Rapid Separation of Polychlorinated Biphenyls from DDT and Its Analogues on Silica Gel

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Polychlorinated biphenyls (PCB's), which are used in industry worldwide (1), have been found as residues in numerous wildlife species (2-7). Because of the similarity in chemical characteristics, PCB compounds interfere with gas liquid chromatographic (GLC) analysis of certain chlorinated hydrocarbon insecticides (8). In the present study, we sought a rapid microanalytical procedure for separation of PCB's from DDT and its analogues before analysis with GLC. A small silica gel column was found to be suitable for removing two of the Aroclor series of PCB's (1254 and 1260) from DDT and its analogues.

Materials

Silica gel used for the columns was grade 950 activated desiccant, 60-200 mesh, from the Davison Chemical Division of W. R. Grace, Baltimore, Maryland. Pentane and benzene, distilled in glass grade, were from Burdick and Jackson Laboratory, Inc., Muskegon, Michigan. Commercial PCB preparations containing 54 and 60 percent chlorine (Aroclor 1254 and 1260) were from the Monsanto Organic Chemicals Division of the Monsanto Co., St. Louis, Missouri. Standards for DDT and its analogues (DDT, DDD, DDE) were from the U.S. Public Health Service Pesticides Repository, Pesticide Research Laboratory, Perrine, Florida.

The Method

Transfer silica gel from a freshly opened can to a glass stoppered bottle and add enough pentane to cover the silica gel with at least 12 mm of pentane. If the silica gel has been previously exposed to air, reactivate it by placing it in an oven at 200° C for 8 hours before mixing it with the pentane.

Quickly add the mixture of silica gel and pentane to a glass-wool stoppered column (1.0 cm ID x 20 cm long). A useful tool for packing the column is a disposable pipette from which the narrow portion of the tip has been removed. Small amounts of silica gel

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are drawn into the pipette with a rubber bulb, and expelled into the column. Gentle tapping of the column facilitates packing. Always keep enough pentane in the column to ensure that the silica gel being added will filter through the pentane, thus eliminating air bubbles. The column must be free of air bubbles or breaks in the packing to ensure proper separation of the DDT complex from the PCB's. A length of 7.7 cm (about 3 g dry weight) of silica gel is required for each column.

Wash the column with 5 ml of pentane. Place 1 ml of sample in pentane or hexane on the column. Rinse the tube which contained the sample twice with 1-ml portions of pentane and place the rinse on the column. After the sample and rinse have been absorbed, collect the following solvent fractions separately in two 50-ml tubes:

Fraction	Solvent	Ml collected	Chemical eluted
A	Pentane	1 - 38	PCB's
B	Benzene	39 - 75	DDT and its analogues

Concentrate each fraction to the desired volume and analyze with GLC.

If the amounts of PCB or insecticide put on the column are large, poor separation results; therefore, only the amounts necessary for determination by GLC analysis should be passed through the column.

Operating conditions for GLC and the methods for extraction and cleanup of fish samples before the extracts are placed on the silica gel column were described by Reinert (9).

Concentrations of Aroclors are determined by planimetric readings of the GLC chromatograms. Areas for all the PCB components collected in the pentane fraction are compared with the areas for known amounts. This method yields a standard curve that is linear on semilog paper.

Efficiency of the Method

Efficiency of the silica gel column was measured by determining percentage recoveries when known amounts of Aroclors 1254 and 1260 and the DDT complex were washed through the column (Table 1). Fraction A recoveries for 1254 and 1260 averaged 97 and 102 percent, respectively. No peaks with retention times similar to those of DDT and its analogues were found in fraction B.

Measured amounts of Aroclors 1254 and 1260 were added to hexane extracts from fish. The fish--one coho salmon, Oncorhynchus kisutch, and two lake trout, Salvelinus namaycush, from Lake Michigan--contained substantial concentrations of DDT and its

TABLE 1

Percentage recoveries for known amounts of Aroclor 1254 and 1260 and the DDT complex after separation on silica gel columns

Fraction and chemical	Concentration ($1X10^{-8}$ g/ml)	Number of trials	Percentage recovery	
			Average	Range
Fraction A				
Aroclor 1254	50.0-100.0	15	97	86-118
Aroclor 1260	50.0	13	102	80-130
Fraction B				
pp DDE	4.0- 10.0	15	89	72-110
op DDT	0.5- 10.0	12	93	78-114
pp DDD	0.5- 10.0	12	96	83-114
pp DDT	4.0- 10.0	12	97	72-118

analogues. Three samples of each of the spiked extracts were analyzed with GLC after separation on silica gel. The silica gel column effectively separated Aroclor 1254 and 1260 from DDT and its analogues in extracts from fish (Table 2).

Chromatograms taken at various stages during the silica gel cleanup of the hexane extract of a lake trout spiked with Aroclor 1254 are shown in Figure 1.

The silica gel column described here rapidly and efficiently separates the two Aroclors tested from DDT and its analogues. Little prior preparation of the silica gel is needed. Because of the small size of the columns, numerous samples can be run simultaneously on individual columns in a small area. Separation is achieved in about 1 hour. Reproducibility of results and quantitative recoveries from samples were good.

TABLE 2

Percentage recoveries from silica gel columns for Aroclors 1254 and 1260 and the DDT complex in hexane extracts from coho salmon and lake trout

Species and chemical component	Concentration ($1X10^{-8}$ g/ml)	Percentage recovery					
		Fraction A			Fraction B*		
		Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
Coho salmon							
Aroclor 1254	50.0	108	108	108	-	-	-
pp DDE	8.0	-	-	-	100	72	94
op DDT	1.0	-	-	-	100	100	62
pp DDD	1.0	-	-	-	100	100	85
pp DDT	4.0	-	-	-	125	114	100
Lake trout							
Aroclor 1254	50.0	90	90	100	-	-	-
pp DDE	13.0	-	-	-	96	76	100
op DDT	1.0	-	-	-	80	100	80
pp DDD	2.0	-	-	-	87	87	67
pp DDT	6.0	-	-	-	91	91	82
Lake trout							
Aroclor 1260	50.0	130	120	110	-	-	-
pp DDE	10.0	-	-	-	80	90	110
op DDT	1.0	-	-	-	83	100	100
pp DDD	1.0	-	-	-	100	83	83
pp DDT	5.0	-	-	-	89	89	110

* Percentage recoveries for the DDT complex were calculated by comparing the amounts of insecticide found in the hexane extracts from fish with the amounts found after the separation procedure on silica gel columns.

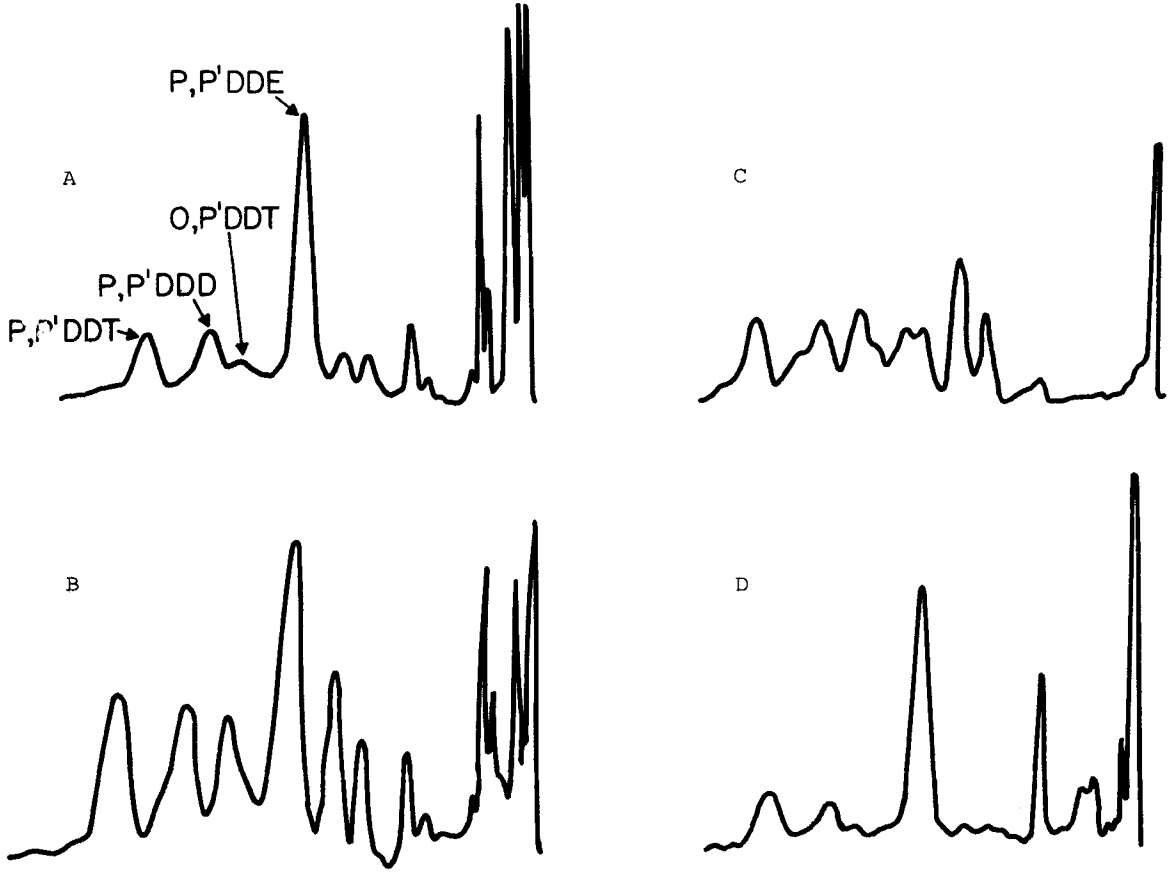

Figure 1. Chromatograms of the hexane extract of a lake trout before and after the addition of 0.5 µg of Aroclor 1254. (A) Hexane extract of a lake trout after the initial cleanup (9), showing DDT and its analogues. (B) Hexane extract after addition of 0.50 µg of Aroclor 1254. (C) Pentane fraction of the hexane extract after cleanup on silica gel, showing Aroclor 1254. (D) Benzene fraction of the hexane extract after cleanup on silica gel, showing DDT and its analogues.

References

(1) C. G. GUSTAFSON. Environ. Sci. and Tech. 10, 814 (1970)

(2) T. W. DUKE, J. F. LOWE, AND A. J. WILSON, JR. Bull. Environ. Contam. and Tox. 5, 171 (1970)

(3) A. V. HOLDEN, and K. MARSDEN. Nature. 219, 1274 (1967)

(4) D. C. HOMES, J. H. SIMMONS, and J. O'G. TATTON. Nature. 216, 227 (1967)

(5) S. JENSEN, A. G. JOHNELS, M. OLSON, and M. GOTTERLIND. Nature. 224, 247 (1969)

(6) J. H. KOEMAN, M. C. TEN NOEVER DE BRAUW, and R. H. DE VOS. Nature. 221, 1126 (1969)

(7) R. W. RISEBROUGH, P. RIECHE, D. B. PEAKALL, S. G. HERMAN, and M. N. KIRVEN. Nature. 220, 1098 (1968)

(8) L. REYNOLDS. Bull. Environ. Contam. and Tox. 4, 128 (1969)

(9) R. E. REINERT. Pest. Monitoring J. 3, 223 (1970)