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AN ELECTROLYTIC REDUCTION METHOD FOR THE DETERMINATION OF FENITROTHION AND METHYL PARATHION

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Fenitrothion or methyl parathion may be determined by polarography in an ethanolic solution at pH=7.0 using a Sorensen's buffer solution as supporting electrolyte and 0.5% gelatin as maximum suppressor at 25±1°. The method can be well adopted even in the presence of malathion, where other analytical techniques are inapplicable.

Key words: Pesticides, Homologues, Reduction.

INTRODUCTION

Pesticides are used to protect crops from the damage caused by pests. Fenitrothion, 0,0-dimethyl-0-(3-methyl-4-nitrophenyl) phosphorothioate, and methyl parathion, 0,0-dimethyl-0-(4-nitrophenyl) phosphorothioate, have found extensive use in agriculture for this purpose. These are commonly determined by a colorimetric procedure [1,3] based upon the reduction of the nitro-group to an amino-group with subsequent diazotisation and coupling with *N*-(1-naphthyl) ethylenediamine to produce a color that may be measured by colorimeter or spectrophotometer. This method has been used for the determination of their residues where 90% recovery is satisfactory but is not suitable for use in the assay of technical materials and formulation because of the interference caused by impurities. Thus a reliable method of analysis is greatly needed for these new compounds in insecticide formulations. As these compounds are aromatic nitro derivaties it seemed likely that these could be analysed by polarography [4,8,11,12,13] because nitrobenzene is easily reduced at the dropping mercury electrode [5] and Bowen *et. al.* [6,7] have already analysed a homologue, parathion using this method. The present method described, differs from Bowen *et. al.* method is being simple and quick. The present method employs simple ordinary electrolysis cell instead of H-cell and Sorensen's buffer solution (pH=7.0) has behaved better than acetone water supporting electrolyte used by Bowen [6] *et al.* Moreover, this method can be effectively used for the determination of fenitrothion or methyl parathion in presence of malathion [9,10].

MATERIALS AND METHODS

1. Cambridge pen-recording polarograph with dropping mercury cathode manufactured by Cambridge Instrument Co. Ltd. A thermostatically controlled water bath maintained the cell at 25±1°. During the recording of the polarograms the air strirrer was stopped in order to eliminate vibration and the heating system was disconnected to remove the possibility of stray current effect [2].

2. *Electrolyte solution.* Sorensen's buffer solution (pH=7.0) was prepared by mixing 60ml of M/15 Na_2HPO_4 with 40 ml of M/15 KH_2PO_4.

3. Ethyl alcohol-95% redistilled.

4. Nitrogen gas: Pure, oxygen free.

5. Gelatin-0.5%.

6. Pure anlytical grade samples of fenitrothion and methyl parathion obtained form Sumitomo Chemical Co. Ltd., Japan.

7. 50% formulation of fenitrothion and methyl parathion (EC) were used.

Preparation of standard curve. A sample of 0.065 gms and 0.104 gms of fenitrothion and methyl parathion respectively were dissolved in 50 ml of ethyl alcohol to give reference solutions containing 1.3 mg/ml and 2.08 mg/ml respectively. Aliquots of 1,3,5,7,8,9 ml of the standard solutions were transferred to 25 ml volumertric flasks. To these flasks ethyl alcohol was added to bring the volume to 10 ml. Four drops of freshly prepared gelatin, were added to these flasks and finally the volume was made to the mark with the buffer solution. 2 ml of the solutions was transferred to the polarographic cell, rinsed with ethyl alcohol, and nitrogen was passed through it for ten minutes. The nitrogen was passed through ethyl alcohol before it reached the cell. For electrolysis the dropping mercury electrode was placed firmly in the cell and the polarograph set to record the wave at −0.6 to −1.5 volts at a sensitivity of 0.003-0.02μ amp. with maximum damping. Wave-heights (diffusion current) were converted to equivalent heights at a suitable sensitivity. Standard curve was prepared by

plotting the concentration (mg/100ml) against the wave-height (cm) Fig. 1.

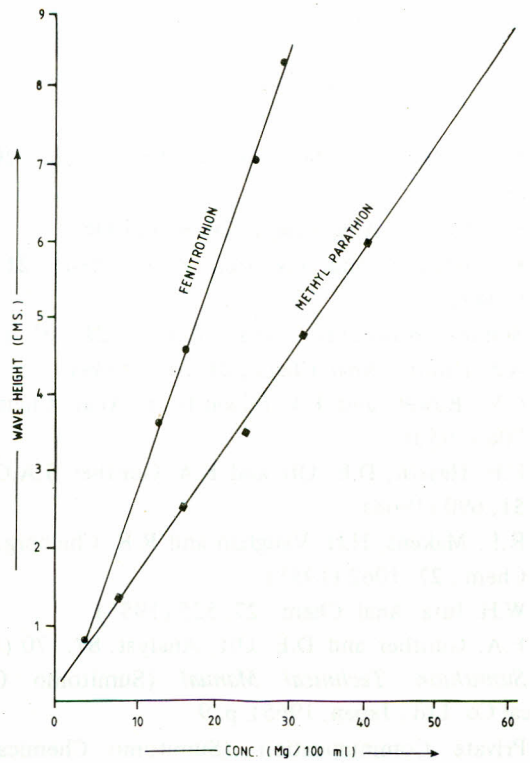

Fig. 1. Relation between concentration and wave-height.

Analysis of samples. Technical and formulation samples containing approximately 1.3 mg/ml and 2.08 mg/ml of fenitrothion and methyl parathion respectively were treated in the same manner as the standard samples and polarographed under the same conditions. Concentrations corresponding to the wave-heights were determined from the standard curve. The results obtained were within the limits of accuracy of the method and are given in Table 1.

RESULTS

The minimum concentrations for the polarograms recorded were 0.104 mg and 0.166 mg for fenitrothion and methyl parathion respectively. When concentration were

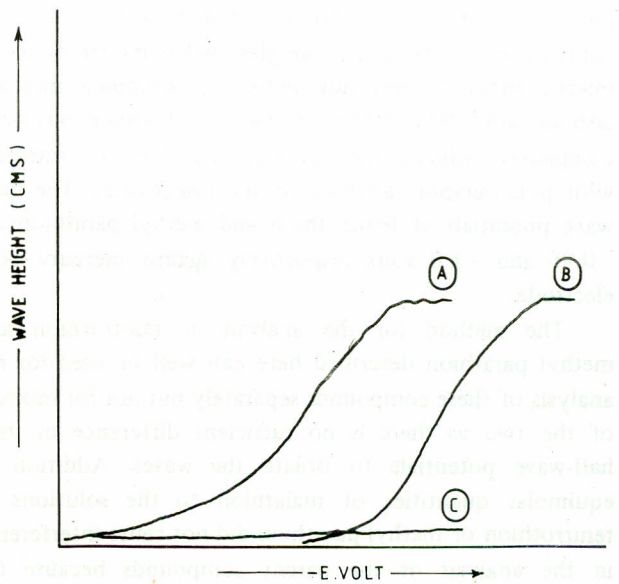

Fig. 2. Typical polarograms of fenitrothion and methyl parathion.

A– Typical polarogram of fenitrothion (Pure) = E½ = –0.95 V.
B– Typical polarogram of methyl parathion (Pure) = E½ = –1.0 V.
C– Blank.

Table 1. Results obained from the analysis of 50% formulations (A,C) and 98% technical samples (B, D)

	Methyl parathion				Fenitrothion			
	A		B*		C		D*	
	50%		98%		50%		98%	
	Found %	Error %	Found %	Error %	Found %	Error %	Found %	Error %
1.	50.0	±0.00	98.3	+0.3	51.0	+2.00	96.66	–1.36
2.	48.0	–4.00	96.16	–1.87	50.16	+0.32	100.00	+2.04
3.	49.46	–1.08	97.85	–0.15	49.22	–1.56	98.21	+0.21
4.	51.0	+2.00			50.18	+0.36		
5.	51.66	+3.32			50.18	+0.36		
6.	51.75	+3.50			48.66	–2.68		

*Technical samples were analysed in the presence of malathion.

plotted against the wave-heights a straight line was obtained showing that concentration is proportional to the wave-height (Fig. 1). Typical polarograms for fenitrothion and methyl parathion are given in Fig. 2.

DISCUSSION

Curves of concentrations against wave-height of the polarograms were obtained with *p*-nitro-phenol, a major contaminant of technical samples which interferes colorimetric method does not reduce at dropping mercury cathode until fenitrothion or methyl parathion has been completely reduced and consequently does not interfere with polarographic analysis of the insecticides. The half-wave potentials of fenitrothion and methyl parathion are −0.95 and −1.0 volts respectively against mercury pool electrode.

The method for the analysis of fenitrothion and methyl parathion described here can well be used for the analysis of these compounds separately but not for mixture of the two as there is no sufficient difference in their half-wave potentials to isolate the waves. Addition of equimolar quantities of malathion to the solutions of fenitrothion or methyl parathion did not cause interference in the analysis of the parent compounds because the half-wave potential was different from those of fenitrothion and methyl parathion.

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