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## Note

# OV-17–QF-1 capillary column for organochlorine pesticide analysis

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The determination of pesticides in general and of organochlorine pesticides (OCPs) in particular is a complex problem. Difficulties arise because the normal extraction method of solvent partitioning and Florisil column "clean-up" is a difficult process to control and yields a complex sample[1,2]. The complexity arises from the large number of compounds which may be present. The ubiquitous distribution of industrial chemicals such as polychlorinated biphenyls (PCBs) further complicates the analysis[3–6].

Recently the potential of cyclic steam extraction as a sample preparation method has been demonstrated and applied[6–9]. Extracts obtained in this manner are sufficiently free from interferents to permit analysis by gas chromatography (GC) directly. Normally chromatographic determination of OCPs is performed by gas–liquid chromatography with an electron-capture detector (GLC–ECD) using packed columns. The liquid phase most commonly used and the one officially recommended[10] is 1.5% OV-17–1.95% QF-1. This unique combination of a partially-phenylated methyl silicone (OV-17), and a trifluoromethyl-substituted methyl silicone (QF-1) is, when correctly prepared, capable of giving a reasonable separation for many OCPs. Difficulties arise, however, when, for example *p,p'*-DDE and dieldrin are present in the same sample. Likewise the presence of minor components is seldom revealed when packed columns are used. For example commercial grade *p,p'*-DDT contains a significant quantity of *o,p'*-DDT and dehydrochlorination (the natural environmental degradation reaction) should therefore yield *o,p'*-DDE. *o,p'*-DDE is seldom identified in chromatograms obtained on packed columns presumably because it co-elutes with another major component (such as aldrin). The obvious solution is to apply capillary GC to the separation of organochlorine compounds. The technology of capillary GC has been the subject of considerable research interest in recent years. Much theoretical consideration has been given to the preparation of the surface prior to coating, to deactivation of the surface prior to coating, to the method of coating the column and to assessment of column performance by means of standard compounds. In our work we have adopted two criteria for assessing column performance. These are: (1) does the column perform the desired separation and (2) does the useful column lifetime justify the time spent in preparation? We now report the simple preparation of a mixed phase (2% OV-17–1.5% QF-1) capillary column which gives superior performance to either OV-17 or SE-30 with respect to organochlorine pesticides.

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## EXPERIMENTAL

### *Reagents*

All solvents were distilled before use. Standard pesticide compounds were obtained from the National Physical Laboratory, Teddington, Great Britain and were used as received. OV-17 and QF-1 were purchased from Jones Chromatography (Llanbradach, Great Britain). The preparation of the mixed phase column is described in detail below.

### *Equipment*

A Fractovap 2151 Series gas chromatograph (Carlo Erba, Milan, Italy), fitted with a splitless injection system and flame-ionisation detector was used. The hydrogen carrier gas flow-rate was 2 ml $min^{-1}$. An injection port temperature of 250°C and a temperature programme of 60°C hold 2 min, then 5°C $min^{-1}$ to 200°C, then 6°C $min^{-1}$ to 225°C, hold 3 min were employed unless other wisestated. Amplifier sensitivities were $\times 32$ for Fig. 1 and $\times 16$ for Fig. 2. PTFE-faced septa were used for *ca.* ten injections each before they began to break up and deposit small particles in the injection port

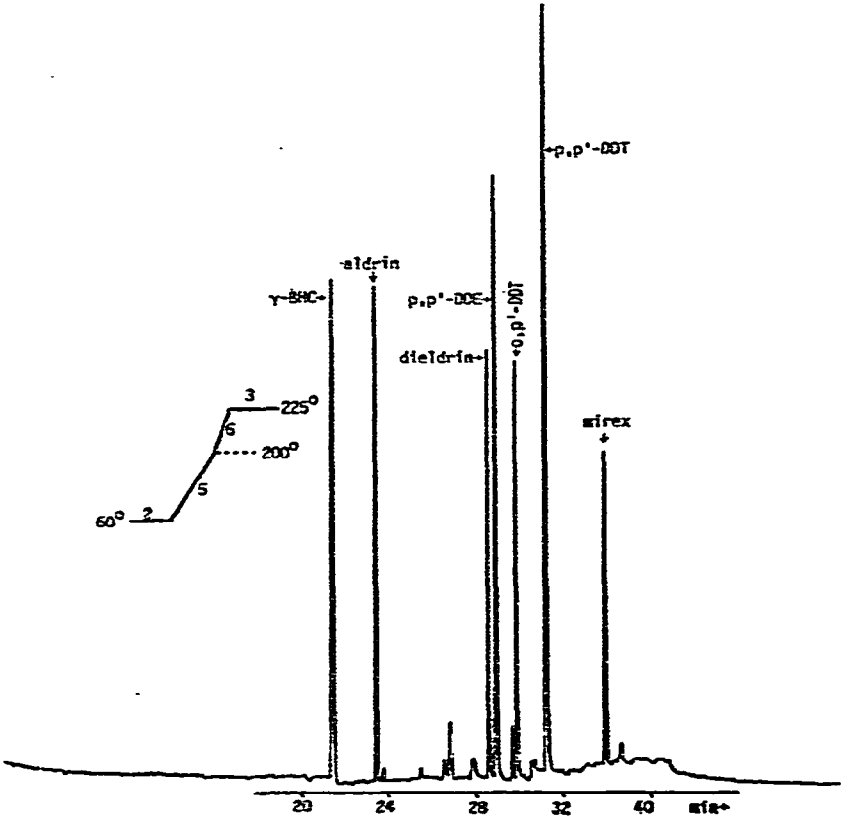


Fig. 1. The mixture of organochlorine pesticides chromatographed on an OV-17–QF-1 capillary column.

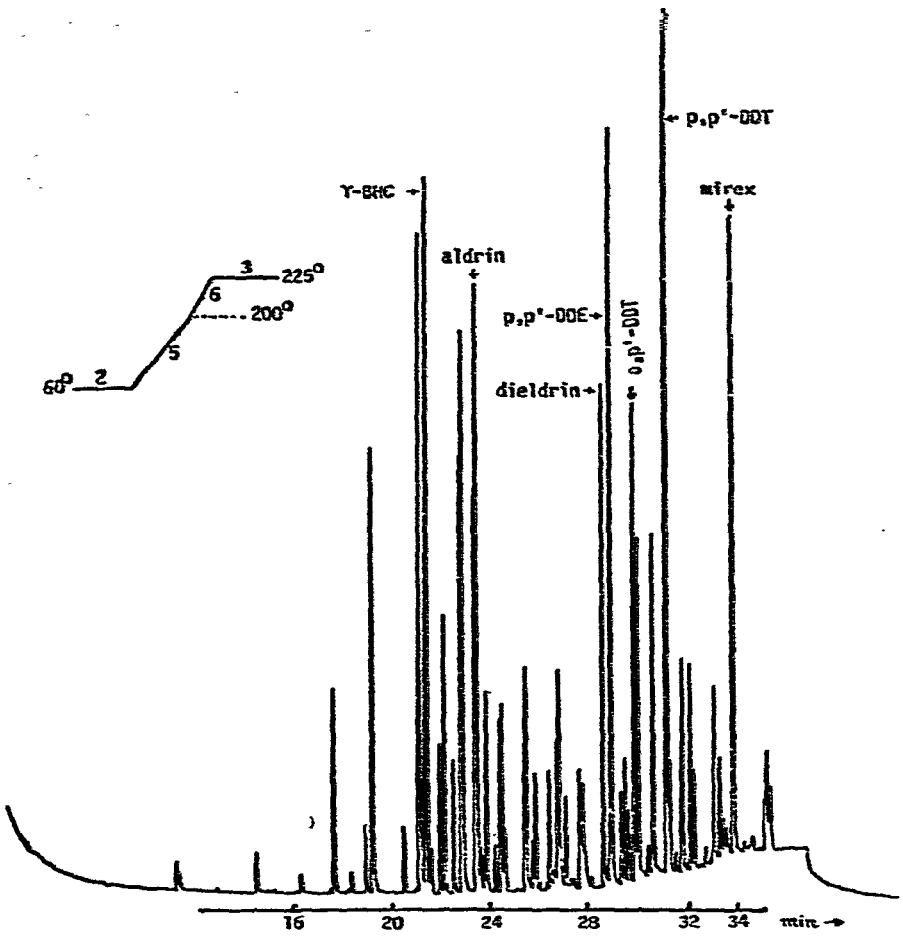


Fig. 2. The mixture of organochlorine pesticides, with Aroclor 1242 and Aroclor 1260 added, chromatographed on an OV-17–QF-1 capillary column.

liner. Septa were replaced and the glass liner cleaned, regularly. Glass capillary columns were drawn on a Hewlett-Packard Model 1045 A drawing machine.

## RESULTS AND DISCUSSION

### *Column preparation*

Columns were drawn from soda glass tubing. Before drawing the inside of the tube was thoroughly washed with freshly prepared chromic acid. The intention was to remove traces of organic material adsorbed on the glass surface but the process may also be beneficial in leaching out unwanted metal ions. After acid washing the tube was cleaned with water, then acetone and finally dried by passage of nitrogen. Capillaries were drawn to give a length of 20 m and an internal diameter of 0.3 mm (nominal). The column was then filled to *ca.* 90% capacity with HCl gas (from a

cylinder, nominal purity 99%), sealed, and heated at 350°C for a minimum of 3 h (refs. 11 and 12).

The etched column was filled to *ca.* 20% with a "plug" of Carbowax 20 M (0.1%), in dichloromethane and this "plug" was pulled through the column by application of a vacuum. The rate of travel of this deactivating solution through the column was carefully regulated by means of a needle valve to one turn per minute. After passage of this solution the column was installed in the gas chromatograph, a flow-rate (2 ml $min^{-1}$) of hydrogen established, and the following temperature programme performed: 50°C hold 30 min; increase 1°C $min^{-1}$ to 280°C; hold 60 min. The whole coating and conditioning procedure was then repeated. The relevance of hydrogen as a carrier gas to this procedure is unknown but it may serve to reduce the possibility of oxidative degradation of the liquid phase (note: if the column is not to be coated immediately after the Carbowax 20 M deactivation treatment then the ends should be sealed until use).

The deactivated capillary was then coated with a solution of 2% OV-17–1.5% QF-1 in chloroform. The column was filled to approximately 20% and the plug pulled through again using vacuum controlled by a needle valve to give a flow-rate of 1 turn $min^{-1}$. A buffer column of about 10 m was placed between the analytical column and the needle valve to ensure a constant coating velocity as the coating solution neared the end of the analytical column. The column was placed in the gas chromatograph and the temperature was slowly raised, (1°C $min^{-1}$), to 230°C and maintained there for about 12 h. The maximum column temperature employed subsequently was 225°C.

*Separation of organochlorine compounds*

A solution (hexane) containing the nominally "pure" standard organochlorine pesticides, $\gamma$-BHC, aldrin, dieldrin, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT and mirex was prepared. These were selected as typical compounds representative of the full range of OCPs. Chromatograms were obtained using a standard injection size (0.6 $\mu$l). A typical chromatogram is shown in Fig. 1. Peak shape and resolution are excellent as illustrated by the resolution to baseline of the dieldrin/*p,p'*-DDE pair. The elution of dieldrin before *p,p'*-DDE is the reverse of that which is usually observed[13]. All peaks were identified by co-injection.

Environmental extracts containing OCP residues are often contaminated by PCB[7–9]. The performance of this mixed phase column with respect to PCB residues is displayed in Fig. 2.

To the standard mixture of OCPs were added the PCB mixtures Aroclor 1242 and Aroclor 1260. Aroclor 1242 was found to elute completely before *p,p'*-DDE and *ca.* 95% of the components of the Aroclor 1260 eluted later than *p,p'*-DDE. Incidentally the separation of Aroclor 1242 on this column was found to be superior to that obtained on a single phase OV-17 column[14]. From the chromatogram (Fig. 2) it can be seen that one component of Aroclor 1242 elutes on the leading edge of the aldrin peak. A comparison of the ratio of peak heights of aldrin and $\gamma$-BHC in the presence and absence of Aroclor 1242 reveals no difference. Thus the aldrin response is not perturbed by the proximity of this component. Quantitation by peak height should thus be possible. All the other organochlorine pesticides are well resolved from PCB compounds. Mirex elutes at the end of the chromatographic run at a temperature of 220°C. The sample preparation procedure which requires column chromatographic

separation of OCP's from PCBs prior to determination on packed columns would thus appear unnecessary if a mixed phase (OV-17–QF-1) capillary column were to be used for the determination.

## CONCLUSION

A mixed phase (OV-17–QF-1) glass capillary column has been prepared by a simple coating procedure which provides excellent separation of organochlorine compounds. In spite of the simple preparation procedure, columns appear stable over long periods of use (> 3 months) and give excellent peak shapes for these mildly polar compounds. Quantitation should therefore be routinely achievable by peak height measurement. To demonstrate this possibility known weights of $\gamma$-BHC (from 5 to 40 ng) were injected and a calibration curve based on peak height was constructed. The regression equation for the line was $y = 3.5x - 4.67$, with a correlation coefficient of 0.9994.

Substitution of OV-210 for QF-1 would allow a higher temperature limit to be employed should this prove necessary.

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