

COLUMN PACKING

Mixed-Phase Silicone Packing for Pesticide Analysis by Gas Chromatography

Twelve chlorinated pesticides were almost completely separated by use of a mixed packing prepared from QF-1 and new phenylmethyl silicone.

RETENTION data for pesticides on a mixed-phase packing were recently reported by Burke and Holswade (7). The packing consisted of equal portions of 15 weight % QF-1 on 80/100 Gas Chrom Q and 10 weight % DC 200 (12,500 cs.) on 80/100 Gas Chrom Q made separately and then thoroughly mixed together. The purpose of the work by Burke and Holswade was to develop a packing with a polarity different from that of the dimethyl silicones (such as DC 200 or SE-30), which would separate a large number of chlorinated pesticides. The present work consists of comparing mixed and individual phases and was prompted by the availability of a new phenylmethyl silicone, OV-17. The results indicate almost complete separation of 12 chlorinated pesticides: lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-TDE, and *o,p'*-TDE.

Experimental

The chromatograph used was a Barber-Colman 5000 equipped with both flame and electron-capture detectors. The columns were 6-foot \times 4-mm. i.d. glass U-tubes, filled with packings prepared with 80/100 and 100/120 Gas Chrom Q and one or more of the following stationary phases: (1) QF-1 (also known as FS-1265), (2) DC 200 (12,500 cs.), and (3) OV-17, a phenylmethyl silicone.

The packings were prepared by the fluidization technique described by Kruppa (2). In the case of mixed-phase packings, the individual packings were first prepared and then subsequently mixed thoroughly in the proper proportions.

Results

The authors' results agreed well with those of Burke and Holswade on the QF-1 + DC 200 packing for the 12

pesticides (Burke and Holswade presented retention data for many more pesticides). The results from the OV-17 packing were different from those of the other packings, but except possibly for special applications, did not seem significantly important. All the packings tested gave separation factors for two or more pairs of pesticides which were too small to result in any appreciable separation. However, the retention data from the OV-17 and the QF-1 packings suggested that the proper mixture of these two packings might separate all 12 pesticides.

The best results were obtained from a

mixture of equal portions of 7 weight % OV-17 and 9 weight % QF-1 on 100/120 Gas Chrom Q. Whether this is the optimum combination for phase loading has not yet been determined. However, all but two of the 12 pesticides were almost completely separated and these two (*p,p'*-DDE and dieldrin) were partially separated. If the column efficiency can be improved (it was 2000 vs. the usual 3000 to 4000 theoretical plates obtained with DC 200), the separation would be appreciably improved.

A chromatogram of the 12 pesticides is shown in Figure 1. Retention times

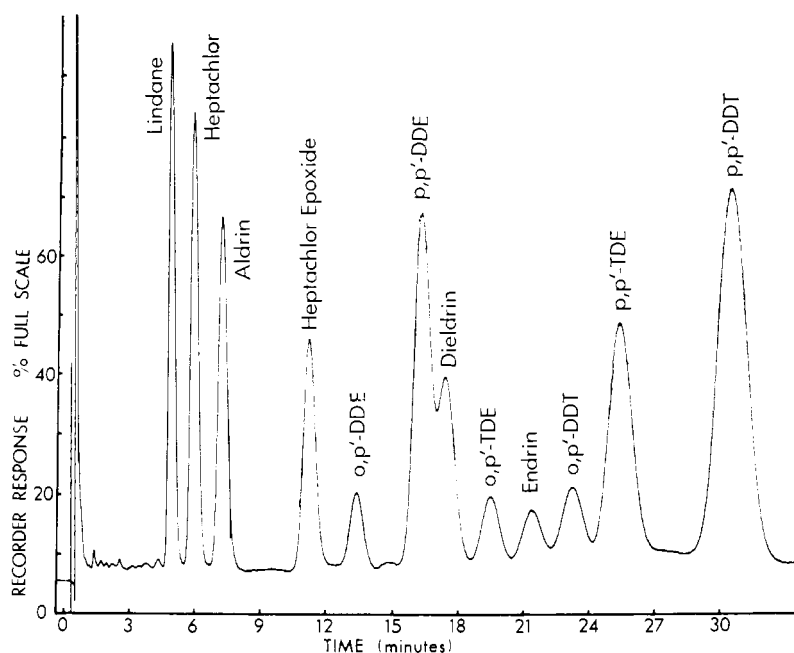


Figure 1. Chromatogram of 12 pesticides

Equal parts by weight of 7 weight % OV-17 and 9 weight % QF-1 on 100/120 Gas-Chrom Q at 200° C. and 20 p.s.i.g.
Column. 6-foot \times 4-mm. i.d. glass U-tube
Electron-capture detector

Table I. Retention Times Relative to Aldrin

	OV-17 ^a + QF-1	OV-17 ^b	QF-1 ^c	DC 200 ^d	DC 200 ^e + QF-1
Lindane	0.66	0.63	0.77	0.48	0.58
Heptachlor	0.81	0.80	0.77 ^f	0.79	0.81
Aldrin	1.00	1.00	1.00	1.00	1.00
Heptachlor epoxide	1.57	1.50	1.80	1.23	1.46
<i>o,p'</i> -DDE	1.89	1.94	1.44	1.47	1.47
<i>p,p'</i> -DDE	2.30	2.39	1.88	1.81	1.88
Dieldrin	2.47	2.35	2.73	1.82	2.22
<i>o,p'</i> -TDE	2.77	2.83	2.25	1.87	2.04
Endrin	3.05	2.93	3.22	2.04	2.50
<i>p,p'</i> -TDE	3.62	3.60	3.20	2.31	2.70
<i>o,p'</i> -DDT	3.30	3.42	2.33	2.41	2.48
<i>p,p'</i> -DDT	4.36	4.44	2.42	3.07	3.28

^a Equal parts of 7% OV-17 + 9% QF-1 on 100/120 Gas Chrom Q at 200° C. and 20 p.s.i.g. Absolute retention time for aldrin, 7.12 min.

^b 9% OV-17 on 100/120 Gas Chrom Q at 205° C. and 40 p.s.i.g. Absolute retention time for aldrin 12.11 min.

^c 12% QF-1 on 100/120 Gas Chrom Q at 200° C. and 35 p.s.i.g. Absolute retention time for aldrin 2.01 min.

^d 10% DC 200 on 100/120 Gas Chrom Q at 200° C. and 30 p.s.i.g. Absolute retention time for aldrin 6.11 min.

^e Equal parts of 10% DC 200 + 15% QF-1 on 80/100 Gas Chrom Q at 200° C. and 30 p.s.i.g. Absolute retention time for aldrin 8.35 min.

^f Not calculated. Heptachlor very close to lindane.

relative to aldrin are presented in Table I for five packings. Separation factors for adjacent pesticides are shown in Table II for the OV-17 + QF-1 and DC 200 + QF-1 mixed packings.

Literature Cited

- (1) Burke, J. A., Holswade, W., *J. Assoc. Offic. Anal. Chemists* **49**, 374 (1966).
- (2) Kruppa, R. F., Henly, R. S., Supina,

Table II. Separation Factors between Adjacent Pesticides

OV-17 + QF-1		DC 200 + QF-1	
Lindane		Lindane	
Heptachlor	1.23	Heptachlor	1.40
Aldrin	1.24	Aldrin	1.23
Heptachlor epoxide	1.57	<i>o,p'</i> -DDE	1.46
<i>o,p'</i> -DDE	1.20	Heptachlor epoxide	1.01
<i>p,p'</i> -DDE	1.22	<i>p,p'</i> -DDE	1.28
Dieldrin	1.08	<i>o,p'</i> -TDE	1.08
<i>o,p'</i> -TDE	1.12	Dieldrin	1.09
Endrin	1.10	<i>o,p'</i> -DDT	1.12
<i>o,p'</i> -DDT	1.09	Endrin	1.03
<i>p,p'</i> -TDE	1.10	<i>p,p'</i> -TDE	1.06
<i>o,p'</i> -DDT	1.20	<i>p,p'</i> -DDT	1.22

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RESIDUE DETERMINATION

Determination of Small Quantities of 2,6-Dichloro-4-nitroaniline (Dichloran)

A procedure for the colorimetric determination of dichloran and for detecting dichloran spots on thin-layer chromatographs, based on diazotization and dye-coupling, is described. A modification of the Kilgore colorimetric method for dichloran is given.

DICHLORAN, 2,6-dichloro-4-nitroaniline, DCNA, Botran (The Upjohn Co.) has been used for the control of certain fungus diseases of fruits and vegetables, and gas chromatographic and colorimetric methods for its determination in small quantities have been developed. Beckman and Bevenue (1) reported the determination of dichloran by gas chromatography with a thermal conductivity detector, and recently, Cheng and Kilgore (2) reported a similar determination with greater sensitivity using an electron-

capture detector. The gas chromatographic determination of dichloran has been reported by The Upjohn Co. (4), and, in this laboratory, the method using both detectors has been used for the past 2 years. The sensitivity and rapidity of the electron-capture gas chromatography method for the determination of dichloran often makes it the method of choice in spray residue work.

Kilgore, Cheng, and Ogawa (3) have described a colorimetric method for dichloran in processed fruits based on

the yellow color formed by adding potassium hydroxide to a solution of the sample in acetone. In applying this method, the authors found that the samples as prepared for the spectrophotometer were frequently fogged due to the precipitation of carbonate, which is insoluble in acetone. Furthermore, acetone containing an alkali may develop a yellow color on standing.

The authors modified the Kilgore method by substituting dimethylformamide (5) for acetone as the sample solvent, and Hyamine 10-X hydroxide