SEPARATION OF PCB CONGENERS USING ACTIVE COAL COLUMNS

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Numerous analytical techniques today are being investigated for the isolation, identification and quantification of the various PCB congeners. It has long been recognized that specific congener analysis provides more meaningful information with regard to exposure assessment[1] . The analyses however, have always been complicated owing to a number of factors.

1. The complex nature of the biological matrices in which the PCBs exist.
2. The large number of isomers for each degree of chlorination of a biphenyl molecule.
3. Individual PCB congeners have different toxicological, ecological and kinetic properties.
4. The non-ortho (planar) congeners, identified as the most toxic, occur at concentrations several orders less than the more abundant congeners.
5. Poorly resolved clusters of congeners on a given chromatographic column give rise to ambiguous quantification[2] .

The affinity of active coal for the planar PCB congeners has been utilized for their structural separation from other PCBs, thereby eliminating the potential interferents and improving the quality of analytical data. This technique, together with the use of dual column system[3] , is being developed at the National Food Administration for monitoring PCB congener levels in fish and other biological materials of interest. Analyses are performed using two electron capture detectors fitted with two columns of different characteristics.

With two micro active coal columns, non-ortho-, mono-ortho- and di-ortho-PCBs in a sample extract, can be separated into three fractions prior to final determination by HRGC and/or GC/MS. Quantification and congener identification is carried out by comparison with an external standard. Confirmation of the presence of PCB congeners is provided partially by the second of the dual GC columns, and partially by GC/MS (non-ortho congeners).

Method: The sample is homogenized and extracted , and the fat content determined. For the purpose of recovery tests the sample is fortified with:

1. IUPAC No 53 for the 2-4-ortho PCB congeners.
2. IUPAC.No 189 for the mono-ortho congeners.
3. Three $^{13}C_{12}$-PCB congeners for the three coplanar PCBs of interest, that is, IUPAC No 77, 126 and 169.

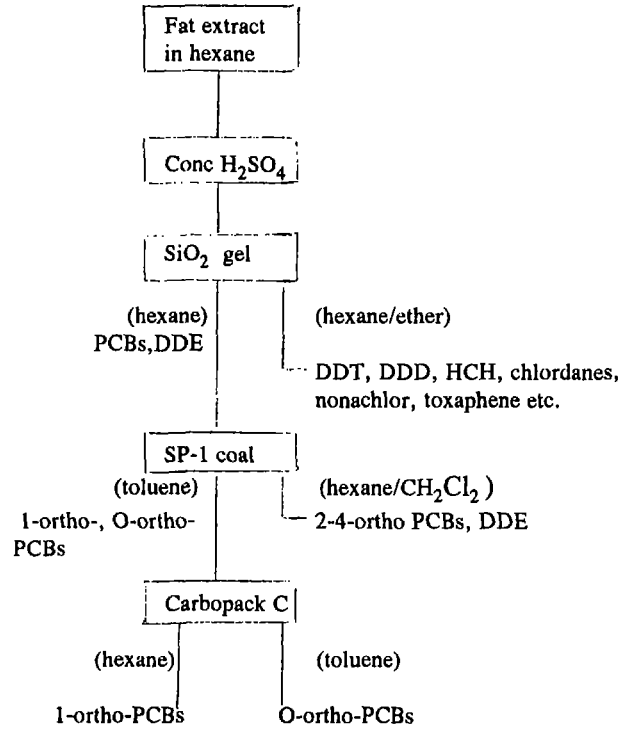
The fat extract dissolved in hexane is cleaned using concentrated sulphuric acid, followed by elution through a silica gel chromatographic column (4.5g of 3% water deactivated silica gel).Subsequent cleanup steps include

(i) Separation of the mono-ortho- and the coplanar PCBs from 2-4-ortho PCBs on an SP-1 coal/chromosorb chromatographic column.

(ii) Separation of the mono-ortho- from the coplanar PCBs on a carbopack/ celite column. The coplanar PCB fraction is concentrated to 200 ul for analysis.

Fig. 1 shows a flow diagram of the cleanup and separation process. The analyses of the specific PCB congeners, performed on a Hewlett-Packard Model 5890 Gas Chromatograph, using dual capillary column system, is achieved by comparing responses and retention times to calibration standards for each analyte of interest.

Fig 1 A Schematic Diagram of the Cleanup/Separation Method



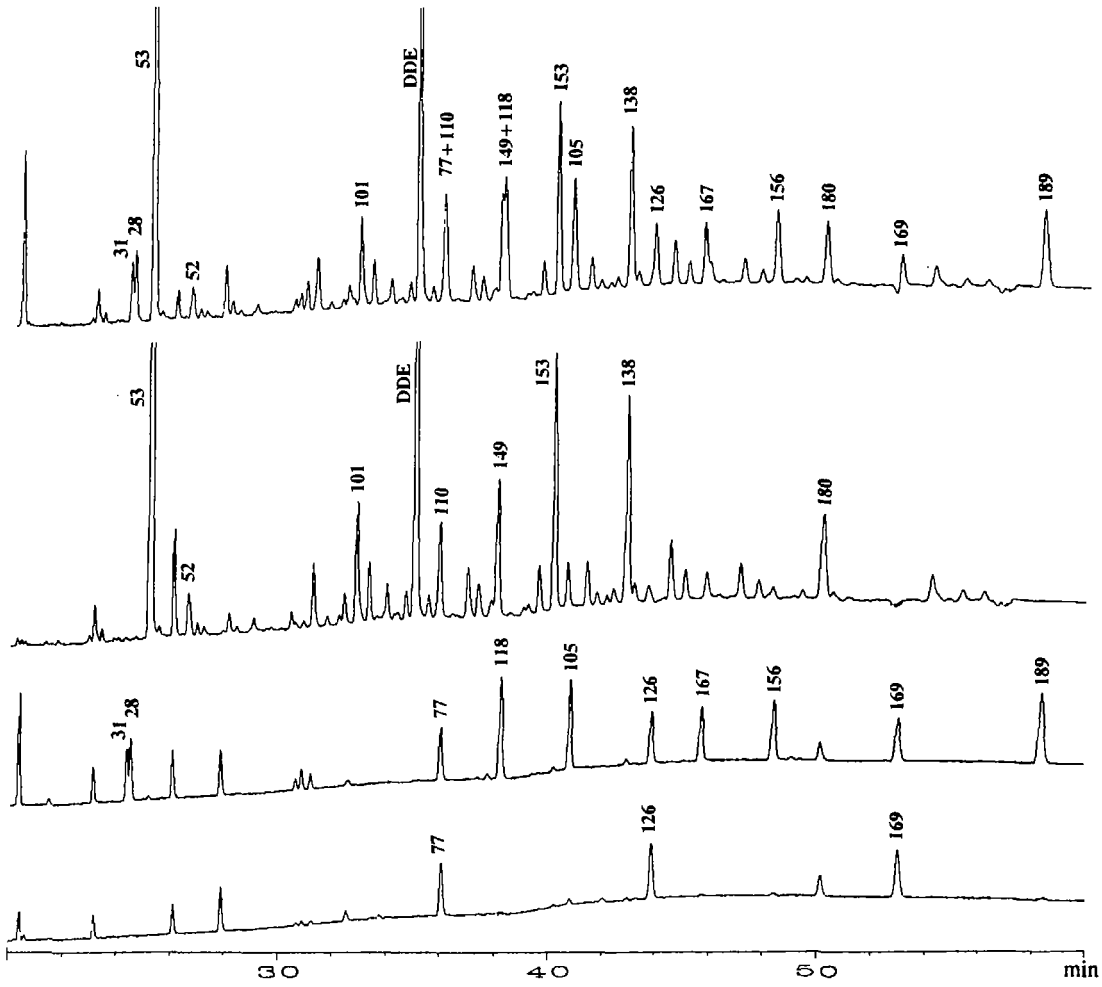


Fig. 2 Chromatograms of different fractions of a spiked herring sample . Column: Ultra-2 (Hewlett-Packard), 50m(l) and 0.20mm (i.d.)

A. Silica gel column, fraction 1 (hexane)
B. SP-1 column, fraction 1 (hexane/CH_2Cl_2 4:1)
C. SP-1 column, fraction.2 (toluene)
D. Carbopack column fraction 2 (toluene)

Further confirmation of the coplanar PCBs is by GC/MSD. Two ions characteristic of the selected non-ortho PCB and the respective labelled standards are monitored for an analysis. Confirmation of the PCBs is based on both retention times and the comparison of the ratios of the characteristic ions with theoretical values.

Application of the methodology to standard and spiked solutions yielded recoveries of the various congeners of interest between 90 and 100%. Fig. 2 shows the chromatograms obtained after the separation process of a spiked sample.

Specific congener analysis has been performed on a number of herring samples from previous assessment studies. Among the congeners determined are IUPAC No. 77, 126, 169 (non-ortho-), No 28, 118, 105, 156 (mono-ortho-) and 52, 101, 153, 138 and 180 (2-4-ortho). The results of this study will be fully reported separately.

REFERENCES

1. De Voogt P, Wells D.E, Reutergårdh L, Brinkman U.A.Th. Biological Activity, Determination and Occurrence of Planar, Mono- and Di-ortho PCBs. Intern J Environ Anal Chem 1990; 40:1-46
2. Durell G.S, Sauer T.C. Simultaneous Dual-Column, Dual Detector Gas Chromatographic Determination of Chlorinated Pesticides and Polychlorinated Biphenyls in Environmental Samples. Anal Chem 1990; 62: 1867-1871.
3. Duinker J.C, Schulz D.E, Petrick G. Multidimensional Gas Chromatography with Electron Capture Detection for the Determination of Toxic Congeners in Polychlorinated Biphenyl Mixtures. Anal Chem 1988; 60: 478-482.