values obtained by the gas chromatographic method proposed in AOAC official methods of analysis[16], for pure pesticides were also obtained for comparison purposes. Comparison of the results indicates that the values obtained for the pure pesticides by both methods are in close agreement.

TABLE I Estimation of Benfluralin and Trifluralin in Formualtions by Differential Pulse Polarography

Compound	*Labelled amount (mg)*	*Amount found (mg)*	*Recovery* %	*R.S.D (%)*	*AOAC Method [16]*
Benfluralin Formulation					
Benefex	2.00	1.90	97.5	0.26	1.90
	6.00	5.85	97.6	0.13	5.84
	10.0	9.90	99.0	0.10	9.82
	15.0	14.7	98.0	0.14	14.6
	20.0	19.6	98.0	0.08	20.0
Balan	3.00	2.94	98.0	0.47	2.91
	5.00	4.88	97.6	0.22	4.88
	7.00	6.94	99.1	0.10	6.94
	10.0	9.89	98.9	0.12	9.80
	12.0	11.92	99.3	0.14	11.9
Trifluralin Formulation					
Treflan	2.00	1.92	98.5	0.78	1.91
	6.00	5.85	98.0	0.17	5.85
	10.0	9.89	98.9	0.09	9.89
	15.0	14.8	98.6	0.12	14.4
	20.0	19.6	98.0	0.11	19.9
Elancolan	3.00	2.96	98.6	0.23	2.96
	5.00	4.86	97.2	0.08	4.86
	7.00	6.92	98.8	0.15	6.91
	10.0	9.92	99.2	0.09	9.92
	12.0	11.9	99.1	0.14	11.9

* Each value is an average of three determinations.

Analysis of benfluralin and trifluralin in grains and soils

Known amounts of benfluralin and trifluralin (pure and formulation) were sprayed on grain (rice or wheat) samples (25g) or soil sample (10g) and left for 1–2 hrs. The extracts were prepared by treatment of a crushed sample with two 50 ml portions of acetone and evaporated to dryness. The residue of benfluralin and trifluralin was dissolved in dimethylformamide and transferred to a 100 ml volumetric flask. Results obtained for the determination of the herbicides in grains and soil are presented in Table II. Recoveries of benfluralin and trifluralin ranged from 96.8 to 99.3%, which indicates the accuracy and reproducibility of the proposed differential pulse polarographic method.

TABLE II Recoveries of Benfluralin and Trifluralin in Grains and Soils

Pesticide	*Amount added (mg)*	*Recovery %* *		
		Wheat	*Rice*	*Soil*
Benfluralin (pure)	1.0	99.0	99.1	99.3
	3.0	98.9	98.5	97.9
	5.0	99.0	90.0	98.8
	8.0	97.8	97.3	98.7
Trifluralin (pure)	1.0	98.6	98.8	99.0
	3.0	98.8	98.4	97.2
	5.0	98.2	97.2	96.9
	8.0	98.5	98.2	99.2
Benefex (Benfluralin formulation)	1.0	99.1	97.6	98.9
	3.0	99.0	98.8	97.6
	5.0	99.1	97.3	98.1
	8.0	97.2	98.4	99.1
Balan (Benfluralin formulation)	1.0	98.7	99.2	97.4
	3.0	98.5	98.1	96.9
	5.0	96.8	98.3	98.9
	8.0	99.0	98.5	99.2
Treflan (Trifluralin formulation)	1.0	98.0	97.8	97.5
	3.0	98.5	98.9	97.8
	5.0	97.7	98.2	98.9
	8.0	98.6	99.1	97.9
Elancolan (Trifluralin formulation)	1.0	97.5	97.8	97.2
	3.0	98.5	98.1	98.7
	5.0	98.8	98.3	98.7
	8.0	97.4	99.1	98.6

* Each value is an average of three determinations.

The same procedure is applied for the analysis of residues of benfluralin and trifluralin in real samples. For this, the grains (rice and wheat) and soil fields were sprayed with 500g a.i./ha of herbicidal formulations. The spraying was done with foot sprayer. Nozzle was adjusted carefully to deliver uniform deposit. Then the samples (25g of wheat and rice, 10g of soil) were collected in randomised manner from the respective fields and left for 1–2 hours. The extracts were prepared by treatment of a crushed sample with two 50ml portions of acetone. The extract was evaporated to dryness. The residue of benfluralin and trifluralin was dissolved in dimethylformamide and transferred to a 100ml volumetric flask. The residues of benfluralin and trifluralin were determined by DPP method. The samples of grains and soil were drawn at 0, 3 and 6 days after the application to study the carry-over of the residues. Results were presented in Table III. With time the residue levels of these herbicides are gradually reduced.

TABLE III Residues of Benfluralin and Trifluralin in grains and soil

Pesticide	*Dosages g a.i./ha*	*Sampling interval (days)*	*Residue level mg kg^{-1}*			*Standard deviation*			*Relative standard deviation*			*Recovery %*		
			Wheat	*Rice*	*Soil*	*Wheat*	*Rice*	*Soil*	*Wheat*	*Rice*	*Soil*	*Wheat*	*Rice*	*Soil*
Benefex	500	0	5.04	4.92	4.54	0.02	0.01	0.04	0.52	0.20	0.96	99.1	97.5	97.4
(Benfluralin formulation)		3	1.02	1.06	1.03	0.01	0.01	0.01	0.98	0.98	0.97	95.2	91.2	90.0
		6	0.08	0.07	0.05	0.00	0.00	0.00	0.00	0.00	0.00	90.1	87.4	84.2
Balan	500	0	4.97	5.05	4.83	0.03	0.05	0.04	0.72	1.02	0.93	98.7	99.2	97.3
(Benfluralin formulation)		3	1.01	1.13	1.02	0.01	0.01	0.01	0.99	0.88	0.98	93.4	92.8	90.4
		6	0.06	1.00	0.04	0.00	0.01	0.00	0.00	1.00	0.00	89.2	88.9	83.3
Treflan	500	0	5.23	5.16	4.92	0.03	0.05	0.04	0.57	0.95	0.97	97.9	97.7	97.5
(Trifluralin formulation)		3	1.09	1.01	1.00	0.01	0.01	0.01	0.91	0.99	1.00	93.2	92.8	91.2
		6	0.08	0.07	0.03	0.00	0.00	0.00	0.00	0.00	0.00	89.6	89.8	85.4
Elancolan	500	0	4.96	4.84	4.62	0.01	0.04	0.04	0.20	0.88	0.97	97.5	97.8	97.2
(Trifluralin formulation)		3	1.00	1.03	1.02	0.01	0.01	0.01	1.00	0.97	0.98	92.8	93.0	91.4
		6	0.06	0.06	0.03	0.00	0.00	0.00	0.00	0.00	0.00	88.9	89.5	86.7

The initial average deposits of benfluralin applied to rice, wheat and soil at 500g a.i./ha was found to be 4.92, 5.04 and 4.54 for benefex and 5.05, 4.97 and 4.83 for balan respectively. Similarly the initial average deposits of trifluralin applied to rice, wheat and soil are as follows: 5.16, 5.23 and 4.92 for treflan and 4.84, 4.96 and 4.62 for elancolan respectively. For further sampling intervals (3rdand 6th day) the deposits were shown in Table III. These results suggested that even after 6 days of application of the herbicides fell within the detection limit. Residues of benfluralin and trifluralin range from 99.1 to 83.3% which indicates the accuracy and reproducibility of the proposed differential pulse polarographic method. The proposed method is simple, rapid, reliable, sensitive and free from the interferences of other herbicides and hence can be used in environmental samples.

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