

## Notes

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### Gas-liquid chromatography of pesticides on OV-17 stationary phase

The most widely used stationary phases for gas chromatographic analysis of pesticide residues are the organosilicones SE-30, QF-1, DC-200 (ref. 1) and the mixture QF-1 + DC-200 (refs. 2 and 3). The use of OV-17—a phenylmethyl silicone containing 50% phenyl groups, a product of Applied Science Laboratories—has also been proposed recently, either mixed with QF-1 (ref. 4) or alone<sup>5,6</sup>. Good separations were obtained for twelve chlorinated hydrocarbon pesticides<sup>4,5</sup>.

During more extensive studies regarding the level of pesticide contamination of surface and potable waters in Italy, we experimented with this new stationary phase for a number of herbicides, organochlorine and organophosphate insecticides and related compounds.

#### *Experimental*

The gas chromatograph used was a Carlo Erba C-model, equipped with an electron-capture detector (tritium source) and a glass column 2 m × 4 mm I.D., packed with 3% OV-17 on 80-100 mesh Gas Chrom-Q. The column was conditioned for three days at 250° with a moderate N<sub>2</sub> flow rate operating.

Chromatographic operating conditions were as follows: temperatures: the column, 198°; injection block, 220°; detector, 200° ± 1° (lagged); carrier gas, N<sub>2</sub> at  $p = 1.22 \text{ kg/cm}^2$  (70 ml/min); detector voltage, 30 V d.c. ( $3.1 \times 10^{-8}$  A, attenuation × 100 × 4) at which 1 ng of aldrin causes 1/2 a full scale recorder deflection.

Under the conditions described the column efficiency was 2050 theoretical plates in relation to *p,p'*-DDT; for good quantitative performance the column should be saturated with  $\mu\text{g}$  quantities of the various compounds to be separated.

Standard pesticide solutions were prepared in *n*-hexane. The first standards of methyl- and ethyl-guthion, methylparaoxon and dimethoate, all substances only slightly soluble in *n*-hexane, were prepared in concentrations less than 200  $\mu\text{g/ml}$ .

The photodieldrin (hexachlorohexacyclo isomer of dieldrin) was prepared as described by ROBINSON *et al.*<sup>7</sup>, the methyl esters of 2,4-D, 2,4,5-T, and silvex were obtained by diazomethane methylation.

#### *Results and discussion*

Table I shows the retention times relative to aldrin for the various compounds examined and the respective amounts (ng) approximately required to obtain 50% of the full scale recorder deflection with an attenuation × 100 × 4.

A temperature of 198° was chosen for the operation of the column for routine analyses, since it permits satisfactory separations to be obtained in a fairly short time.

TABLE I

RETENTION TIMES RELATIVE TO ALDRIN AND RESPONSE DATA OF PESTICIDES AND RELATED COMPOUNDS FOR A COLUMN (3% OV-17 ON GAS-CHROM Q, 80-100 MESH) OPERATING AT 198°

No.	Pesticide	Retention time relative to aldrin <sup>a</sup>	Response (ng) for $\frac{1}{2}$ f.s.d. <sup>b</sup>
1	DDVP	0.09	18-19
2	Phosdrin	0.23	45-50
3	2,4-D (methyl ester)	0.37	5-7
4	Thimet	0.42	18-20
5	$\alpha$ -BHC	0.45	0.6
6	Vegadex	0.48	1.6
7	Silvex (methyl ester)	0.50	1.6
8	Diazinon	0.59	90-100
9	$\gamma$ -BHC	0.61	0.7
10	2,4,5-T (methyl ester)	0.64	1.7
11	Di-Syston	0.67	65-70
12	$\beta$ -BHC	0.74	3.2
13	Heptachlor	0.79	0.8
14	$\delta$ -BHC	0.89	1.1
15	Aldrin	1.00	1.0
16	Methyl paraoxon	1.03	400-450
16a	Methyl paraoxon <sup>c</sup>	1.24	—
17	Ronnel	1.05	2.8
18	Dimethoate	1.07	60-80
19	Methyl parathion	1.19	20-22
20	Dursban	1.38	2.0
21	Heptachlor epoxide	1.52	1.7
22	Malathion	1.52	40-45
23	Parathion	1.54	24-26
24	Kelthane	1.57	—
25	Paraoxon	1.64	170-190
26	Perthane (technical)	1.72 ; 2.64 ; 3.39	—
27	$\gamma$ -Chlordane	1.79	2.1
28	Endosulfan I	1.98	—
29	$\alpha$ -Chlordane	1.99	2.7
30	<i>o,p'</i> -DDE	2.04	4.5
31	Dieldrin	2.46	3.0
31a	Dieldrin <sup>c</sup>	2.77	—
32	<i>p,p'</i> -DDE	2.53	3.4
32a	<i>p,p'</i> -DDE <sup>c</sup>	2.99	—
33	Captan	2.55	14-15
34	<i>o,p'</i> -TDE	3.03	9.0
35	Endrin	3.10 ; 4.85 ; 8.15	—
36	<i>o,p'</i> -DDT	3.77	7.1
37	Endosulfan II	3.87	—
38	<i>p,p'</i> -TDE	4.06	9-10
39	Methyl trithion	4.32	17-19
40	Ethion	4.87	30-31
41	<i>p,p'</i> -DDT	4.95	9.2
42	Trithion	5.42	18-20
43	<i>p,p'</i> -Methoxychlor	10.38	70-80
44	Photodieldrin	11.90	36-40
45	Methyl guthion <sup>d</sup>	12.94	450-500
46	Ethyl guthion <sup>d</sup>	15.86	200-250

<sup>a</sup> Retention time approximately 7.8 min.

<sup>b</sup> Approximate quantity (ng) necessary for 50% full scale recorder deflection at  $\times 100 \times 4$  (3.1  $\times 10^{-8}$  A).

<sup>c</sup> Column temperature 175°. Aldrin retention time 17.2 min.

<sup>d</sup> Column temperature 220°. Aldrin retention time 3.8 min.

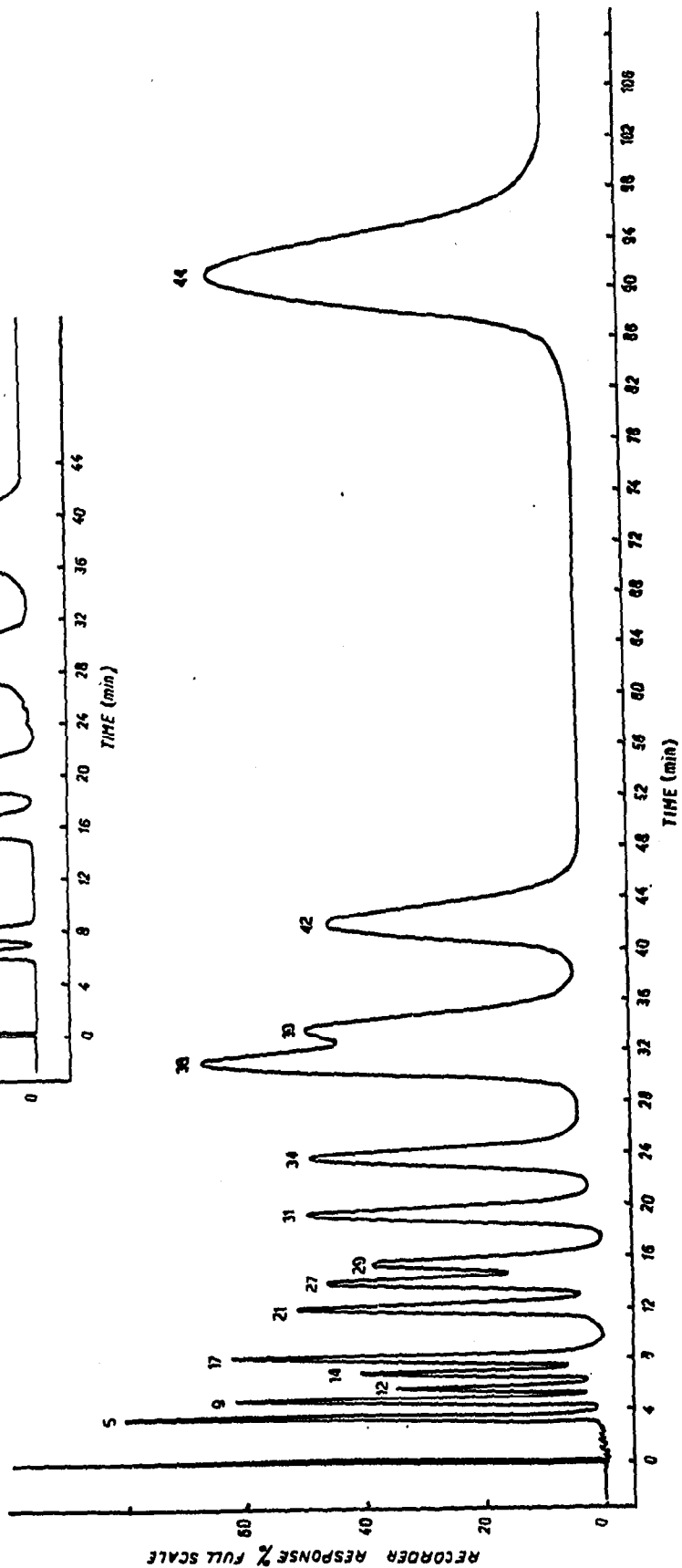
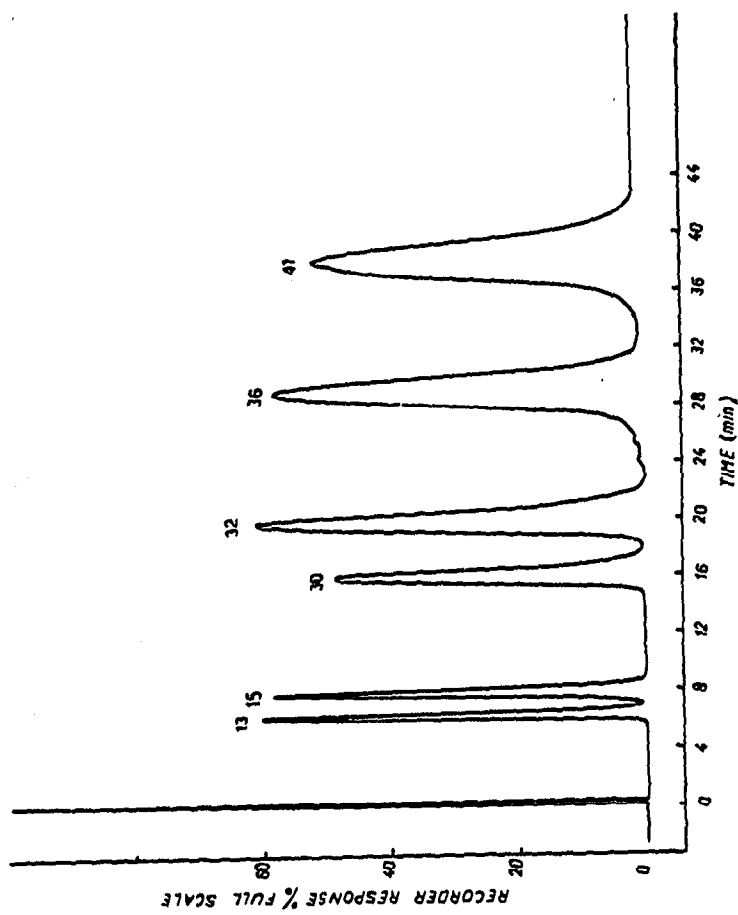


Fig. 1 and 2. Comparison of the components of two samples of material on an OV-17 column at 100°C. Note the difference in peak positions.

The results obtained at 198° with the OV-17 stationary phase are comparable with those obtained at lower temperatures with the mixed phase QF-1 + DC-200; however OV-17 often permits one to obtain better separations. For example, it is superior for the four BHC isomers, for the methyl ester of some herbicides, and for compounds of the DDT series; however, the dieldrin/*p,p'*-DDE separation is not satisfactory at 198° whereas it is at 175° (Table I).

The use of OV-17 as a stationary phase has contributed to the solution of some of the problems in pesticide residue analysis, for example, the systematic analysis of pesticides in water (to be published). The pesticides are first separated into four groups, and the components of the first two groups are separated very well on the column with OV-17 (Figs. 1 and 2).

In addition, excepting for dimethoate, paraoxon and methylparaoxon, all the compounds listed in Table I are regularly eluted and give symmetrical peaks. There is, however, some disadvantage to this column since larger amounts of substances are necessary to obtain detector responses equivalent to those obtained when using other stationary phases such as the mixed QF-1 + DC-200 phase.

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- 1 B. J. GUDZINOWICZ, *The Analysis of Pesticides, Herbicides and Related Compounds using the Electron Affinity Detector*, Jarrel-Ash Co., Waltham, Mass., 1965.
- 2 J. A. BURKE AND W. HOLSWADE, *J. Assoc. Offic. Agr. Chem.*, 49 (1966) 374.
- 3 R. E. DUGGAN, *Pesticide Analytical Manual*, Vol. I. U.S. Department of Health, Education and Welfare, Food and Drug Administration, 1968.
- 4 R. S. HENLY, R. F. KRUPPA AND W. R. SUPINA, *J. Agr. Food Chem.*, 14 (1966) 667.
- 5 C. M. MENZIE AND R. M. PROUTY, *J. Gas Chromatog.*, 6 (1968) 64.
- 6 C. A. BACHE AND D. J. LISK, *J. Assoc. Offic. Anal. Chem.*, 51 (1968) 1270.
- 7 J. ROBINSON, A. RICHARDSON, B. BUSH AND K. E. ELGAR, *Bull. Environ. Contam. Toxicol.*, 1 (1966) 127.

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### Thermal decomposition of some methyl substituted benzhydrols

Recently pyrolysis gas chromatography has been developed as a valuable method of analysis<sup>1,2</sup>, suitable for a wide variety of volatile<sup>3-7</sup> and non-volatile substances<sup>8-12</sup>, especially polymers<sup>13</sup>. This method was chosen for a study of the thermal decomposition of some methyl substituted benzhydrols. The pyrolysis was performed by means of an electrically heated gold tube (Fig. 1), constructed in such a way that this furnace could easily be attached to the injection port of a Varian-Aerograph 1521-1B gas chromatograph. The pyrolysis temperature was  $600 \pm 5^\circ$ .

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