Electroanalytical Determination of the Fungicides Folfet, Phosmet, and Dialifos in Grains and Soils

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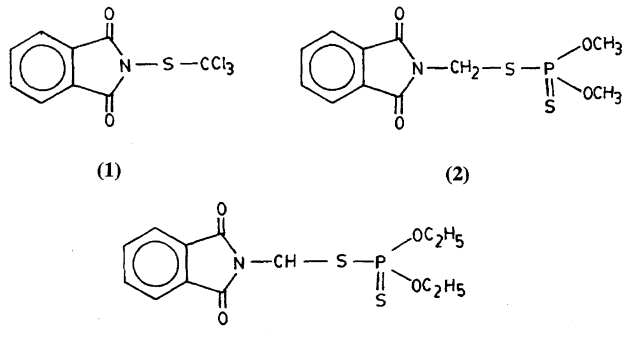
The electrochemical behavior of the fungicides folfet, phosmet, and dialifos was studied using differential pulse polarography in unversal buffers of pH 2.0 to 6.0. The cathodic peak observed for folfet, phosmet, and dialifos is attributed to the reduction of the carbonyl group, and was shown to be pH-dependent. Differential pulse polarography was used to estimate folfet, phosmet, and dialifos in agricultural formulations, grains and soil samples. Both standard addition and calibration methods were used for the analytical measurements. The lower detection limits were found to be 1.9×10^{-9}, 1.72×10^{-9}, and 2.12×10^{-1} M, respectively.

Folfet (**1**), phosmet (**2**), and dialifos (**3**) are effective fungicides, and are useful for the treatment of foliar soil and seed-borne diseases, including apple scab, grape, mildews, cornseed infection and many fruits, vegetables, and ornamental plant diseases.[1,2] (Chart 1)

Literature reviews[3—6] indicate that a number of fungicides have been determined in tomatoes, cucumbers, and apples using such techniques as column chromatography with an electron-capture detector in vegetables and fruits by capillary gas chromatography and in food by gas liquid chromatography. Phosmet was determined in foliar residue leaves by Blewett et al.[7] Folfet has been determined by high-pressure liquid chromatography[8] and gas liquid chromatography in fruits and vegetables.[9]

In comparison with UV, GC, TLC, and HPLC, the main technique employed in this study, the electroanalytical procedures are faster, easier, and cheaper to carry out. Moreover, they can be successfully employed for the analysis of colored materials or samples containing dispersed solid particles.[10] Electroanalytical techniques are widely used for the determination of carbonyl-group (>C=O) containing compounds.[11,12] However, no discussion has been given concerning our understanding of the differential pulse polarographic behavior of folfet, phosmet, dialifos, and to determine these compounds using differential pulse polarography.



(1) (2)

(3)

Chart 1.

The aim of this work was to study the electrochemical behavior of such fungicides as folfet, phosmet, and dialifos using differential pulse polarography on a dropping mercury electrode (DME) in order to establish an electroanalytical procedure for determining folfet, phosmet, and dialifos in formulations, grains, and soil samples.

Experimental

Differential pulse polarograms were measured with a Metrohm E 506 polarecord connected an E 616 VA Scanner. The three-electrode assembly consisted of a dropping mercury electrode (of area 0.0223 cm^2) as a working electrode, saturated Ag/AgCl(s), Cl^-, and a platinum wire as an auxiliary electrode. All of the experiments were performed at 25±1 °C; pH measurements were carried out using an Elico digital pH meter. Dissolved air was removed from the solutions by degassing with oxygen-free nitrogen for 10 min.

Folfet, phosmet and dialifos were supplied by "Promochem" (West 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 ethanol. Universal buffers of pH 2.0 to 12.0 were prepared using 0.2 M (1 M = mol dm^{-3}) boric acid, 0.05 M citric acid, and 0.1 M tri sodium orthophosphate.[13] All of the chemicals used were of Anala R grade.

Results and Discussion

These fungicides were found to be give a single well-defined peak in both acidic and neutral ($2.0 \leq$ pH ≤ 6.0) buffer systems. This peak is attributed to facile simultaneous reduction of two carbonyl groups present in the fungicides folfet, phosmet, and dialifos in a four-electron reduction process to the corresponding hydroxy derivative. No reduction was

observed in the basic medium ($8.0 \leq pH \leq 12.0$) due to a precipitation of the electroactive species. Typical differential pulse polarograms for phosmet are shown in Fig. 1.

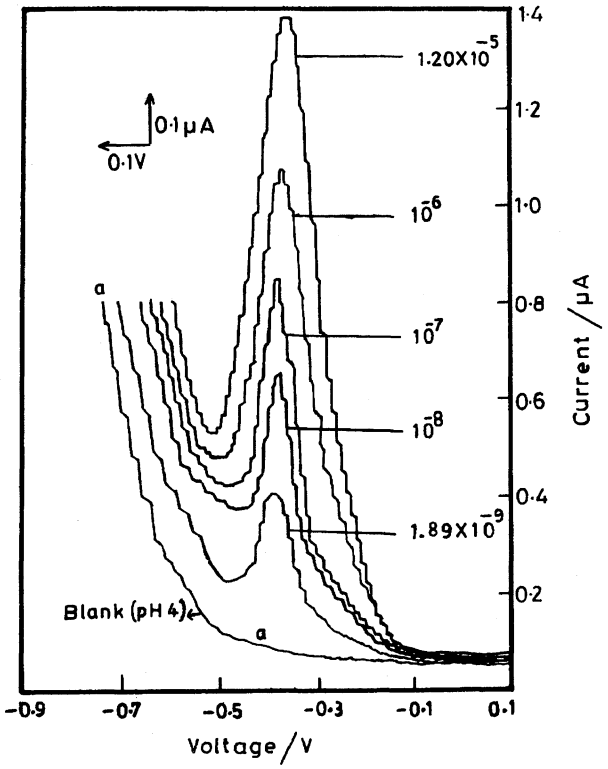


Fig. 1. Typical differential pulse polarograms of phosmet in pH 4.0.
Concentration = 1.2×10^{-5} M—1.89×10^{-9}M, Drop time = 2 s, Pulse amplitude = 50 mV, a : Blank solution of pH 4.0.

The reduction process in the fungicides folfet, phosmet, and dialifos was found to be diffusion-controlled and adsorption-free in the buffer systems studied, as evidenced from the linear plots of i_m versus $t^{2/3}$ (where i_m is the maximum current and t is the drop time) passing through the origin.[14] The marginal variation of the peak-potential (E_m) 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 proton involvement in the electrode process. The variation of the E_m values towards more negative potentials upon increasing the concentration of folfet, phosmet and dialifos[15,16] indicated the irreversibility of the electrode process.

Analysis. The polarographic peaks obtained in pH 4.0 for the respective compounds were well-resolved and used for the analysis. For a quantitative estimation of the three compounds, both calibration and standard addition methods were used. The peak heights were found to be linear over the range 1.0×10^{-5} to 2.0×10^{-9} M, 1.2×10^{-5} to 1.89×10^{-9} M and 1.15×10^{-5} to 2.4×10^{-9} M for folfet, phosmet, and dialifos, respectively. The lower detection limits were found to be 1.9×10^{-9} M, 1.72×10^{-9} M, and 2.12×10^{-9} M for the respective compounds. The detection limit (*dl*) was calculated using the expression[17] $dl = 3$ sd/m, where sd is the standard deviation and m the slope of the calibration plot.

Recommended Analytical Procedure. A stock solution (1.0×10^{-5} M) was prepared by dissolving an appropriate amount of the electroactive species in ethanol. One ml of the standard solution was transferred into a 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 (0.2 ml) of the standard solution were recorded after each addition under

Table 1. Determination of Folfet, Phosmet, and Dialifos in Formulations by Differential Pulse Polarography

Compound	pH of the supporting electrolyte	Labelled amount mg	Amount found mg	Recovery[a] %	Standard deviation
Folfet formulation					
Phaltan	4.0	2.0	1.98	99.00	0.012
	4.0	5.0	4.96	99.20	0.010
	4.0	8.0	7.85	98.13	0.011
	4.0	10.0	9.82	98.20	0.014
Phosmet formulation					
Imidan	4.0	2.0	1.97	98.50	0.015
	4.0	5.0	4.97	99.40	0.012
	4.0	8.0	7.83	97.88	0.010
	4.0	10.0	9.81	98.10	0.009
Dialifos formulation					
Torak	4.0	2.0	1.98	99.00	0.013
	4.0	5.0	4.95	99.00	0.011
	4.0	8.0	7.86	98.25	0.018
	4.0	10.0	9.87	98.90	0.016

a) Each value is an average of three determinations.

Table 2. Recovery of Folfet, Phosmet, and Dialifos Added to Grains and Soil

Compound	Amount added/mg	Recovery/%[a)]		
		Wheat	Rice	Soil
Folfet	5.0	98.92	99.18	99.20
	10.0	98.90	98.40	98.20
	15.0	98.70	98.25	98.80
	20.0	99.10	99.15	99.06
Phosmet	5.0	97.75	98.25	98.85
	10.0	98.00	98.70	98.80
	15.0	98.64	99.05	98.65
	20.0	97.68	99.38	99.25
Dialifos	5.0	97.55	97.95	97.76
	10.0	98.50	98.95	97.85
	15.0	98.90	99.05	98.70
	20.0	97.35	98.35	98.95

a) Each value is an average of three determinations.

similar conditions. In the present study, the best precision was obtained in the pH range of 4.0 with a drop time of 2 s, a pulse amplitude of 50 mV, and applied potentials of −0.30 V, −0.38 V, and −0.44 V (versus Ag/AgCl(s)), respectively, for the respective compounds. The relative standard-deviation values and correlation coefficients were found to be 1.14% and 0.995, 1.42% and 0.997, and 1.35% and 0.998 for the respective compounds.

This procedure was successfully used for determining these compounds in their formulations (phaltan, imidan, and torak) at different pH zones.

Analysis of Formulations. The required quantity of formulation corresponding to a stock solution of 1.0×10^{-3} M was accurately measured and transferred into a 100 ml calibrated flask containing 50 ml ethanol. A solution of approximately 1.0×10^{-5} M was prepared by diluting this stock solution with the universal buffer. The assay results for folfet, phosmet and dialifos in formulation in pH 4.0 are given in Table 1.

Analysis of Pesticides in Grains or Soils. Grain (rice or wheat) samples (50 g) or soil sample (25 g) were sprayed with known amounts of folfet, phosmet or dialifos and left for 2—4 h. The extracts were prepared by extracting a crushed sample with 100 ml of acetone. The extract was evaporated to dryness. The residue of folfet, phosmet or dialifos was dissolved in ethanol and transferred to a 50 ml volummetric flask.

The results obtained for the determination of the pesticides in grains and soils are presented in Table 2. The recoveries of folfet, phosmet, and dialifos ranging from 97.35 to 99.04%, obtained with the proposed differential pulse polarographic method, indicate its accuracy and reproducibility.

The data incorporated in Tables 1 and 2 suggests that the ingredients present in formulations in addition to folfet, phosmet, and dialifos, and other constituents present in grains and soil do not interfere in the proposed method. The proposed method describes the successful application of an electroanalytical technique for the analysis of folfet, phosmet, and dialifos in agricultural formulations, grains, and soil samples. It also demonstrates that differential pulse polarography at a dropping mercury electrode can be conveniently used for the quantitative determination of these fungicides in those environments. The method shows good reproducibility and high accuracy, and does not involve the elaborate clean-up procedures required by the other methods.

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