Polychlorinated Terphenyls in Paperboard Samples

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Introduction

This paper describes the detection, estimation and confirmation of identity of polychloroterphenyls (PCTs) as well as polychlorobiphenyls (PCBs) in paperboard and food packaging material.

PCTs which are used in similar industrial applications to PCBs, have not received the same widespread attention as the latter. However, their presence has recently been reported in environmental samples (1,2). Aroclor® is one trade name applied to these polychlorinated polyphenyls. [Aroclor series 25 and 24 contain mixtures of PCB and PCT, while the 54 series contains only PCT. The last two digits indicate the chlorine content of the material, e.g. 5460 is a PCT with 60% chlorine. Undistilled PCTs are also available as Aroclor 50 series. The Aroclor 60 series are blends of Aroclor 5460 and PCB Aroclor 1221. The last two digits indicate the percentage of Aroclor 5460 in the blend, e.g. Aroclor 6062 is a blend containing 62% Aroclor 5460 and 38% Aroclor 1221 (3).]

As an analytical service for Industry and Government, our laboratory has carried out a large number of PCB analyses on pulp, paper, paperboard, and food packaging materials. At an early stage in this PCB service work, gas chromatography (GC) column difficulties were encountered with some extracts due to the presence of components having high electron capture affinities, very lengthy retention times, and poor resolution under normal PCB operating conditions. PCTs were suspected, and further examination confirmed their presence. We developed two GC systems for the estimation of PCTs, both being satisfactory.

Experimental

The procedure used is an extension of Reynolds' method (4,5). The sample is blended, and a representative aliquot (10 g: when available) is Soxhlet extracted with hexane (150 ml) for 2 hours in thimbles that are precleaned by exhaustive Soxhlet extraction. The extract is then concentrated, cleaned-up on Florisil (elution with 250 ml of hexane), and subjected to a "PCB split" on Florisil

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(elution with 80 ml of hexane). Florisil used was 60/100 mesh, pesticide grade, supplied by the Floridin Co., and stored at 130°C until ready for use.

For waxy samples, the hexane extract from the Soxhlet extraction is concentrated, and the residue dissolved in 5% benzene in acetone (100 ml) with slight warming. The solution is chilled in a dry ice/methanol bath for 3 minutes and the flocculent precipitate obtained filtered off through Na_2SO_4 (with a glass wool plug), rinsing with benzene/acetone solution (50 ml). The filtrate is then concentrated and put through the Florisil cleanup and "PCB split" as described above.

The cleaned up sample extract (hexane eluate) is injected for screening and quantitation of PCT using one of the following GC parameters. (1) 6' X 1/8" coiled glass column containing a mixture of 3% SE 30 (Ultra phase) and 3% OV 210 on Chromosorb W (AW; DMCS; 60/80 mesh) and operated at 250°C with an injection temperature of 275°C and a detector temperature (tritium foil) 220°C. (2) 6' X 1/8" coiled glass column packed with 3% Dexsil 300 on Chromosorb W (AW; 60/80 mesh) and operated at 300°C with an injection temperature of 310°C and a detector temperature (Ni^{63}) of 320°C. Nitrogen was used as the carrier gas in both columns at a flow rate between 30-40 ml/min.

Results and Discussion

Figures 1 and 2 show the GC-EC chromatograms obtained with Standard Aroclor 5460 when chromatographed on the respective GC columns mentioned above. It can be seen that there is a characteristic pattern for the PCT profiles. The retention time of decachlorobiphenyl under the GC parameters used is shown by arrow in Figure 1. Figure 1 also shows a GC-EC profile of a cleaned up extract of a paperboard sample. The similarity between the sample extract profile and that of standard Aroclor 5460 is readily apparent.

The choice of clean up procedure depends on whether organochlorine pesticide residues are present and are to be determined in addition to PCB and PCT levels; if so, elution from the Florisil cleanup column is made with 20% ether in hexane. In the case of paperboard samples calling for determination of PCB/PCT only, the use of hexane as eluant is preferred since cleaner extracts are obtained with good recoveries. Also, relatively large volumes of hexane can be used to ensure elution of all PCTs from the respective Florisil columns. Using the volumes specified above, essentially total recoveries of fortified PCTs were obtained.

Our current procedure is to screen all paperboard and food packaging sample extracts for PCTs prior to PCB analysis. If PCTs are present, quantitation is achieved with either the use of a disc integrator and estimation of the whole area under the GC profile; or the comparision of two or more major peak heights. The figure obtained is compared to that obtained from the injection of a known

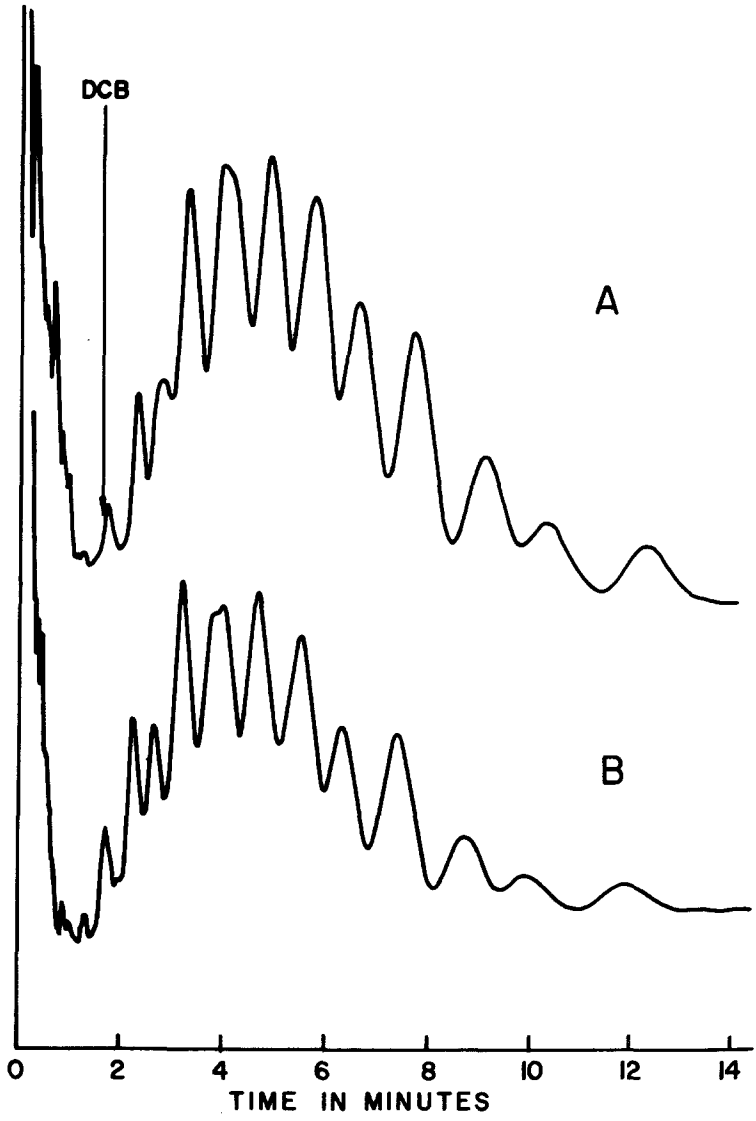

Figure 1. GC-EC chromatograms obtained using mixed 3% SE30/3% OV 210 column.
A, Aroclor 5460 (5 ng); B, typical cleaned up extract of paperboard sample.

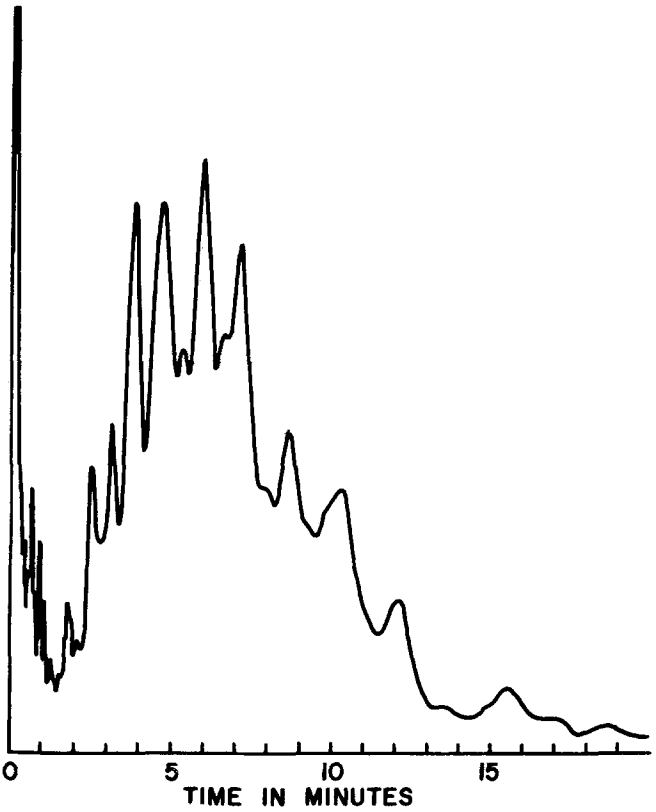

Figure 2. GC-EC chromatogram of Aroclor 5460 (3 ng) obtained using 3% Dexsil 300 column.

amount of standard Aroclor 5460. The chromatogram from the PCT screening also provides a rough estimate of the PCB present, and the extent of possible GC problems with the PCB analysis and quantitation. If no PCTs are detected the extracts are analysed for PCBs using our general purpose column (4). If both PCTs and PCBs are present, we have found that either of the columns detailed above can be used to quantitate the PCBs after appropriate GC parameter changes. Very low concentrations of PCTs will not interfere with normal PCB analysis.

It is of interest to note that we have been able to use the tritium detector quite satisfactorily for the estimation of PCTs even though the column temperature during operation is at 250°C. The need for frequent cleaning of the detector has not arisen even after prolonged use for the estimation of PCTs.

We use GC-Mass Spectrometry (MS) as a means of confirming PCB residues in environmental samples. We have not attempted to put PCTs through our GC-MS system. We have, however, separated PCTs from other contaminants by Silicic acid/Celite chromatography (6) and used the solid probe for the direct insertion of the isolated PCT into the MS source. The spectra were identical to the spectrum of Standard Aroclor 5460, also obtained by means of solid probe insertion into the MS source. Both PCBs and PCTs give intense molecular ions and a characteristic isotope pattern depending on the number of chlorines substituted on the aromatic rings. The spectra of these compounds are readily identified (7).

In addition to the use of two GC columns and MS, the PCT residues were also confirmed by perchlorination with $SbCl_5$ in sealed glass tubes (8). We found that two major tetradecachloroterphenyl isomers are produced with retention times of 10.94 and 12.31 relative to decachlorobiphenyl, respectively, when chromatographed on the mixed phase column. Identical peaks were obtained from similarly treated Aroclor 5460.

We have analysed approximately 100 paperboard samples in which the levels of PCTs ranged from 0-163 ppm and the levels of PCBs ranged from 0-20 ppm. Our analytical procedures and preliminary results of work on food packaging material were reported at the 164th ACS National meeting in New York City, (9,10).

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