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Note

Adsorption liquid chromatography of DDT and polychlorinated biphenyls

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DDT isomers and the higher chlorinated biphenyls frequently overlap and interfere with each other during the gas–liquid chromatographic (GLC) determination of chlorinated hydrocarbons[1–9], which are frequently found in environmental samples. Polychlorinated biphenyls (PCBs) containing 54 and 60% of chlorine constitute the majority of the environmental PCBs[1,10].

In GLC, the higher chlorinated PCB species show longer retention times than the biphenyls with lower chlorine content[1]. The same is apparently true with reversed-phase partition liquid chromatography (LC)[11,12]. These two forms of partition chromatography (gas–liquid and reversed-phase liquid–liquid) resemble each other in two respects: firstly, the PCBs form many individual peaks with widely differing retention times, which makes their elution as a group nearly impossible, and secondly, the PCBs of higher chlorine content exhibit longer retention times than those of lower chlorine content. This causes overlaps to occur between DDT peaks and the peaks of those PCBs which occur most frequently in the environment.

Group separations are often achieved more easily by adsorption chromatography. We therefore wanted to investigate whether adsorption LC might be of advantage for the group separation of DDT from the higher chlorinated PCBs.

Collins *et al.*[13] were able to separate the PCBs from the DDT isomers by conventional silica gel chromatography, and determined the PCBs after oxidation of the interfering residual *p,p'*-DDE to the corresponding benzophenone. Several workers[2,8,9] obtained good separations of Aroclors 1254 and 1260 from *p,p'*-DDE and the DDTs, but other workers[7] found it difficult to repeat these separations.

Using adsorption LC, Von Spulak[14] investigated the retention of a few individual chlorinated biphenyls, and separated a number of chlorinated insecticides under conditions that were not directly comparable. Eisenbeiss and Sieper[4] showed an adsorption chromatographic separation (Perisorb A in hexane) of PCBs from DDT. The chlorine content of the PCBs used was not stated.

In order to investigate whether a group separation of the PCBs from DDT by adsorption LC was feasible, the adsorption liquid chromatographic relative retentions of the various PCBs and DDT isomers were determined and their separation was demonstrated by obtaining test chromatograms.

EXPERIMENTAL

Standards of *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, Aroclor* 1232, 1242, 1248, 1254, 1260 and 1268 and a sample of cardboard known to contain PCBs were obtained from Poly Science Niles, Ill., U.S.A., or were gifts from Prof. A. N. Sagredos**. Solutions of 1 mg/ml of the standards in heptane were prepared and between 3 and 20 μl of mixtures of these solutions were injected directly into the column.

Merckosorb SI 60 of average grain diameter 10 μm was used as the column filling material. The liquid chromatograph was home-built from individually purchased parts and consisted of a solvent reservoir, pump (Milton Roy 196-100), septum injection head, glass column of dimensions *ca.* 30 cm × 3.5 mm I.D., and a Zeiss PMQ II spectrophotometer, which was equipped with a Hupe and Busch micro flow-cell of dead volume 8 μl and used as a variable wavelength UV detector.

Dry light petroleum (Petroleumbenzin 1775, b.p. 40–60°; E. Merck, Darmstadt, G.F.R.) was used as the solvent. A pre-column (*ca.* 58 cm × 6 mm) filled with alumina was used for further drying of the solvent. The column back-pressure generated was usually about 15–20 atm. The signal from the 10-mV outlet of the PMQ II detector was converted to 1 mV via a Pye eluant collector and recorded on a Philips PM 8000 1-mV recorder. An absorption–absorbance converter was not used.

The flow-rates used were about 0.6 ml/min. Injections were made into a 2-cm layer of glass beads on top of a 27–28-cm sorbent filling. The linear velocity was about 1 mm/sec.

RESULTS AND DISCUSSION

Preliminary investigations on the most suitable adsorbent type, solvent and water content of the solvent led to the choice of 10-μm Merckosorb SI 60 and dry light petroleum. Apparently straight-chain saturated hydrocarbons give the best results in the adsorption LC of chlorinated hydrocarbon pesticides. A number of workers[1,6,8,15] have shown that the water content of the adsorbent–solvent system is important for the success or failure of a separation. We found that even blends made of 75% of dry hydrocarbon plus 25% water-saturated hydrocarbon led to a rapid decrease in k' values and eventually to the elution of all components in the unretained peak.

When the column was dry-filled with Merckosorb SI 60 as received, *i.e.*, without prior activation of the sorbent, and equilibrated by pumping dried solvent through the column for periods of 5–8 h, separations of the type shown in Fig. 1 were achieved. The calculated plate numbers were usually about 1200–1500 for k' values of 1.7–5, equal to about 5000 plates/m.

Fig. 1 shows that, while the separation of the peaks of PCBs with average chlorine contents of 54 and 60% (*i.e.*, those most prone to interference in GLC) from the less retained DDT isomer is very good (R_s = 3.8), their separation from the major DDT metabolite, *p,p'*-DDE is not as good (R_s = 1.2). This separation could possibly be further improved by activation of the sorbent.

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Fig. 2 shows the LC retention characteristics of various Aroclor samples with chlorine contents ranging from 32 to 68%. This adsorption LC retention behaviour of the PCBs is in sharp contrast to their GLC behaviour, where the retention increases with chlorine content. Adsorption LC should permit an easy separation of DDT from the higher chlorinated PCBs, while PCBs with low chlorine content, *e.g.*, Aroclor

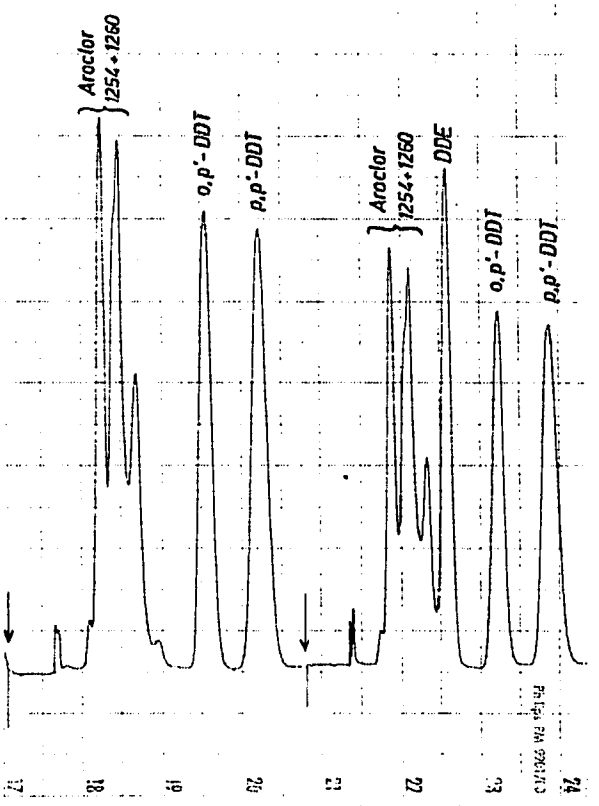

Fig. 1. Adsorption LC separations of the DDTs and DDE from PCBs of average chlorine content 54 and 60%. Peaks measured at 235 nm correspond to about 3 μg of each compound.

1232, will overlap with the DDT group, *i.e.*, the opposite behaviour to that observed in GLC. It is presumed that the clean-up separation by a small conventional silica gel column used in a number of pesticide analysis schemes[6,8,15] is governed by the same principles.

From a packing board that was known to contain PCBs, the chlorinated hydrocarbons were extracted following conventional clean-up procedures[16] including the use of a Florisil column. The final Florisil column eluate was subdivided into a first and second fraction, which were concentrated to about 50 μl and injected. Fig. 3 shows the liquid chromatograms obtained from the two fractions. The second fraction contained the PCBs present. No peaks for DDT were seen. A parallel GLC investigation showed that the PCBs in this packing board were similar to Aroclor 1242. An attempt to omit the Florisil column clean-up stage and to replace it with the LC procedure failed because large amounts of wax were present in this sample. The analytical LC column was overloaded by the wax alcohols that were still present in

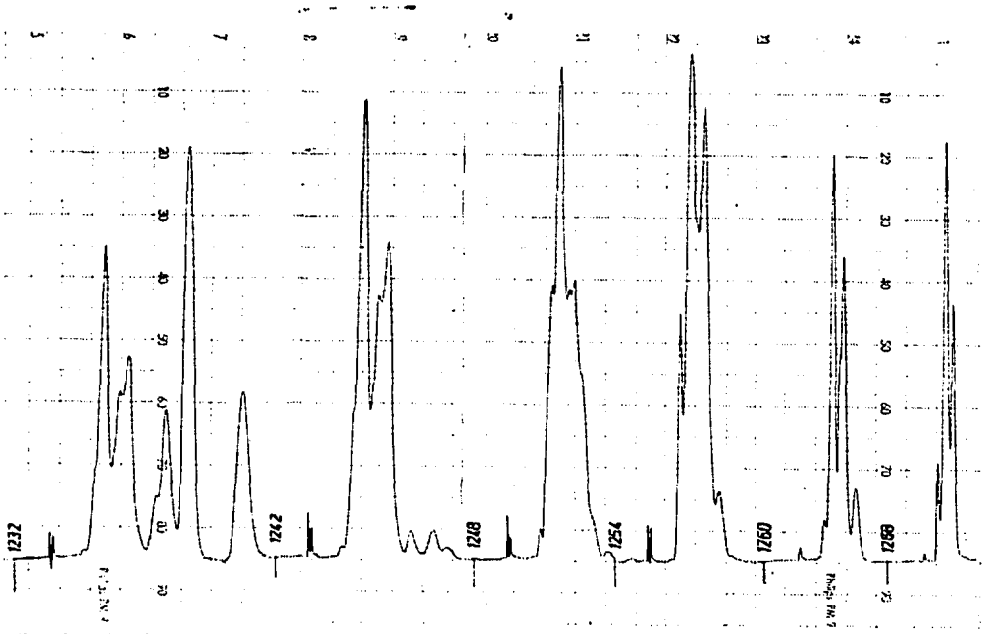

Fig. 2. Liquid chromatograms of individual PCB samples of chlorine content 32–68%. Aroclor 1232, 1242, 1248, 1254, 1260 and 1268. Amounts injected ranged from 15 μg for Aroclor 1232 to 3 μg for Aroclor 1268. The wavelength used (235 nm, chosen for DDT) is not optimum for the PCBs. Better sensitivity may be obtained at 210–215 nm.

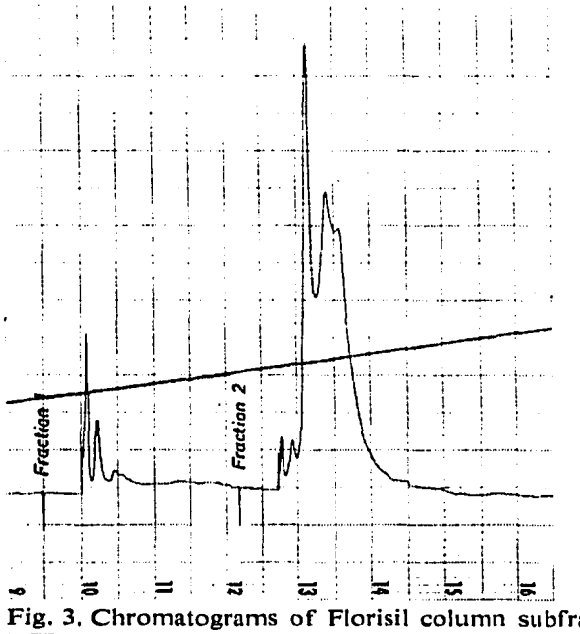

Fig. 3. Chromatograms of Florisil column subfractions of cardboard extract. Fraction 2 contains PCBs.

the extract after saponification. The Florisil column removed the bulk of the wax alcohols.

As the sensitivities of available LC detectors are lower by about three orders of magnitude than those of GLC detectors[4,10], LC will not be able to replace GLC as the final determination step in trace residue analysis. It may, however, be of advantage in special cases when larger amounts of PCBs or DDT are present or as a clean-up stage in which those PCBs which interfere in the GLC determination of DDT can conveniently be removed. Whenever the saponified extracts do not contain large amounts of hexane-soluble lipid material, the more selective LC procedure may replace the Florisil column clean-up stage.

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