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COMPARISON OF GAS CHROMATOGRAPHY COLUMNS FOR PESTICIDE RESIDUE ANALYSIS

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Four column packings, 10% DC-200 or 15% QF-1 on 80–100 mesh celite and mixtures of the two, were tested for electron-capture gas chromatographic assay of 25 insecticides or alteration products.

Detection of insecticides on the 15% QF-1 column was usually more sensitive than on 10% DC-200 column and relative retention times on the two columns differed.

A packing made by mixing equal amounts of celite coated with 10% DC-200 or 15% QF-1 more nearly resembled the 15% QF-1 packing than the 10% DC-200 packing. A second packing of similar composition made by mixing the silicone polymers before applying to celite more closely resembled the DC-200 packing but generally detection was less sensitive.

Since the retention times on the columns differ they provide additional ways of identifying and separating insecticides.

To distinguish pesticide residues by their retention times, most gas-liquid chromatographic analyses utilise a stationary phase of a nonpolar methyl silicone polymer such as DC Hi-Vac grease, SE-30, DC-200, DC-11, SF-96. These versatile stationary phases separate a large number of pesticide chemicals[1–3] but they all chromatograph pesticide chemicals in the same sequence and with a similar degree of separation. In general the reasons for choosing any of these phases in preference to another are minor. DC-200 has been used in our laboratory for gas chromatographic assay of chlorinated pesticides and several organophosphorus compounds but it is well known that chromatographic analysis by a single system gives only a tentative identification which must be confirmed in at least any other system. Gas chromatography is a most convenient method for analysis of pesticides and it was desirable to have an alternative gas chromatographic system.

A number of liquid phases other than DC-200 have been tried to change order of elution or effect different separations.[6] Retention times and response data are available for organophosphorus pesticides[4,5] on silicone-type columns used mainly for the analysis of chlorinated hydrocarbon pesticides. Epon-1001 and QF-1 have been used by some laboratories, but the number of pesticides they will chromatograph well is limited.[8,9] Goulden *et al.*[10] have reported the use of five columns, each with a different liquid phase, Beroza and Bowman[7] reported the relative retention times of 25 organophosphorus insecticides on three silicone columns and on a diethyleneglycol succinate column. McCully and McKinley[11] tested 6% QF-1 and 4% SE-30 mixed prior to application to chromosorb-W for use in residue analysis, and demonstrated the potential value of mixtures of liquid phases for the gas-chromatographie separotion[12] and confirmation[13] of the identity[14] of pesticides residues. More recently Watts and Storherr[15] reported the use of the mixture of QF-1 and DC-200 on Gas chrome-Q for the analysis of organophosphorus pesticides residues, and Burke and Holwade[5] reported its use for chlorinated compounds.

This paper describes the investigations of the retention times and sensitivity of detection of chlorinated and organophosphorus insecticides using column of QF-1 and DC-200 both alone and mixed together on celite in gas chromatography equipment available in this laboratory.

Experimental

Apparatus.—A Philips gas chromatograph Model PV-4000 Series, equipped with an electron capture detector, was used with high purity nitrogen as carrier gas at 25 lb/in^2 giving a gas flow of 40 ml/min. Stock solutions of 1 mg/ml of pure insecticides (Table 1) were prepared in n-hexane, stored in all-glass-stoppered bottles in a refrigerator. Dilutions were made as necessary.

Columns.—To compare different types of column packings, columns were prepared with either 15% QF-1 or 10% DC-200 coated on to celite as stationary phases and with mixtures made in two different ways. One mixed column (A) was prepared by mixing equal amounts of supports treated with 15% QF-1 and with 10% DC-200. A second mixed column (B) contained the same quantities of QF-1 and DC-200 but it was prepared by mixing the liquid phases together before application to the solid support.

The silicone polymers were dissolved in chloroform and 80–100 mesh celite was added to give a slurry in a round-bottomed flask. The solvent was evaporated by warming in a water bath at about 60°C while the flask was rotated to ensure a uniform coat of polymer on celite. The dried coated solid was air-elutriated to separate the

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small particles which restrict gas flow. When prepared stationary phases were packed with vibration in stainless steel columns of 2 mm internal dia $\times 1.2$ m in length. Columns were preconditioned at 170°C overnight before use to eliminate traces of slightly volatile materials which affect electron capture detector.

Results and Discussion

Most of the 25 important organochlorine and organophosphorus compounds tested were chromatographed on each of the four columns prepared. The purity of the compounds, listed in alphabetical order, is given in Table 1. The quantities to give 20% full scale deflection (FSD) for the 18 substances tested on all four columns are listed in section A and the remaining 7 substances in section B. Retention times are given in Table 2.

The amounts of insecticide causing 20% full scale deflection varied from substance to substance and from one column to another. Detection of oxy-demeton Methyl and Demeton-S-Methyl were exceptionally insensitive (always above 300 ng) and they were not detected on using DC-200 columns and will not be discussed further.

Generally much smaller quantities of other insecticides could be measured although Dicrotophos was not detected using the column prepared from mixed liquid phases and it was not tested on the unmixed columns. Usually smaller amounts of any substance could be measured on the QF-1 column (range 0.1–45 ng) than on the DC-200 column (range 1.2–150 ng.) (Table 1). The amounts measured, using the column made by mixing coated solids (range 0.1–53 ng), were similar to those which were measured on the QF-1 column whereas the column made by mixing liquids (range 0.9–143 ng) was more similar to the DC-200 column (Table 1 section A), although usually less

TABLE 1.—COMPARISON OF SENSITIVITY OF DETECTION OF ORGANOPHOSPHORUS AND ORGANOCHLORINATED INSECTICIDES BY GAS CHROMATOGRAPHY USING FOUR STATIONARY PHASES.

Pesticides	Response (ng) for 20% FSD				
	Purity %	10% DC-200	15% QF-1	Mix A	Mix B
Section A					
Bromophos	100	104	45.5	20	143
Gamma-BHC	100	0.6	0.1	0.13	0.91
Demeton-S-methyl		ND	1000	700	1600
Diazinon	100	12.8	3.3	5.6	35
Dieldrin	100	1.2	0.14	0.315	4.0
DDE	99.3	2.2	0.3	0.32	3.47
p, p'-DDT	99.8	3.8	0.72	0.5	6.0
Dicofol	100	5.0	1.1	1.45	10.5
Dimethoate	95	150	46.5	53	143
Endrin	100	6.6	2	2.2	30
Endosulfan	96.5	1.8	0.32	0.44	4
Fenitrothion	96.8	3.5	1.7	2.4	13.6
Formothion	100	104	45.5	20	143
Malathion	99.5	10	11	1.65	14.5
Methyl parathion	98	3	1.15	2.5	2.45
Oxy-demeton-methyl	93.4	ND	1000	335	1700
Phorate	100	23.4	5.85	10.7	10.6
Section B					
Aldrin	100	0.1	—	0.3	1.53
Dicrotophos	95	—	—	30	ND
o, p'-DDT	99.8	—	—	1.37	6.25
Heptachlor	98.6	—	—	0.1	1.2
Imidan	100	—	—	59	Poor response
Phosphamidon	100	17	4.55	5.3	—
TDE	99.8	—	—	0.83	6.0
Telodrin	100	—	—	0.57	3

ND. not detected; Mix A. coated solid phases mixed; Mix B. solid coated with mixed liquid phases.

TABLE 2.—COMPARISON OF RETENTION TIMES OF DETECTION OF ORGANOPHOSPHORUS AND ORGANOCHLORINATED INSECTICIDES BY GAS CHROMATOGRAPHY USING FOUR STATIONARY PHASES. (INSECTICIDES ARRANGED IN ORDER OF INCREASING RETENTION TIME ON DC-200).

Pesticides	10% DC-200 min	15% QF-1 min	Mix A min	Mix B min
Phosphamidon	1.0	2	0.5	—
Phorate	2.5	2.5	3	3
Gamma-BHC	3	3	3	5.25
Dicrotophos	—	—	1	ND
Diazinon	4	3	4	6.5
Oxy-Demeton methyl	ND	4	3	4
Demeton-S-methyl	ND	4	3	4
Methyl parathion	4.5	10	10	10
Formothion	5	13	10	17
Heptachlor	—	—	5	8
Dimethoate	6	16	14	16
Aldrin	7	—	6	10
Malathion	7.5	12.5	11	18
Fenitrothion	7.6	12	11	18
Dicofol	8	8	9	14
Bromophos	8.5	7	9	16
Endasulfan	12	10	12	20
Telodrin	—	—	8	12
Dieldrin	16	11	16	25
DDE	18	10	14	22
o, *p*-DDT	—	—	20	30
TDE	—	—	20	34
TDE	—	—	20	34
p, *p*′-DDT	30	18	26	44
Imidan	—	—	64	Poor response
Endrin	22	16	18	35

ND. not detected; Mix A, coated solid phases mixed; Mix B, solid coated with mixed liquid phases.

could be measured than on the single phase column. However, frequently less could be measured on the column prepared by mixing the coated solids than on the QF-1 column although the reverse was sometimes true as for example with Diazinon and Phorate.

Perhaps the most important reason for examining different columns is to improve and confirm the identification of unknown insecticides. The retention times of most insecticides on the four columns tested do not differ greatly (Table 2) but there are some useful differences in the retention time of insecticides on the several columns, for example the retention time of Phosphamidon on DC-200 is half that on QF-1 and twice that on the mixed solids (Mix A) in contrast phorate, has a similar retention time on all the four columns. Although Malathion and Fenitrothion have similar retention times on all four columns and may be confused with Endosulfan on three columns they can be distinguished from Endosulfan on the DC-200 column. Also *p*,*p*′-DDT and Endrin, not separated on the QF-1 column are distinguishable on the other three columns.

Conclusion

Retention times on columns prepared from mixtures of two components differ with the mode of preparation. Although retention times are often intermediate between those for the two components or the same as for one component they may be completely different.

Sensitivity with columns containing mixed packings may be better or worse than those prepared from the individual components.

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