Estimation of Traces of Polychlorobiphenyl Compounds (PCB)

1. SCOPE

The method is applicable to water. A modification applicable to fish is described and a reference given to a modification applicable to sediments.

2. PRINCIPLE OF METHOD

PCB's are extracted with hexane, the extract clean-up from interfering co-extractives by column chromatography or solvent partition and the PCB's estimated gas chromatographically by reference to standard materials (8.1).

3. REAGENTS

Hexane; sodium sulfate, anhydrous; silica gel.
Also, for fish; acetone; dimethylformamide; alumina.

4. APPARATUS

Gas chromatograph; Kuderna-Danish evaporators; chromatographic columns; Soxhlet extraction apparatus (for fish).

5. PROCEDURE

5.1 *Water*

Shake ca. 2l water with 100ml of hexane for 15mins. Allow the mixture to stand until the two phases have completely separated. Run off the lower water layer and pass the hexane through a short column of granular, anhydrous sodium sulfate into a Kuderna-Danish evaporator. Wash the sodium sulfate column with hexane and concentrate the combined washings and sample extract to 1.0ml. Inject 5µl of this final solution into two different GLC columns. Compare the retention times of the chromatographic peaks with those obtained from a standard PCB preparation. If there are a number of peaks with retention times equivalent to that of pp'-DDT and longer and which agree with those of PCB, then the presence of PCB can be suspected and a separation of the PCB from other pesticide residues must be carried out by column chromatography on silica gel as described in para. 7.2.

5.2 *Fish*

Finely comminute 10g of sample and dry it with granular anhydrous, sodium sulfate. Place the prepared material in a preextracted Soxhlet thimble and then extract for 3hr with a 2 + 1 mixture of hexane and acetone in the Soxhlet apparatus. Pass the extract through a short column of granular, anhydrous sodium sulfate into a Kuderna-Danish evaporator. Wash the sodium sulfate well with more hexane and then concentrate the combined extract and washings to ca. 5ml. Transfer the concentration solution to a 100ml volumetric flask and make up to the mark with hexane. Clean up 25ml of this solution by dimethyl formamide partition and alumina column chromatography in the manner detailed by de Faubert Maunder et al (8.2). Examine the cleaned-up extract on two different GLC columns. If there is a series of peaks, with retention times corresponding to ca. pp′-DDT and longer, then the presence of PCB is indicated. Use the method given in para. 7.2 to separate the PCB from the other pesticide residues.

5.3 *Sediment*

Holden (8.3) uses a mixture of hexane and propan-2-ol for extraction.

6. CALCULATION OF RESULTS

6.1 Only an approximate result can be calculated since commercial PCB preparations differ and the composition of individual preparations "age" in different ways on exposure.

When the pp′-DDE and the PCB's have been separated from the other chlorinated residues by silica gel column, examine the concentrated extract by GLC, preferably on an Apiezon column. Insofar as their retention times are identical with those of a standard preparation, all the peaks following that of pp′-DDE are assumed to be PCB compounds. If pp′-DDE appears to be present and it is thought that there may be a peak due to a PCB compound at exactly the same retention time which will significantly affect the calculated amount of pp′-DDE, then oxidise the pp′-DDE to pp′-DCBP. On chromatography, the pp′DDBP will give an earlier retention time peak and leave the PCB's unaffected. Calculate the amount of PCB's in the sample injection in the following manner:

(a) Determine the retention times (Rt) and peak heights (Ht) of all the compounds which appear to be PCB compounds.

(b) Multiply the individual retention times (Rt) by the peak heights (Ht) and sum all the products so obtained:

$$\Sigma Rt_n . Ht_n = Rt_1 \cdot Ht_1 + Rt_2 \cdot Ht_2 + Rt_3 \cdot Ht_3 + \ldots \text{etc.}$$

(c) Divide this sum by the product of the peak height x retention time for 1 ng pp′-DDE. This will give an estimate of the total amount of PCB (in ng) in the sample injection.

If a silicone column has to be used for the estimation, divide the sum of the Rt's x Ht's by the product of Rt x Ht for 1 ng dieldrin.

6.2 Because it is usual for the chromatographic patterns of the PCB compounds eluted from samples to be different from those of the manufacturers' preparations, it is impossible to use individual peaks in the standard material and determine the amount of PCB by simple proportion.

6.3 A determination of the area per nanogram for the whole range of PCB preparations gives a figure which is very close to that determined for 1 nanogram of pp'-DDE on an Apiezon column, i.e. the *mean* electron-capture response for PCB's is very similar to that for pp'-DDE. If only single PCB compounds are being determined, there will in some cases be a large error. On silicone columns, the mean electron-capture response is nearer to that of dieldrin. This is because the PCB compounds produce different peak patterns on this liquid phase. The view that the mean electron-capturing power of PCB's is similar to that of pp'-DDE is confirmed by Zitko et al (8.4).

7. SPECIAL CASES

7.1 *Separation of PCB's from DDT and other pesticides*

7.1.1 Preparation of the column

Use either silica gel, BDH (material for chromatographic adsorption) or silica gel, Hopkin & Williams, MFC. Dry the silica gel at 110°C for at least 2hr, place the material in a desiccator and when cooled, quickly weigh out the required amount of adsorbent into a tared, stoppered bottle or flask. Add 2.5% v/w of distilled water and shake the material for 1½hr or shake for ½hr and leave the material in the stoppered bottle until next day. Weigh out 5.0g of the prepared gel and cover it immediately with hexane. Shake the mixture to release any air bubbles and wash the preparation into a narrow, glass chromatographic column (7mm I.D.), using hexane. Run the surplus hexane through the column until its meniscus is just touching the surface of the silica gel.

7.1.2 Separation of pesticide residue

Add the sample extract to the column in about 2.0ml of solvent. Allow the solution to run into the column until the meniscus is just touching the top of the gel. Wash the sample container with 1.0ml of hexane and transfer this washing to the column. Elute the column with 45ml of hexane at the rate of 1 drop per second, stopping the elution when the meniscus just reaches the gel. Concentrate the eluate and examine it by GLC. It should contain all

PCB-type compounds, pp′-DDE and HCB. After changing the receiver under the gel column, further elute the silica gel with 50ml of hexane containing 10% v/v of diethyl ether. Concentrate this second eluate and examine it by GLC. It should contain pp′-DDT and all the more polar residues as far as dieldrin.

8. REFERENCES

8.1 Report of the Government Chemist 1969, p. 81. H.M. Stationery Office, London 1970.

8.2 de Faubert Maunder, M. J., Egan, H., Godly, E. W., Hammond, E. W., Roburn, J. and Thomson, J. *Analyst*, **89**, 168, 1964.

8.3 Holden, A. V. *Nature*, **228**, 1,220, 1970.

8.4 Zitko, V., Hutzinger, O. and Safe, S. *Bull. Envir. Contam. Toxicol.*, **6**, 160, 1971.