Gas-Liquid Chromatography—Mass Spectrometric Characterization of Aroclor 1242 and 1254 Components

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The recently discovered toxic hazards of PCB have encouraged a search for alternative chemicals but the millions of pounds of PCB already produced will continue to pose a threat for many years. PCB residues are virtually ubiquitous and to attempt enforcement of very low tolerance levels would impose tremendous hardships on several industries and geographical locations (e.g., communities where fish from Lake Michigan are dietary staples). Thus, it is necessary to establish the toxic hazards of low level PCB intake, the rates of accumulation and depletion of residues, and the most offensive and persistant components of the complex mixtures introduced into the environment. In order to accomplish these goals, a monitoring system which will discriminate among the various components of these complex mixtures must be developed.

Several laboratories (HUTZINGER et al. 1970, SISSONS and WELTI 1971, STALLING and HUCKINS 1971, ROTE and MURPHY 1971, WEBB and McCALL 1972, and ROTE and MORRIS 1973) are investigating the PCB components in commercial mixtures and are using GC-MS methods for analysis and confirmation of PCB. This laboratory is investigating the pharmacokinetics and tissue residues of the individual components after administration as Aroclor 1242 or 1254. This should single out the more persistant components of the mixtures and provide metabolic profiles of the PCB to permit more precise recognition of PCB after exposure to biological systems. Since each batch of Aroclor differs slighty from other batches, this paper is intended to characterize the Aroclor mixtures we will use in all subsequent investigations and to introduce our peak identification system for future reference. A subsequent publication (WELBORN et al., in press) will discuss extraction and quantitation procedures.

MATERIALS AND METHODS

The designation of peaks by letters a through t are based on the tritium electron capture gas chromatography (EC-GC) tracing of both Aroclor 1242 and 1254 combined in equal amounts by weight. The later peaks (longer RRT) of 1242 and the early peaks (shorter RRT) of 1254 occur at similar retention times; thus, some letter codes appear in the standard tracings of both Aroclors (Figure 1). The instrument used was a Varian Aerograph Model 2700 with 6' x $\frac{1}{4}$" glass columns packed with 3% OV-1

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on 100/120 chromosorb W. Nitrogen carrier gas flow was adjusted to give a standard retention time for peak j, and injector, column, and detector oven temperatures were maintained at 240°C, 200°C, and 240°C respectively.

In order to determine the percentage of chlorine found in each component of Aroclor 1242 (peaks a through p) and Aroclor 1254 (peaks g through t), a mass spectrum of each Aroclor was obtained. The present study was carried out on a Hitachi-Perkin Elmer mass spectrometer RMU-6E with Varian 1200 gas chromatograph. The stainless steel column (6' x 1/8" O.D.) was packed with 3% OV-1 on 80/100 chromosorb W HP. The mass spectra were recorded at 22 ev electron energy with 1875 v accelerating voltage and filament emission current was 3.2 uA. Helium carrier gas flow rate was 35 mls/min and injector and column temperatures were maintained at 290°, 280° respectively. The mass spectra were scanned magnetically over the range of m/e 600.

To determine the amount of PCB contributed by each component (peak) to the total Aroclor, a tracing for each Aroclor was obtained from thermal conductivity gas chromatography (TC-GC). Even though EC-GC is the most sensitive method for detecting chlorinated biphenyls, the peak areas do not necessarily correspond to the amount of each component present in the mixture. The peak areas obtained by TC-GC are directly proportional to concentration and can be used to calculate the percentage that each component contributes to the total amount injected. Thus, if peak n contributes 16.7% to the total Aroclor 1254 mixture, then a 2.0 ng injection of 1254 will contain 0.167 x 2.0 = 0.334 ng of component n.

A Varian Autoprep A-700 gas chromatograph with a thermal conductivity detector was used. The 5' x 1/4" stainless steel column was packed with 20% SE 30 on 60/80 AW DMCS chromosorb W with column-oven, injector and detector temperatures maintained at 225°, 280°, 380° respectively. The flow of helium was 240 mls/min.

To confirm that the peaks used for area calculation were indeed the same peaks designated on the EC-GC tracing, fractions from TC-GC, corresponding to those peaks were collected. Retention times relative to p, p'-DDE were identical to those of the Aroclors.

RESULTS AND DISCUSSION

Figure 1 illustrates the EC-GC profiles of the Aroclors, while Figures 2 and 3 represent the TC-GC profiles. Peaks are identified by letters (a through t) for later reference. The samples from which the figures were produced and which will be used in subsequent investigations were supplied by Monsanto Chemical Company (Electrical Grade, Lot Numbers: 1242, KB-05-415; 1254, KB-04-612). These samples differed slightly from other

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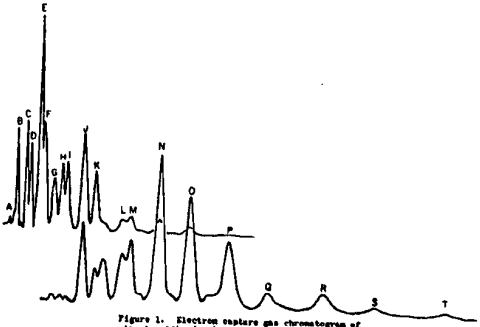


Figure 1. Electron capture gas chromatogram of Aroclor 1242 (top) and Aroclor 1254 (bottom).

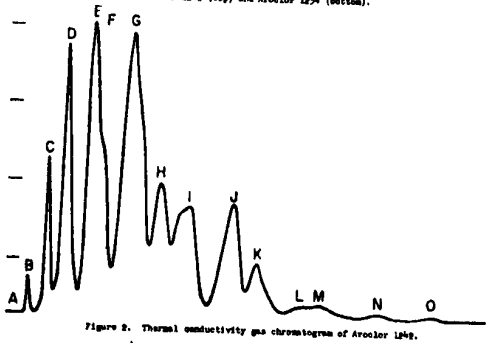


Figure 2. Thermal conductivity gas chromatogram of Aroclor 1242.

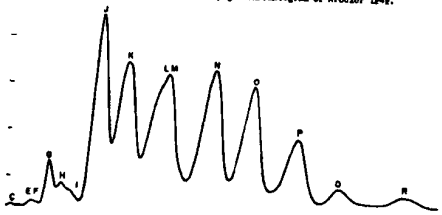


Figure 3. Thermal conductivity gas chromatogram of Aroclor 1254.

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Table I Peak Composition and peak contribution to total Aroclor 1242

Peak	RRT[1)]	Per cent composition of peak					% Total PCB
		1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	
a	13	100	--	--	--	--	T
b	21	2.7	97.3	--	--	--	0.5
c	26	--	100	--	--	--	3.4
d	31	--	--	100	--	--	8.8
e	37	--	--	100	--	--	15.5
f	41	--	--	90.3	9.7	--	5.7
g	48	--	--	24.2	75.8	--	27.4
h	53	--	--	26.9	73.1	--	11.0
i	57	--	--	3.8	96.2	--	11.5
j	70	--	--	--	13.9	86.1	9.0
k	84	--	--	--	11.6	88.4	4.2
l	99	--	--	--	3.9	96.1	1.1
m	105	--	--	--	--	100	1.2
n	127	--	--	--	--	ND	0.5
o	149	--	--	--	--	ND	0.3
p	176	--	--	--	--	ND	T

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Table II Peak Composition and peak contribution to total Aroclor 1254

Peak	RRT[1)]	Per cent composition of peak					% Total PCB
		3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	
c	26	--	--	--	--	ND	T
d	31	--	--	--	--	ND	T
e	37	--	--	--	--	ND	
f	41	--	--	--	--	ND	.2
g	48	--	100	--	--	--	2.0
h	53	3.8	96.2	--	--	--	1.0
i	57	3.8	96.2	--	--	--	0.8
j	70	1.7	98.3	--	--	--	16.1
k	84	--	96.8	3.2	--	--	16.4
l	99	--	--	100	--	--	
m	105	--	--	97.3	2.7	--	20.2
n	127	--	--	87.5	12.5	--	16.7
o	149	--	--	77.6	22.4	--	13.7
p	176	--	--	5.5	94.5	--	8.2
q	208	--	--	12.0	88.0	--	2.1
r	253	--	--	--	75.7	24.3	1.9
s	286	--	--	--	--	100	0.6
t	332	--	--	--	--	ND	T

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samples obtained from Monsanto and from the lots (not designated by number) analyzed by WEBB and McCALL (in press). The industrial process by which Aroclors are produced will introduce minor variations between lots; these variations, however, are small compared to the profile changes introduced when the PCB is subjected to light and/or biological systems (COOK 1972; WELBORN et al., in press; BORCHARD et al., in press).

Tables I and II show quantitative comparisons of the Aroclors based on TC-GC and GC-MS determinations. The composition of the peaks in terms of the number of chlorine atoms as well as the percent contribution of each peak to the total PCB are presented. Thus, in Lot KB-05-415 of Electrical Grade Aroclor 1242, peak g is the predominant component, constituting over 27 percent of the total PCB; it is composed of 25 percent trichloro- and 75 percent tetrachlorobiphenyls. On the other hand, in the Aroclor 1242 examined by WEBB and McCALL (in press), component g (RRT = 47) constituted less than 9 percent of the total PCB and was composed entirely of tetrachlorobiphenyls as is the same peak in Aroclor 1254. The symmetrical analog, 2,2',5,5'-tetrachlorobiphenyl, has been confirmed as the major component of this peak (WEBB and McCALL, 1972).

In Aroclor 1254, the major components are peaks j through p, primarily tetra-, penta-, and hexa- chloro-biphenyls. As might be expected, the analog composition of peaks with the same retention times varies from Aroclor to Aroclor as well as from batch to batch (Tables I and II); thus, rates of metabolism or accumulation of components (peaks) may be expected to change as peak composition is altered by the biological systems. Blood levels of peaks k and o, for example, parallel each other up to fifteen hours after administration of an i.v. bolus of Aroclor 1254 to sheep; changes in rates of disappearance between 14 and 24 hours, however, result in the reversal of relative concentrations of the two components (BORCHARD et al., in press).

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