Analysis of Polychlorinated Biphenyls by Gas Chromatography and Ultraviolet Irradiation

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An ultraviolet irradiation method developed to aid in the identification of chlorinated insecticides was applied to a commercial mixture of polychlorinated biphenyls (PCB's) (Aroclor 1254). Following gas chromatographic separation, each PCB peak was trapped, irradiated, and rechromatographed. In most cases, the degradation pattern of the PCB peak differed from the degradation pattern of the insecticide having the same retention time. A mixture of the chlorinated insecticides and PCB's was trapped, irradiated, and rechromatographed to note any interferences or changes which might occur when both are present together. Samples of herring and salmon oil, containing both PCB's and insecticides, were analyzed by this method.

Polychlorinated biphenyls (PCB's), first identified in wildlife samples by Jensen (1966), are widespread environmental contaminants (Holden and Marsden, 1967; Holmes *et al.*, 1967; Jensen *et al.*, 1969; Koeman *et al.*, 1969; Risebrough *et al.*, 1968). Due to their similarity to DDT, they are carried through the cleanup methods normally used for chlorinated insecticides (CI's) and give a similar response using gas chromatography–electron capture (gc–ec) analysis. As a result they have often been mistaken for CI's, especially DDT and DDE.

Jensen and Widmark (1967) used nitration as a means to differentiate PCB's and CI's. Reynolds (1969), trying to duplicate these results, found that there was a loss of some of the lower chlorinated PCB's and that some of the insecticides did not nitrate. Several investigators tried using column chromatography to separate the PCB's from the CI's. Florisil was ineffective (Armour and Burke, 1970; Reynolds, 1969), but a silicic acid–Celite column separated PCB's and CI's (Armour and Burke, 1970), provided deactivation of the silicic acid with water was precise (Stalling and Huckins, 1971).

In this study an ultraviolet method for the identification of certain CI's (Kaufman *et al.*, 1972) was applied to the identification of PCB's alone and in the presence of CI's. The method involved trapping the component as it eluted from the gas chromatograph, exposing it to laboratory ultraviolet (uv) light, and rechromatographing the resulting products.

EXPERIMENTAL SECTION

Gas Chromatographic Operating Conditions. All analyses were performed on an F&M (Model 810) gas chromatograph equipped with a pulsed tritium electron capture detector and a 122 cm × 4 mm i.d. glass column packed with a 1:1 mixture of 4% SE-30 and 4% QF-1 on 70/80 mesh Anakrom ABS. The injector and detector were held at 200° and the column was held at 180°. The carrier gas was 95% argon–5% methane with a flow rate of 60 ml/min. A detector purge flow of the same gas at a rate of 60 ml/min was employed. The effluent splitting and trapping assemblies were the same as those described by Kaufman *et al.* (1972). This system provides a means of trapping individual gas chromatographic peaks in a short length of Teflon tubing. Trapped components can be irradiated directly in the tubing after the addition of solvent.

Procedure. Characteristic "fingerprint" degradation patterns and the optimum irradiation time (OIT) were determined for each peak. For this work, the OIT was defined simply as the irradiation time which yielded the best characteristic degradation pattern. Ten microliters of a solution of Aroclor 1254 (Monsanto Chemical Co.) in hexane (6 ppm) were injected into a gas chromatograph and the individual peaks were trapped in Teflon tubes as they eluted from the column. After the addition of 50 μl of hexane, the trapped components were irradiated for varying periods of time with a 100-W, medium pressure uv lamp (Hanovia, Model 616A) followed by reinjection into the gas chromatograph.

For the irradiation of PCB's and insecticide simultaneously, insecticide standards were added to a hexane solution of Aroclor 1254 (15 ppm) in the range of 0.2–0.6 ppm. Five microliters of this solution were injected into a gas chromatograph and treated as above.

Sample Extraction and Cleanup. The PCB's and CI's were extracted from salmon and herring oil by petroleum ether–acetonitrile partitioning (Pesticide Analytical Manual, 1968). The extracted sample was further purified by using a Florisil column and eluting with petroleum ether. DDT and DDD were retained on the column, while DDE eluted with the PCB's.

RESULTS AND DISCUSSION

Separation of Aroclor 1254 on an SE-30/QF-1 column yielded 13 peaks, each of which represents more than one PCB compound or isomer (Sissons and Welti, 1971). On this column the retention times of peaks 2, 3, and 6 of the PCB mixture correspond to the retention times of aldrin, heptachlor epoxide, and dieldrin, respectively (Figure 1). Peaks 4 through 9 of the PCB mixture correspond to the *o,p* and *p,p'* isomers of DDT, DDE, and DDD.

Table I gives the OIT for each PCB peak which interferes with the analysis of the CI's mentioned above. The OIT and fingerprint degradation patterns for the CI's were

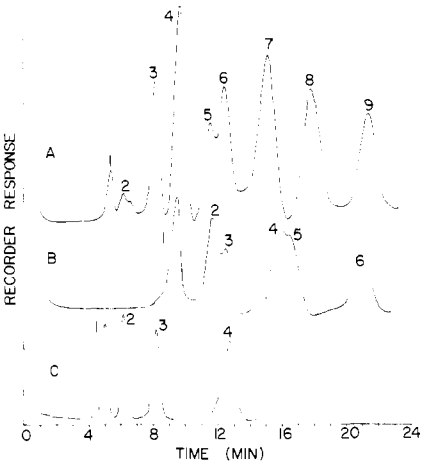

Figure 1. A. Aroclor 1254 (peaks 10, 11, 12, 13 not shown). B. (1) *o,p'*-DDE, (2) *p,p'*-DDE, (3) *o,p'*-DDD, (4) *o,p'*-DDT, (5) *p,p'*-DDD, (6) *p,p'*-DDT. C. (1) heptachlor, (2) aldrin, (3) heptachlor epoxide, (4) dieldrin. See text for instrumental conditions.

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Table I. Optimum Irradiation Time of Component Peaks of Aroclor 1254[a]

Peak no.	Retention time relative to aldrin	Optimum irradiation time, sec
1	0.89	120
2	1.02	60
3	1.33	120
4	1.56	120
5	1.87	30
6	1.98	45
7	2.39	45
8	2.80	90
9	3.34	30

[a]First 9 peaks of 13 total as separated on an SE-30/QF-1 column.

presented in the previous publication by Kaufman *et al.* (1972).

The rate of degradation was independent of the concentration of PCB in hexane at concentrations below 100 ppm. As shown in Table I, the OIT varied from 30 to 120 sec. The less chlorinated compounds generally required a longer time to degrade than the more highly chlorinated compounds.

Using the irradiation times listed in Table I, each PCB peak gave a characteristic fingerprint degradation pattern,

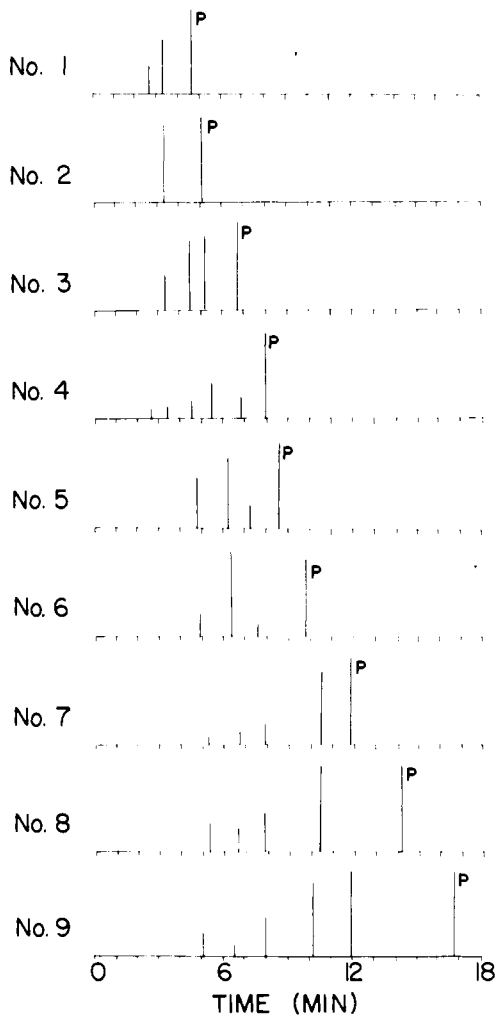

Figure 2. Degradation patterns of peaks 1–9 of Aroclor 1254 presented as peak area *vs.* retention time. Parent peak designated as P. See text for instrumental conditions.

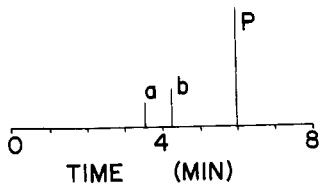

Figure 3. Aroclor 1254 peak 2 plus aldrin irradiated 75 sec. (a) PCB degradation peak; (b) aldrin degradation peak.

presented in Figure 2 as a bar graph of peak area *vs.* retention time. As the intensity of the uv source decreases with age, the extent of degradation will also decrease if the irradiation time is held constant. Thus, it is desirable to frequently, or even routinely, irradiate a standard concurrently with the sample.

When CI's and PCB's are present simultaneously in environmental samples, it may be difficult to recognize that both are present. In most cases, the analyst would wish to carry out a prefractionation of CI's and PCB's on a silicic acid–Celite column (Armour and Burke, 1970) before proceeding to the gc and photolysis of trapped components. However, even without prefractionation, uv treatment of a trapped peak can yield information about the components. The degradation pattern and/or the ratio of the degradation peak area to parent peak area (DPA/PPA) may be indicative of the presence of more than one compound.

Table II presents the data obtained when the individual trapped peaks of a mixture of PCB and insecticide were irradiated. The irradiation time was selected to yield the best differentiating pattern for the mixture. For instance, the characteristic *o,p'*-DDE peak disappears upon longer irradiation, so it is important to keep the irradiation time close to that of the OIT of *o,p'*-DDE.

Heptachlor and PCB peak 1 have been omitted from the table because they do not coincide exactly. When only one is present, the degradation pattern may be used to determine which one. There are no insecticide degradation peaks listed for heptachlor epoxide because the degradation products are not separated on this column (Kaufman *et al.*, 1972).

The cyclodiene insecticides aldrin and dieldrin were easily distinguished from the corresponding PCB peaks 2 and 6, respectively, since both insecticides gave a degradation product which was completely separated from the PCB degradation products. Figure 3 presents the degradation pattern for a mixture of PCB peak 2 and aldrin.

In the DDT family more emphasis is placed on the DPA/PPA ratio, since in most cases the corresponding insecticide and PCB have overlapping degradation peaks. These are noted in the third column of Table II. *o,p'*-, *p,p'*-DDD, and *o,p'*-DDT do not have any characteristic peaks which do not coincide with a PCB degradation peak, while *o,p'*-, *p,p'*-DDE, and *p,p'*-DDT have one characteristic degradation peak which is separated from

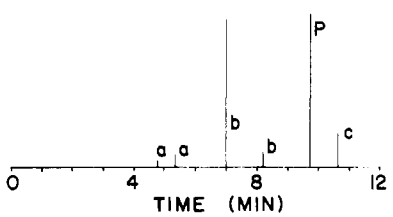

Figure 4. Aroclor 1254 peak 5 plus *p,p'*-DDE irradiated for 30 sec. (a) PCB degradation peaks; (b) PCB and *p,p'*-DDE degradation peaks; (c) *p,p'*-DDE degradation peak.

Table II. Degradation Patterns of PCB and Insecticide Irradiated Together

	Retention time, min				
	PCB degradation peak	Insecticide degradation peak	Overlapping PCB and insecticide degradation peaks	Remaining PCB and insecticide	DPA/PPA[a]
PCB peak 2 +	3.54				0.19
aldrin irra-		4.09			0.30
diated 75 sec				5.20	
PCB peak 3 +	3.54				0.12
heptachlor ep-	4.65				0.13
oxide irradiated	5.43				0.16
120 sec				6.93	
PCB peak 4 +	4.65				0.03
o,p'-DDE irra-			5.51		0.09
diated 30 sec		6.30			0.03
	7.01			8.19	
PCB peak 5 +	4.80				0.03
p,p'-DDE irra-	5.43				0.07
diated 30 sec			7.01		0.96
			8.19		0.01
				9.76	
		11.58			0.19
PCB peak 6 +			5.28		0.18
o,p'-DDD irra-			6.77		0.49
diated 60 sec	7.87				0.15
				10.32	
PCB peak 6 +	5.35				0.12
dieldrin irra-	6.77				0.34
diated 60 sec	7.80				0.11
		8.82			0.26
				10.79	
PCB peak 7 +			5.43		0.36
o,p'-DDT irra-	7.01				0.15
diated 45 sec			8.66		0.50
			11.02		2.68
				13.39	
PCB peak 8 +	5.59				0.09
p,p'-DDD irra-			6.93		0.16
diated 120 sec	8.27				0.17
	11.02				0.41
				14.17	
PCB peak 9 +		6.93			0.07
p,p'-DDT irra-	8.98				0.03
diated 15 sec	11.81				0.08
	13.54				0.31
				18.66	

[a]Degradation peak area/parent peak area.

Table III. Analysis of Salmon Oil and Herring Oil

Degradation pattern peak no.	Retention time relative to parent	DPA/PPA	Retention time relative to parent	DPA/PPA	Retention time relative to parent	DPA/PPA
	PCB peak 4[a]		Salmon oil peak 2[a]		Herring oil peak 2[a]	
1	0.42	0.01	0.43	0.01	*c*	
2	0.55	0.05	0.55	0.04	0.55	0.06
3	0.67	0.10	0.67	0.10	0.67	0.13
4	0.84	0.07	0.84	0.05	0.84	0.05
5	1.00		1.00		1.00	
	PCB peak 7[b]		Salmon oil peak 4[b]		Herring oil peak 4[b]	
1	0.43	0.08	0.45	0.05	*c*	
2	0.54	0.09	0.56	0.12	*c*	
3	0.64	0.07	0.67	0.17	*c*	
4	0.70	0.07	*c*		0.69	0.08
5	0.85	1.29	0.89	0.40	0.92	0.34
6	1.00		1.00		1.00	

[a]Trapped component irradiated for 120 sec. [b]Trapped component irradiated for 45 sec. [c]Degradation peak not detected.

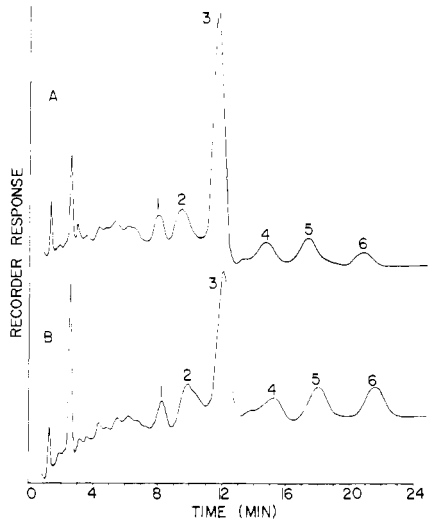

Figure 5. A. Salmon oil. B. Herring oil. Instrumental conditions given in text.

the rest. The degradation pattern for a mixture of *p,p'*-DDE and PCB peak 5 is presented in Figure 4.

Analysis of Salmon and Herring Oil. Figure 5 shows the chromatograms of salmon and herring oil extracts. The pattern for Aroclor 1254 was recognizable, but the ratio of the peak areas was not the same as the standard. Since the uv degradation of the PCB's is independent of the concentration, the degradation pattern will be the same for environmental samples as it is for standards unless preferential metabolism or degradation of some of the PCB's has occurred.

In analyzing salmon and herring oil, the peaks that apparently contained only PCB's yielded degradation patterns with the same peak area ratios as the standard. An example of this is given in Table III, salmon and herring oil peak 2 and PCB peak 4. When some other compound was present, or perhaps preferential metabolism had occurred, the pattern was similar to the standard but the ratios were different. This can be seen by looking at the results in Table III for salmon and herring oil peak 4 and PCB peak 7.

Peak 3 of the oils was shown to contain PCB peaks 5 and 6 and *p,p'*-DDE. When the entire peak was trapped and irradiated, the degradation pattern could be used for the identification of only peak 6 and *p,p'*-DDE. By making two trappings of this peak, the first trap being removed at the top of the peak and replaced with a second trap, the presence of peak 5 was demonstrated.

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Mass Spectrometric Identification of the Hepta- and Octa-Chlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Technical Pentachlorophenol

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Analytical measurements indicate that technical pentachlorophenol, a widely used pesticide, contained chlorinated dibenzo-*p*-dioxins. High-resolution mass spectrometry was used to determine the elemental composition of ions present in the spectrum of the mixture obtained as a cleaned-up neutral fraction from technical pentachlorophenol. Hepta- and octachlorodibenzo-*p*-dioxins were identified in the sample, as were hepta- and octachlorodibenzofurans.

Mass spectrometry is continuing to gain in importance as a method for determination of the structures of pesticides and their transformation products. Spectra can be obtained with isolated samples or with individual components of mixtures if a gas chromatograph is linked with the mass spectrometer through a suitable interface (Hutzinger *et al.*, 1971).

High-resolution mass spectrometry permits determination of the accurate masses of ions produced in the mass spectrometer; consequently the elemental composition of individual peaks in the spectrum can frequently be elucidated. The spectrum afforded by a mixture of compounds in the high-resolution mass spectrometer is complex, but potentially provides a method by which the individual components of a mixture can be recognized. Lovins (1969)

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