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THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) RESIDUES IN ENVIRONMENTAL SAMPLES USING GLASS CAPILLARY GAS CHROMATOGRAPHY $(GC)^2$

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ABSTRACT

The major problems of determining polychlorinated biphenyl (PCB) residues in environmental samples are highlighted. A microcolumn adsorption chromatography method for the 'clean-up' and isolation of PCB residues from organo-chlorine pesticides using 3 g of 5% deactivated alumina and 2 g of 5% deactivated silica with n-hexane and 2% tetrahydrafuran as solvents is described.

The application of temperature programme high resolution glass capillary column using hydrogen carrier gas to the routine analysis of PCB residues is shown to greatly improve the resolution of PCBs compared to that of conventional packed columns without increasing the analysis time.

The quantitation of PCB residues by summation of designated peak heights is shown to be a method applicable to routine automated analysis.

INTRODUCTION

The determination of polychlorinated biphenyl (PCB) residues in environmental samples using electron capture gas-liquid chromatography presents the analyst with two major problems which need to be critically assessed if accurate measurement of the PCB residues is to be achieved. The first is the isolation of the PCB residues from unwanted co-extracted material (mainly lipid and organo-chlorine pesticides) which may interfere with the analysis. The second problem is one of quantification. Because the PCB residues undergo degradation in the environment the relative amounts of different chlorophenyl compounds are altered compared with

the original PCB, and PCB profile will vary from sample to sample. It is therefore not possible to calibrate the PCB extract against an identical standard. This paper describes the methods used by this Laboratory to overcome these two problems.

METHODS

Clean-up and Separation

The isolation of PCB residues from co-extracted materials is achieved by adsorption chromatography, using a method derived from that published by Holden and Marsden (1969) followed by glass capillary gas chromatography $(GC)^2$.

Apparatus and Reagents for Adsorption Chromatography

Borosilicate glass chromatography columns 150 x 6 mm ID with a solvent reservoir at the top and a 2 mm bore tip.

Cotton wool (Hexane washed) plug.

Silica-Merck No. 7764 (70-325 mesh ASTM) - supplied by BDH, Poole, Dorset.

Alumina-Merck No. 1077 (70-230 mesh ASTM) - supplied by BDH, Poole, Dorset.

N-hexane - glass distilled grade - supplied by Rathburn Chemicals, Walkerburn, Scotland.

Acetone - glass distilled grade - supplied by Rathburn Chemicals, Walkerburn, Scotland.

Tetrahydrofuran - Analar grade - supplied by BDH.

Preparation

The alumina is sieved prior to activation, the 64-125 µm portion being retained. The silica is activated by firing for two hours at 600°C and the alumina by firing for four hours at 800°C. Both are cooled in a vacuum dessicator to room temperature and partially deactivated with 5% distilled water (hexane washed). Once deactivated the alumina and silica are stored in stoppered glass jars in a dessicator cupboard and discarded or reactivated after seven days.

All glassware is soaked overnight in a bath of 5% nitric acid, then rinsed in distilled water, solvent washed with acetone followed by n-hexane, and then air dried.

The alumina columns are prepared by pouring 3 g of the 5% deactivated alumina into a cotton wool plugged column and gently tapping the sides. The silica columns are prepared in a similar fashion except that only 2 g of silica is used.

Procedure

A 10 ml aliquot of the organochlorine residue extract is evaporated

to 1 ml under a stream of air. The extract is then applied to the top of the alumina column and followed by the addition of 20 ml of n-hexane. The first 16 ml of the eluant from the column is collected in a graduated centrifuge tube and its volume reduced to 1 ml by evaporation. The 1 ml of sample extract is then applied to the silica column followed by the addition of 20 ml of 2% V/V tetrahydrofuran in n-hexane.

Three fractions are collected from the silica columns. The first fraction (4.5-5.5 ml) contains HCB, Aldrin, pp'DDE and the PCBs; the second fraction (8.5-9.5 ml) contains αHCH, γHCH, heptachlor epoxide, dieldrin, pp DDD and pp DDT; the third fraction is normally free of organochlorine residues. All fractions are then concentrated to 2 ml and analysed.

The precise volumes of the individual fractions collected from the silica column are first determined by subjecting a prepared standard containing Arochlor 1254, αHCH and ppDDT to silica column separation, followed by analysis of the eluant at various stages of elution as shown in Table 1.

Table 1

	I	II	III
Fraction 1	4.5 ml	5 ml	5.5 ml
Fraction 2	9.5 ml	9 ml	8.5 ml
Fraction 3	2 ml	2 ml	2 ml

Gas Liquid Chromatography

During the silica column separation the PCBs are separated from most of the organochlorine compounds except HCB, Aldrin and pp DDE. HCB elutes very early during gas chromatography and does not interfere with the PCBs. Aldrin is very rarely found in environmental samples since it rapidly undergoes epoxidisation to form dieldrin. DDE interferes with the analysis and measurement of PCBs using the conventional (2 m) packed columns (Thompson et al., 1971) because it cannot be resolved from one of the major components of Arochlor 1254, which is used as a standard by most laboratories carrying out routine PCB analyses. However, DDE can be separated from Arochlor 1254 by further column chromatography (Armar and Borte, 1972) or by oxidisation to the more polar dichlorobenzophenone (Trotter, 1975) prior to column chromatography. Unfortunately, these additional steps significantly increase the time taken to isolate the PCB fraction and may cause additional problems due to contamination of the sample or losses from incomplete recovery.

It has been found that separation of DDE from PCB residues can be achieved using high resolution glass capillary columns with temperature programming and hydrogen as the carrier gas. The run time is similar to that resulting from analysis on a conventional (2 m) packed column, but the PCB profile is much improved and hence measurement is more precise. Examples of chromatograms of a typical PCB compound (Arochlor 1254) analysed by both conventional packed columns and glass capillary columns are shown in Figures 1-3. For a more general appreciation of the relative merits of capillary and packed column techniques reference should be made to Grob and Grob (1979).

Conditions of Analysis for Packed Columns

A Hewlett Packard 5730A series gas chromatograph equipped with dual linearised ^{63}Ni electron capture detectors is used. The columns are 2 m long and 7 mm outside diameter of borosilicate glass. Column A is packed with 1.5% SP-2250/1.95% SP-2401 and column B with 4% SE-30/6% SP-2401. The liquid phases are supported on 100-120 mesh Supelcoport. The carrier gas is argon 95%/methane 5% at a flow rate of 35-50 ml/min. Detector, oven and injection port temperatures are 300, 200-215 and 250°C respectively. The oven temperature and carrier gas flows are optimised to give an analysis time of 18-20 minutes.

Conditions of Analysis for Capillary Columns

The instrument used is a Carlo Erba Fractovap series 2150 fitted with a micro volume ^{63}Ni electron capture detector operated in the constant current mode with a 0.5 μs pulse width at a temperature of 275°C. The column is 20 m long, has an internal diameter of 0.3 mm and is coated with SE-54. The carrier gas is hydrogen at an inlet pressure of 0.3 kg/cm^3. Argon 95%/methane 5% at an inlet pressure of 1.25 mg/cm^3 is required as a make-up gas for the detector.

The injection port temperature is held at 250°C and used in the splitless mode. The oven is temperature programmed as follows: ambient temperature for 30 s, ballistic heating to 185°C, then to 235°C at 6°C/min. These conditions result in an analysis time of 18-20 min.

Quantification

PCBs are complex mixtures of up to 209 possible individual components (Pomerantz et al., 1978) and there are a large number of techniques available for their estimation. Chau and Sampson (1975) surveyed the most popular methods available for packed column analysis and sought to provide a uniform approach to quantification. However, the performance characteristics of capillary columns (fast eluting peaks with small areas) make the resultant chromatograms unsuitable for conventional methods of integration

such as peak area measurement or triangulation and can, if the response of the output device (chart recorder, printer-plotter) is slow, result in peaks being missed entirely.

The use of a desk top computer to handle the output from the $(GC)^2$ column has helped considerably to overcome these difficulties. After investigating a number of possible methods of estimation such as designated peak area summation, individual peak area measurement and slice width measurements, the method eventually adopted was based on the summation of the heights of designated peaks. Although these methods are not novel and can be carried out using suitable integrators or even manually, the combination of $(GC)^2$ and the use of a desk top computer has allowed the analysis of PCB residues to be automated to a much greater extent than was possible using conventional packed column chromatography.

DISCUSSION

The use of $(GC)^2$ for the determination of PCB residues has implications for the analysis of organochlorine residues as a whole. The present methods of preparation and analysis using conventional packed columns are relatively labour intensive and time consuming, requiring several GLC runs before the various residues can be determined. Using a suitable $(GC)^2$ technique it is possible to reduce considerably the number of GLC runs because of the greatly improved resolution of capillary columns. If the $(GC)^2$ instrumentation can be coupled to an automatic injection system and a data system it is possible to process samples outside normal working hours under the control of the data system. Besides the savings in labour costs and improvements in precision, this arrangement also optimises the use of the instrument by releasing it during working hours for non-routine applications or maintenance.

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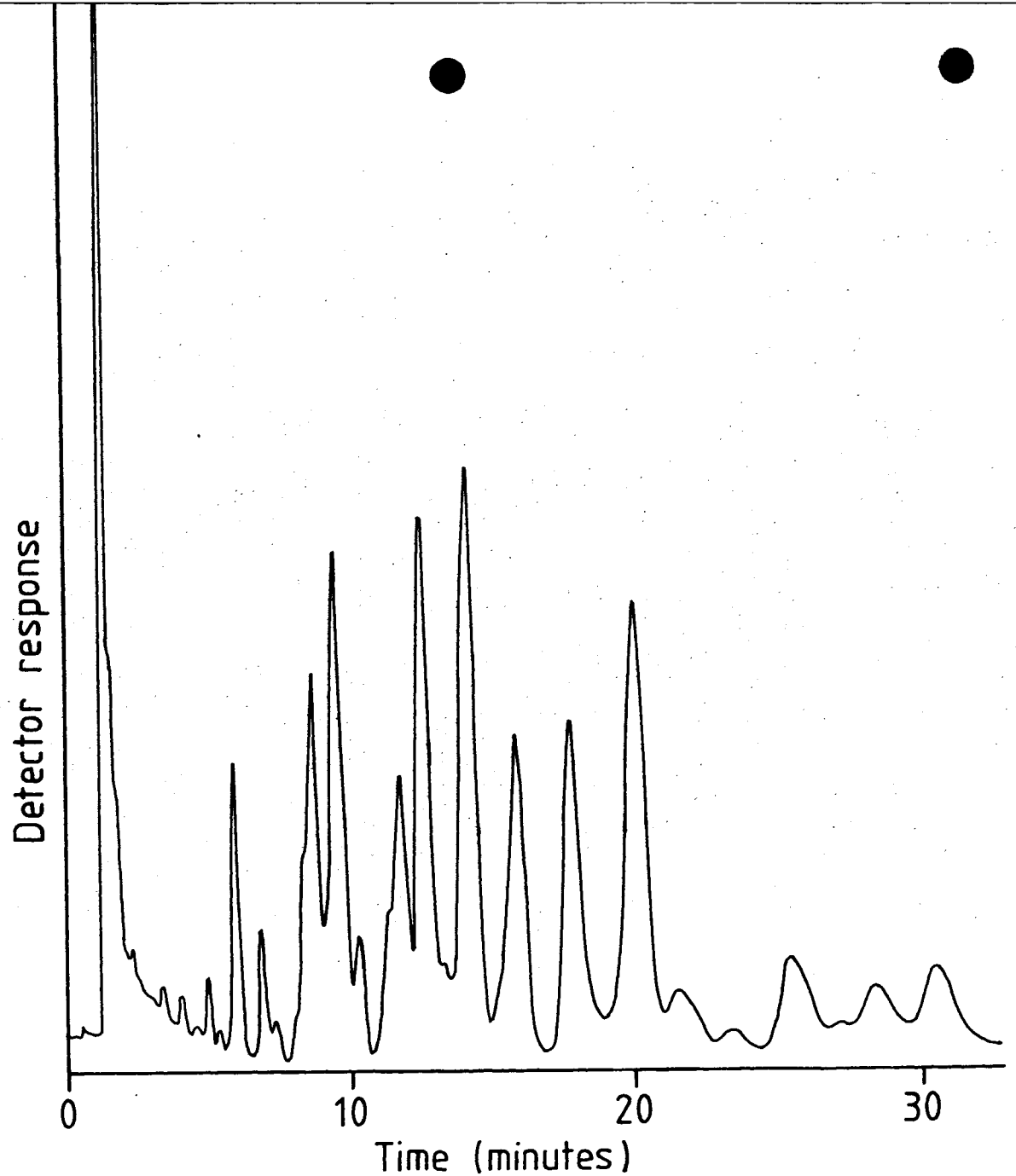

Figure 1 Column A, 2 ng/10 µl Aroclor 1254 (for conditions see text).

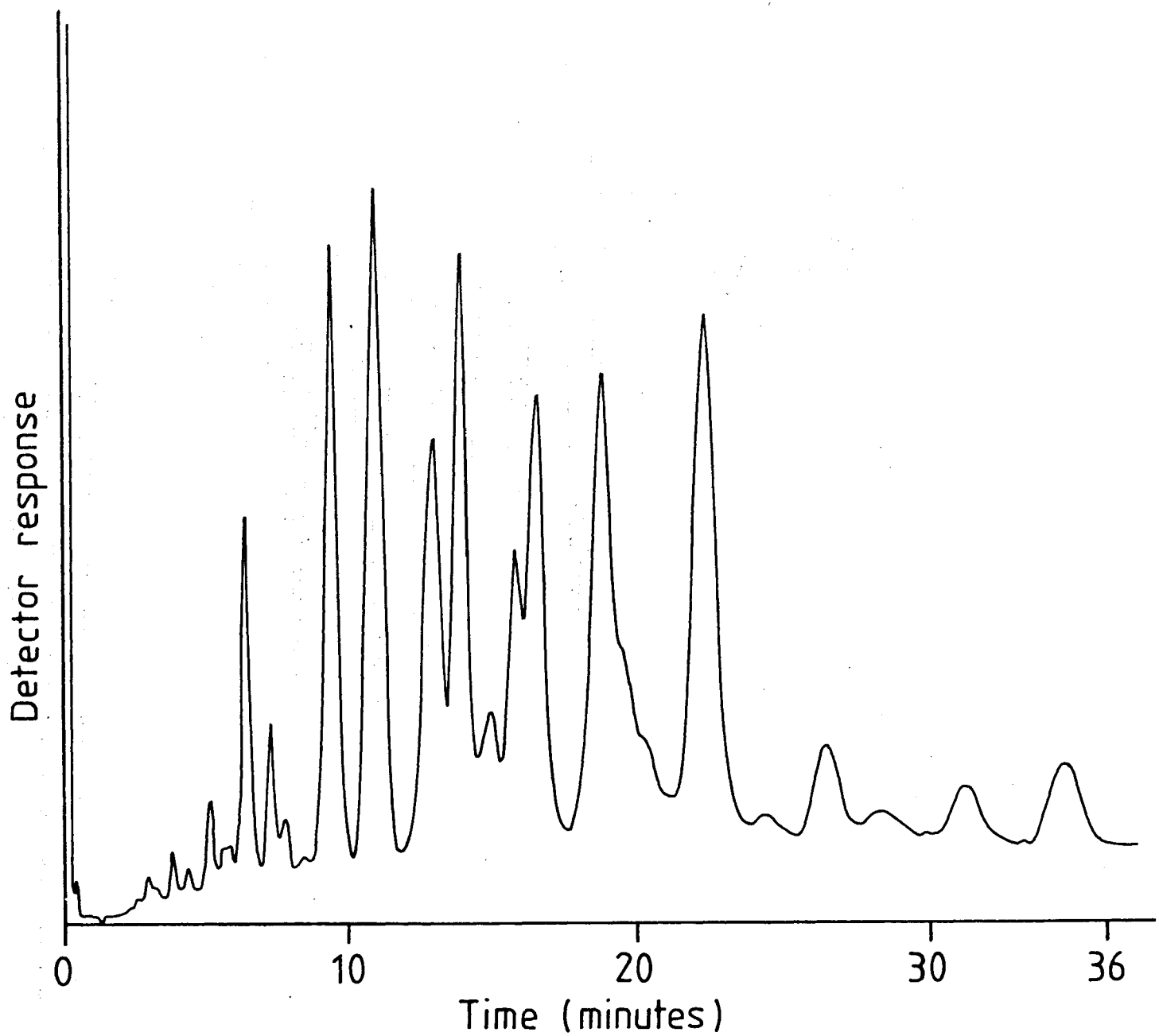

Figure 2 Column B, 2 ng/10 µl Aroclor 1254 (for conditions see text).

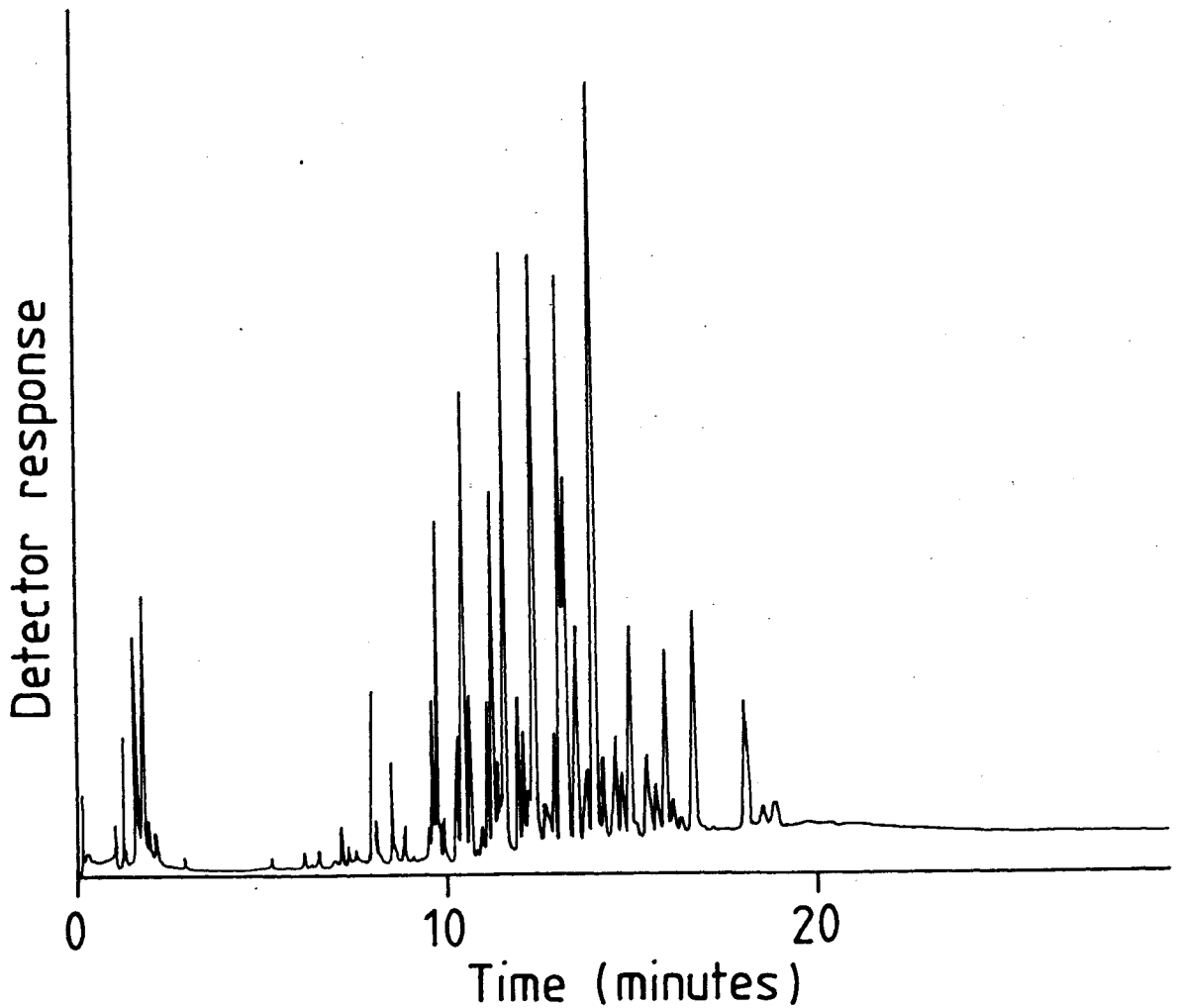

Figure 3 Capillary column, 2 ng/ 1 µl Aroclor 1254 (for conditions see text).