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Design of a column for the gas chromatographic analysis of chlorinated hydrocarbon pesticides

The mixed silicone–fluorosilicone column of BURKE AND HOLSWADE[1] commonly used for pesticide residue analysis does not sufficiently separate hexachlorobenzene (HCB) and α-benzene hexachloride (α-BHC), which is the isomer normally used in estimation of total benzene hexachloride. Occurrence of peaks for these compounds necessitates re-analysis on another, more polar column, which may not be satisfactory for separation of the other chlorinated hydrocarbons of interest because of peak overlaps or impractically long retention times.

Theory

Separation of pesticides in order of their vapour pressures alone is not readily feasible. The most direct way to an ideal column would be by selection of suitable solute–solvent interactions, using differences in the structure, size or shape of the molecule. Data of this kind is not always easily available, and is rather complex to apply.

Many effective chromatographic systems have been designed by trial and adjustment, but the bewildering array of commercially available stationary phases complicates the choice, and many workers tend to use certain favourite phases already on their shelves[1]. Some guidance can be obtained by using the classification of stationary phases described by BROWN[2], who ascribed to a number of compounds vectors of electron-acceptor, electron-donor, and non-polar properties. From retention data found by experiment on a range of compounds with different characteristics on a BROWN plot, several stationary phases may be chosen as closest in properties required for best separation of the solutes of interest. Intermediate properties closer to ideality may then be obtained from mixtures of these phases, the retention data being predictable by methods such as those used by HILDEBRAND AND REILLEY[3].

Mixed stationary phases are tailored by manipulating retention times directly by changing composition. This is done by standardising or normalising other variables. If liquid volume (V_l) in a column is much smaller than gas volume (V_g), it will be linear with partition ratio (k), thus:

$$k = K \frac{V_l}{V_g}$$

where K is the partition coefficient.

Partition ratio is the relation between solute retention time (t_R) and that of an unsorbed material, usually air (t_A), the solute retention time having been corrected for the air peak.

Partition ratios for experimentally different columns may be normalised for gas volume (V_g) and packing weight (w) as follows:

$$k = k_{(\mathrm{exp})} \times \frac{V_{g(\mathrm{exp})}}{V_{g(\mathrm{norm})}} \times \frac{w_{(\mathrm{norm})}}{w_{(\mathrm{exp})}}$$

where (exp) means experimental and (norm) normalised.

Thus t_R becomes a linear function of V_l.

For two stationary phases (A and B) in one column, $V_l = V_{lA} + V_{lB}$, and $t_R = t_{RA} + t_{RB}$. Then

$$\frac{t_{RA} + t_{RB}}{V_{lA} + V_{lB}} = \text{constant}$$

As the stationary phase composition is altered from all "A" to all "B", the retention time will change in a linear fashion from t_{RA} to t_{RB}. Therefore t_R (and hence k) can be predicted for any solute for any column composition.

The optimum mixture may be found for any pair of solutes from the separation factor (SF), which is the ratio of the larger to the smaller of the two partition ratios. It is a useful guide to separating power, as the lower the SF, the more highly efficient must be the column, to effect resolution. Plotting SF against column composition will show the optimum proportions of the mixture.

In practice, the use of mixed phases may introduce several difficulties, *viz.* (1) Differing temperature stabilities can change column characteristics by preferential bleeding or chemical alteration of one component. (2) Interaction between components can result in anomalous behaviour. Series or mixed-bed packing can minimise this problem. (3) Series packing itself can introduce differences in pressures gradients in different sections of the column, and change partition ratios.

Experimental

The phases selected for study have a variety of positions of the BROWN plot. They are: DC-200 (methyl silicone); QF-1 (trifluoro propyl methyl silicone); XE-60 (cyanoethyl methyl and dimethyl silicone); Zonyl E-7 (fluoroalkyl pyromellitic ester); NPGS (poly(neopentyl glycol succinate), (HI-EFF 3B)).

Retention data were collected for the pesticides on the selected stationary phases under the following conditions: instrument, Packard Model 803; detector, electron capture; column, glass, 6 ft. × 4 mm I.D.; support, Gas-Chrom Q, 80–100 mesh; temperature, 200°; flow rate, 200 ml of nitrogen per min.

Some results are shown in Table I.

TABLE I

GC RETENTION TIMES OF CHLORINATED HYDROCARBON PESTICIDES ON SELECTED PHASES

Retention times are corrected for retention of unsorbed solute by using measurements from the solvent peak.

Phase	*Retention time relative to Dieldrin = 100 (RRTD)*				
	10% DC-200	*10% QF-1*	*10% XE-60*	*10% Zonyl*	*2% NPGS*
HCB	22	19	18	22	11
α-BHC	24	25	30	25	30
Lindane	28	31	41	36	44
DDE	100	69	81	136	92
Dieldrin	100	100	100	100	100
DDD	140	116	192	341	257
DDT	171	127	192	—	222

Discussion

Of those phases which satisfactorily separate HCB, α-BHC and lindane, XE-60 and QF-1 do not distinguish sufficiently between DDD and DDT, and Zonyl appears to cause some breakdown of DDT. NPGS seems more useful, although separation of DDE and Dieldrin is inadequate. As QF-1 selectively retains the oxygenated compound Dieldrin, the possibility of using it to modify a column of NPGS emerged.

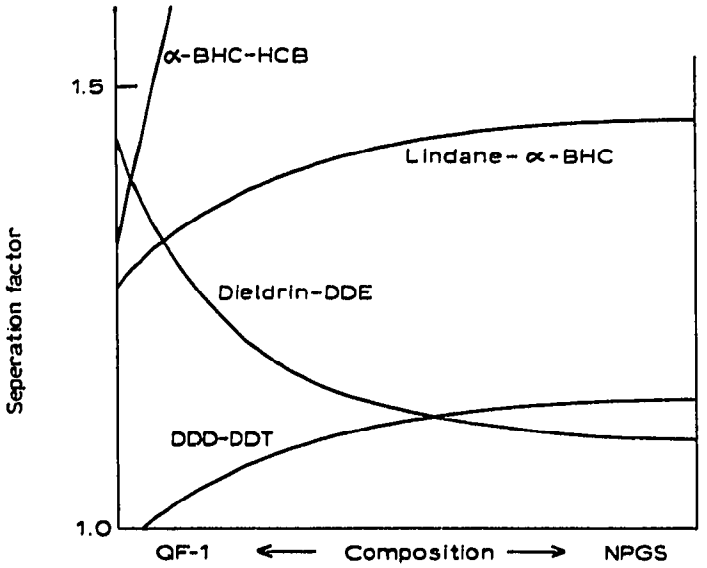

Fig. 1. Plot of separation factors to find optimum substrate composition.

Partition ratios for each solute were calculated for both pure stationary phases from experimental results, then predicted for a range of mixtures from 2% QF-1–0% NPGS to 0% QF-1–2% NPGS. Separation factors were calculated for pairs of pesticides, and plotted against column composition, as shown in Fig. 1. It would appear that optimum separation is available at close to equal proportions of the two constituents.

Confirmatory experiments

A column was made, to contain 2% QF-1 and 2% NPGS. The method of coating

TABLE II

RELATIVE RETENTION TIMES OF CHLORINATED PESTICIDES ON PROPOSED COLUMN

Pesticide	*RRTD*	*Pesticide*	*RRTD*
HCB	13	Heptachlor epoxide	68
Methoxychlor	27, 420	Chlordane	74, 27
Chlordane	27, 74	DDE	88
Heptachlor	28	Dieldrin	100
α-BHC	29	Endrin	113
Aldrin	29	DDT	209
Lindane	41	DDD	235
Telodrin	42	Methoxychlor	420, 27

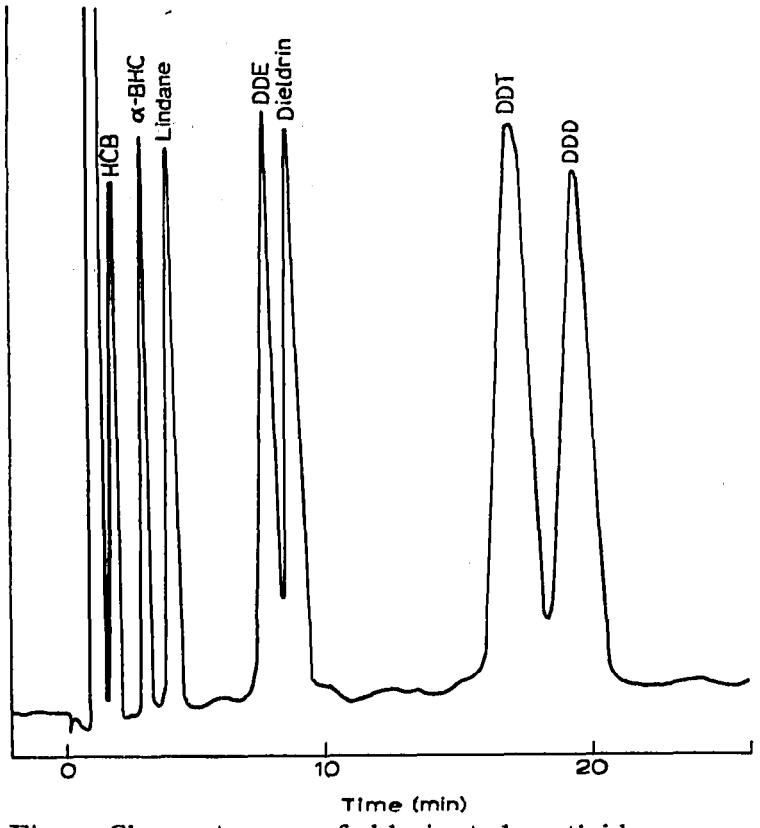

Fig. 2. Chromatogram of chlorinated pesticides on a column of 2% QF-1 and 2% NPGS.

was as follows: Dissolve the required weights of QF-1 and NPGS in acetone and chloroform, respectively. Mix and dilute to approximately 100 ml with acetone in a conical flask. Add 10 g of Gas-Chrom Q (80–100 mesh). Boil for a few minutes until support appears to be degassed. Remove solvent by evaporation and dry by gentle agitation in a stream of dry nitrogen.

This column exhibited retention characteristics close to those predicted. The pesticides are satisfactorily separated under the conditions used. A chromatogram is shown in Fig. 2. It has since been discovered that total column loading may be reduced to 1% without loss of retention characteristics or peak symmetry. Very rapid analyses are possible at this level.

Retention data

Experimentally found retention times, relative to Dieldrin, of a range of chlorinated pesticides, are collected in Table II.

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