CHROM. 8768

Note

Analysis of organophosphorus pesticides by capillary gas chromatography with flame photometric detection

WILLEM KRIJGSMAN and CORNELIS G. VAN DE KAMP

Laboratory for Toxicology, National Institute for Public Health, P.O. Box 1, Bilthoven (The Netherlands)

(Received September 3rd, 1975)

Several methods exist for the analysis of the wide range of organophosphorus pesticides in various materials, and in recent years the preferred method of determination has been gas chromatography after solvent extraction of the pesticide from the substrate. In 1969, Watts and Storherr[1] described the gas chromatography of over 60 organophosphorus pesticides and their degradation products with the aid of a potassium chloride thermionic detector. In 1970, Bowman and Beroza[2] published a survey on the gas chromatographic retention times of 138 pesticides and metabolites containing phosphorus and/or sulphur. They used several packed columns and a flame photometric detector. These tables of retention times are valuable for the identification of unknown compounds. For the analysis of organochlorine pesticides, Schulte and Acker[3] developed a gas chromatographic method with glass capillary columns. The detection was performed with flame ionization and electron-capture detectors.

As far as we know, capillary gas chromatography has not previously been used for the separation of phosphorus esters. Because of their structural similarities, the separation of many of these components in a single step is difficult, and capillary gas chromatography can be a useful method for this purpose.

In this work, we used capillary columns coated with SE-30. This stationary phase can easily be coated on to the glass column and kept in operation for a long period (at least 3 months). The column was connected to a flame photometric detector.

Goretti and Possanzini[4] have described the coupling of the flame photometric detector and a capillary column in the trace analysis of sulphur compounds but practical details of this coupling were not given. We chose a flame photometric detector because it is selective, sensitive and gives better relative molar responses than a thermionic detector. By using an inlet splitting system, it is possible to prevent the solvent flame-out phenomenon.

EXPERIMENTAL

Apparatus

A Tracor Model 550 instrument, equipped with a flame photometric detector, was modified for capillary column operation. On the injection side, the column was connected with a splitter system, as previously described by Schulte and Acker[3].
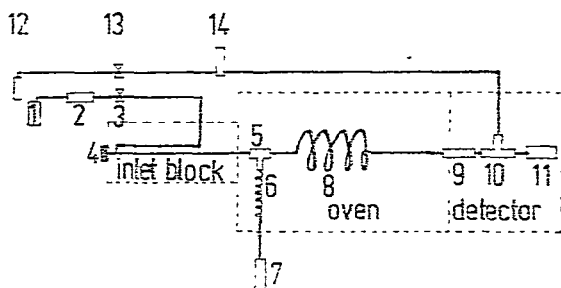
Fig. 1. Gas flow diagram of the gas chromatographic system. 1, Cylinder of carrier gas; 2, Oxisorb cartridge; 3, flow controller VCD 1000, Porter; 4, septum; 5, union tee, 1/16 in., Swagelok; 6, restriction coil; 7, flow meter, 150 ml/min; 8, capillary column; 9, low dead volume connector, 1/16 in., Swagelok; 10, male run tee, 1/8 in., with reducer, 1/16 in., Swagelok; 11, flame photometric detector; 12, cylinder of purge gas; 13, flow controller; 14, flow meter, 150 ml/min.

The dimensions of the restriction coil, connected with the splitting system, determines the splitting ratio (see Fig. 1). The detector, installed as close as possible behind the oven wall, was brought into a straight-line position with the separation column, so that the column could be inserted directly into the burner (see Fig. 2). In this way, the dead volume was reduced to a minimum and contact of the components with hot metal surfaces was prevented. The glass capillary column was coated dynamically[3] with SE-30 (GC grade). The oxygen in the carrier gas helium was removed by means of a low-pressure Oxisorb cartridge (Messer Griesheim, Düsseldorf, G.F.R.). This was necessary because at high temperatures, silicone phases are degraded by oxygen, and the removal of oxygen results in longer lifetimes of the liquid phase.
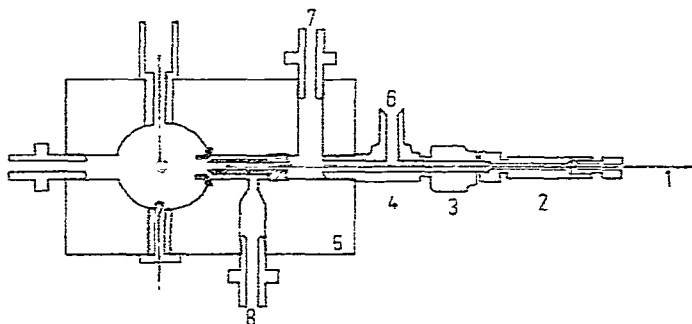

Fig. 2. Connection of capillary column with flame photometric detector. 1, Capillary column; 2, low dead volume connector, 1/16 in., Swagelok, drilled to 1.4 mm; 3, reducer, 1/16 in., Swagelok; 4, male run tee, 1/8 in., Swagelok; 5, flame photometric detector; 6, purge gas inlet; 7, air/O₂ gas inlet; 8, H₂ gas inlet.

Procedure

The gas chromatographic conditions were as follows. Separation column: Pyrex, length 50 m, I.D. 0.35 mm; phase, SE-30 (GC grade). Restriction coil: stainless steel, length 1.40 m, I.D. 0.25 mm. Temperatures: oven, 200° and 240° isothermal, 200–290° at 4°/min with a linear programme; injection block, 220°; detector, 210°.

Gas flows: carrier gas (helium) 4 ml/min; splitting gas (helium) 24 ml/min; detector, hydrogen 200 ml/min, air 80 ml/min, oxygen 10 ml/min; purge gas (nitrogen) 60 ml/min. Injection: 1 μl of mixtures of the organophosphorus pesticides in acetone–light petroleum (b.p. 40–60°) were injected through a septum on to the column.

RESULTS AND DISCUSSION

In Table I the retention times of the pesticides relative to parathion at different conditions column temperatures are given. The retention times of parathion at 200° and 240° isothermal are 7 and 2 min, respectively. In the programmed mode (200–290° at 4°/min), the retention time of parathion is 5 min.

Some components, such as bidrin, mevinphos, omethoate, dimethoate, phosphamidon, vamidothion, triamyphos, ciodrin, menazon and chlorfenvinphos, give

TABLE I

RELATIVE RETENTION TIMES OF PHOSPHORUS ESTERS IN THE ISOTHERMAL MODE AND WITH TEMPERATURE PROGRAMMING (t_R PARATHION = 1)

The mean relative standard deviation was about 1 %.

| Compound	200–290° at 4°/min	Isothermal		Compound	200–290° at 4°/min	Isothermal	
		200°	240°			200°	240°
Trichlorfon	0.26	0.22	—	Bromophos	1.08	1.12	1.09
TEPP	0.28	0.22	—	Pirimithate	1.08	1.15	1.05
Naled	0.30	0.26	—	Trichloronate	1.08	1.13	1.09
Dichlorvos	0.37	0.22	—	Mecarbam	1.14	1.27	1.15
Mevinphos	0.38	0.28	0.51	Bay 77049	1.16	1.28	1.17
Heptenophos	0.47	0.37	0.57	Chlorfenvinphos	1.16	1.27	1.14
Zinophos	0.48	0.39	0.58	Fenthoate	1.17	1.27	1.16
Omethoate	0.51	0.38	0.60	Ciodrin	1.17	1.33	1.14
Prophos	0.53	0.42	0.60	Supracide	1.19	1.35	1 23
Bidrin	0.55	0.44	0.62	Vamidothion	1.24	1.41	1.25
Sulfotep	0.55	0.45	0.62	Bay 77488	1.25	1.42	1.25
Butonate	0.61	0.51	0.59	Tetrachlorvinphos	1.26	1.51	1.27
Dimethoate	0.61	0.50	0.68	Bromophos ethyl	1.27	1.46	1.28
Thiometon	0.61	0.49	0.66	Plondrel	1.30	1.48	1.30
AC 92.100	0.69	0.60	0.74	Triamyphos	1.58	2.38	1.74
Diazinon	0.69	0.60	0.70	Ethion	1.61	2.34	1.73
Cyanthoate	0.70	0.60	0.69	Triazophos	1.61	2.38	1.75
Dyfonate	0.71	0.60	0.76	Carbophenothion	1.72	2.64	1.95
Disulfoton	0.72	0.63	0.75	Menazon	1.95	3.60	2.37
Formothion	0.75	0.66	0.78	Imidan	1.97	3.52	2.44
Dichlofenthion	0.82	0.76	0.83	Phenkapton	2.10	4.21	2.74
Parathion methyl	0.82	0.75	0.83	EPN	2.14	3.94	2.60
Phosphamidon	0.82	0.72	0.81	Azinphos methyl	2.16	4.54	2.98
Prothoate	0.84	0.75	0.84	Phosalone	2.22	4.85	3.09
Fenchlorphos	0.90	0.86	0.91	Azinphos ethyl	2.39	5.95	3.60
Fenitrothion	0.90	0.87	0.85	W 11099	2.57	6.91	3.79
Pirimiphos methyl	0.92	0.90	0.93	Dialifor	2.60	6.48	3.83
Malathion	0.94	0.93	0.94	Coumaphos	2.63	8.23	4.57
Dursban	1.00	1.00	1.00	Abate	4.40	—	18.4
Parathion	1.00	1.00	1.00				
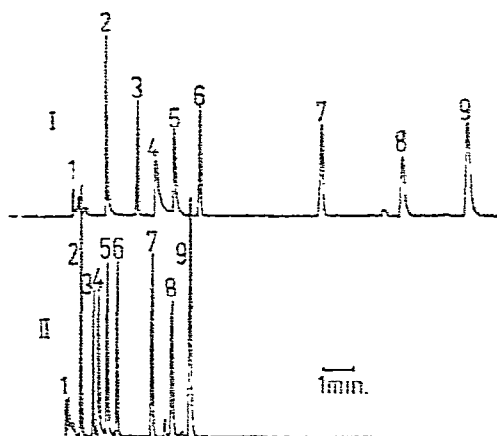
Fig. 3. Temperature effect on tailing of pesticides: I, 200° isothermal; II, 240° isothermal. 1, Solvent; 2. mevinphos; 3, zinophos; 4, bidrin; 5, dimethoate; 6. dyfonate; 7, parathion; 8, chlorfenvinphos; 9. tetrachlorvinphos.

asymmetric peaks when the column temperature is too low. At temperatures above 240°, this tailing effect diminishes. This effect is illustrated in Fig. 3.

The detection limit for the phosphorus esters with a relative retention time of about 1 in the programmed mode is about 100 pg. As an illustration of the possibilities of the proposed method, a gas chromatogram of a mixture of several components is shown in Fig. 4.
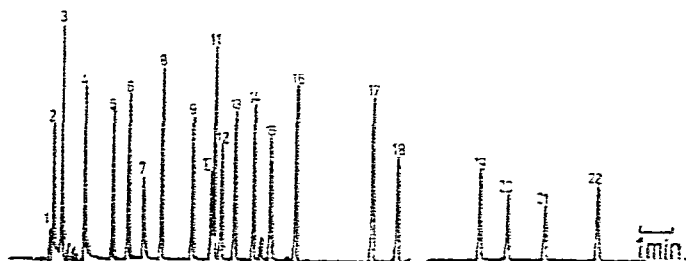
Fig. 4. Illustration of the separation of pesticides with linear programming from 200 to 290° at 4°/min. 1, Solvent; 2, TEPP; 3, naled; 4, mevinphos; 5, zinophos; 6, sulfotep; 7, dimethoate; 8, diazinon; 9, dichlofention; 10. fenchlorphos; 11, fenitrothion; 12, malathion; 13, parathion; 14, bromophos; 15, chlorfenvinphos; 16, bromophos ethyl; 17, ethion; 18, carbofenothion; 19, phenkapton; 20, phosalore; 21, azinphos ethyl; 22, coumaphos.

ACKNOWLEDGEMENT

REFERENCES

1 R. C. Watts and R. W. Storherr, *J. Ass. Offic. Anal. Chem.*, 52 (1969) 513.
2 M. C. Bowman and M. Beroza, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 499.
3 E. Schulte and L. Acker, *Z. Anal. Chem.*, 268 (1974) 260.
4 G. Goretti and M. Possanzini, *J. Gas Chromatogr.*, 77 (1973) 317.