

GAS CHROMATOGRAPHIC DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES IN FORMULATIONS

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Abstract. A gas chromatographic method using electron capture detector is described for the determination of six organophosphorus pesticides in formulations. 5% QF-1 on 60-80 mesh phase Sep-W was used as the GLC column material. The method is rapid, simple and sensitive down to 0.01 μg .

Organophosphorus pesticide chemicals with relatively low mammalian toxicity and rapid metabolism by plants and animals into nontoxic products are gaining wide popularity in the agricultural sector. As newer compounds are introduced into the market by the manufacturers, it is essential to develop reliable analytical methods in order to ascertain the quality of the product supplied to the agriculturist.

The gas chromatography of organophosphorus pesticides has been reported by several workers.¹⁻³ Burke and Holswade⁴ described a mixture of DC 200 and QF-1 as suitable liquid stationary phase in the gas chromatography of 85 pesticide chemicals, using electron capture detector.

There are several other analytical methods available in the literature but most of the techniques either employ expensive equipments, not available in Pakistan, or do not suit our laboratory conditions.

The object of the study was to develop a rapid, sensitive and a reproducible GLC method using electron capture detection system for routine analyses of six organophosphorus pesticides in granular and emulsifiable concentrate formulations. The studied pesticides are commonly used for plant protection work in Pakistan. QF-1 has been found to be a suitable liquid stationary phase in a GLC column.

Methods

Apparatus and Reagents

Gas Chromatograph. Philips model PV-4000, equipped with electron capture detector and a stainless steel column, 1 m long \times 3 mm i.d. packed with 5% QF-1 on 60-85 mesh phase Sep-W (Phase Separations Ltd., Cheshire, England).

Operating conditions. Temperature-column and detector oven 160°C, nitrogen flow-rate 50 ml/min, servoscribe recorder 5 mV, and chart speed 120 mm/hr.

The newly packed column was conditioned at 170°C for 24 hr before use.

Pesticide Standards. The compounds were of analytical grade supplied by the manufacturers. Stock solutions containing 10 $\mu\text{g}/\mu\text{l}$ pesticide standards were prepared in n-hexane. Studied pesticides are chemically identified in Table 1.

n-hexane. Nanograde.

Analysis of Pesticide Formulations. Each sample (0.08-0.1 g) was separately weighed into 10 ml volu-

metric flasks. A small amount of n-hexane was added to each flask and vigorously shaken to dissolve the sample which was then diluted to volume with n-hexane. Appropriate dilutions of stock solutions were prepared in the same solvent.

Each sample was chromatographed 3 times along with its insecticide standard, using 5 μl /injection. The amount of insecticide in each sample was calculated by comparing its peak height with that of the standard. Peak height was calculated by measuring the vertical distance from the peak apex to a line forming the base-line of the peak. All the pesticides were analysed individually but Malathion, Fenitrothion, Diazinon and anyone of the other three insecticides can be analysed in a mixture as well as shown by the GLC retention times: Chlorfenvinfos, 2 min; Diazinon, 3 min; Fenitrothion, 7.5 min, Tetrachlorvinfos, 2.5 min; Malathion, 15 min; Phorate, 2 min. Fig. 1 shows a typical gas chromatogram of Phorate, Diazinon and Malathion. These three insecticides are beautifully resolved from one another.

TABLE 1. CHEMICAL IDENTIFICATION OF PESTICIDES STUDIED.

Common name	Chemical name
Chlorfenvinfos	<i>O,O</i> -Diethyl-[2-chlor-1-(2,4-dichlorophenyl)]-vinyl-phosphate.
Diazinon	<i>O,O</i> -Diethyl- <i>O</i> -[2-isopropyl-4-methylpyrimidinyl-(6)]-phosphorothioate.
Fenitrothion	<i>O,O</i> -Dimethyl- <i>O</i> -(3-methyl-4-nitrophenyl)-phosphorothioate.
Tetrachlorvinfos	<i>O,O</i> -Dimethyl-[2-chlor-1-(2,4,5-trichlorophenyl)]-vinyl-phosphate.
Malathion	<i>O,O</i> -Dimethyl- <i>S</i> -[1-2-biscarbethoxyethyl-(1)]-phosphorodithioate.
Phorate	<i>O,O</i> -Diethyl- <i>S</i> -(ethylthionmethyl)phosphorodithioate.

Results and Discussion

Results of analysis of pesticides in granular and emulsifiable concentrate formulations are presented as average with standard error.

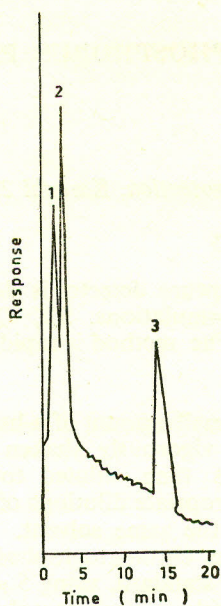


Fig. 1. Gas chromatogram of a mixture of pesticides: (1) Phorate, (2) Diazinon and (3) Malathion.

The concentration of toxic materials in studied formulations had been previously verified by the usual IR spectrophotometric methods and found to conform to the manufacturers' specification in every case. The figures in the last column of the Table 2 are quite satisfactory and fall within an acceptable level of accuracy.

The linearity of the electron capture detector was checked by injecting different amounts of pesticide standards into the gas chromatograph. A plot of peak height against concentration showed complete linearity over the range tried. Inert carrier or solvent

used in the formulation of pesticides does not interfere with the GLC determination.

The method described is rapid, simple and sensitive. The limit of detection of the method was in the range of 0.01–0.14 μg . It is useful for the determination of tested insecticides in nanogram quantities. Although intended primarily for pesticides analysed, it is ex-

TABLE 2. ANALYTICAL DATA OF ORGANO-PHOSPHORUS PESTICIDES STUDIED.

Formulation	Nominal toxicant content(%)	Toxicant found(%)*
Chlorfenvinfos EC†	24	23.6 \pm 0.11
Diazinon G**	10	10.5 \pm 0.05
Fenitrothion EC	50	51.9 \pm 0.05
Tetrachlorvinfos EC	24	23.8 \pm 0.05
Malathion EC	57	55.5 \pm 0.11
Phorate G	10	10.3 \pm 0.15

*Each value is the average of 3 determinations and is reported with standard error. †Emulsifiable concentrate. **Granules.

pected that the method, with perhaps slight variations in the GLC operating parameters, could also be applied to the routine analysis of several other organophosphorus pesticides of related structures in formulations.

References

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