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COMPARISON OF THE COMPOSITIONS OF AROCLOR 1242 AND AROCLOR 1016

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SUMMARY

The complete polychlorinated biphenyl compositions of two American products, Aroclor 1242 and its more modern replacement, Aroclor 1016, have been determined by gas-liquid chromatography (GLC) on twelve liquid phases of differing selectivities. Attempts were made to determine the degree of contamination of these Aroclors with chlorinated naphthalenes, using GLC with multiple ion-monitoring mass spectrometry. Chlorinated dibenzofurans, undetectable in Aroclor 1016, were tentatively identified by negative chemical-ionization mass spectrometry and their retention times relative to dieldrin on two GLC liquid phases. Quantitation of the dibenzofurans was initially accomplished using an electron-capture detector, and confirmed by negative chemical-ionization mass spectrometry. Aroclor 1242 contained less than 0.05 mol. % chloronaphthalenes, while Aroclor 1016 contained less than 0.06 mol. % of these compounds. Aroclor 1242 had approximately 150 ppb* of chlorinated dibenzofurans, of which 43% was the toxic 2,3,7,8-tetrachloro isomer.

INTRODUCTION

Polychlorinated biphenyls (PCBs), ubiquitous environmental pollutants, offer serious difficulties to the residue analyst and toxicologist. The large number of compounds, including isomers, present in the commercial PCB preparations, makes determination of the total PCB content of environmental samples with any degree of accuracy extremely difficult. Most measuring devices, especially halogen-selective gas chromatograph detectors, show extreme variability in molar or weight response to PCBs of different degrees of chlorination or chlorine positions^{1,2}. Any difference between the isomeric composition of the PCB mixture isolated from an environmental sample and the standard mixture used to calibrate the monitoring system is likely to invalidate the quantitation of the environmental sample³.

It is difficult for the toxicologist to interpret results of environmental monitoring for PCBs, since different PCB isomers differ in their biological effects^{4,5}, and in

* Throughout this article the American billion (10⁹) is meant.

general, the isomeric compositions of neither environmental PCB residues nor commercial PCB mixtures are known with any degree of completeness.

In addition to PCBs, commercial PCB preparations generally contain small amounts of chlorinated naphthalenes⁶ and trace amounts of the highly toxic chlorinated dibenzofurans^{7,8}. The dibenzofuran compositions have been reported for the more highly chlorinated PCB preparations^{7,8}, and the total toxicity of the least chlorinated preparations (*e.g.* Aroclor 1221, 21% chlorine) is so low that it is of little concern to most toxicologists. We have previously reported the complete PCB composition of Aroclor 1221 (*ref.* 9).

The commercial PCB preparations with approximately 42% chlorine have been widely used in the manufacture of "carbonless carbon paper", as plasticizers, electrical insulators and heat exchangers. In the present paper we compare the American PCB mixture Aroclor 1242 with its more modern replacement, Aroclor 1016, in terms of their PCB, chlorinated naphthalene and chlorinated dibenzofuran compositions. We hope that knowledge of the typical compositions of these materials will assist the toxicologist in evaluating the possible hazards associated with their occurrence in environmental samples.

MATERIALS AND METHODS

Aroclor 1242, lot No. KA 491 and Aroclor 1016, lot No. KA 706 were obtained from Monsanto (St. Louis, Mo., U.S.A.) in 1970. The PCBs were analyzed as described previously⁹ using the described columns OV-101, OV-3, OV-17, OV-210, OV-225, cyclohexanedimethanol succinate, Poly MPE and Dexil 410. Additionally, a 5 m × 2 mm column packed with 5% SE-52 on 100–120 mesh Gas-Chrom Z was found useful. Apiezon L was chromatographed on Florisil¹⁰, eluting a non-polar fraction with *n*-hexane and a polar fraction with 5% ethyl acetate in hexane. Both fractions, as well as unfractionated Apiezon L were coated at 5% (w/w) on 80–100 mesh Chromosorb W HP. Retention indices were determined on all twelve liquid phases at 200 ± 5° as described previously⁹. Programmed-temperature runs (150–230° at 2° or 4°/min) were also made on all columns to increase resolution of particular pairs of peaks for more reliable quantitation.

Quantitation by measurement of peak areas was facilitated by the use of a Spectra-Physics system IV computing integrator. For each column, that run (isothermal or programmed) giving the best resolution of a given peak was used for its quantitation. Final area percentages were averages of those for a given component from runs on columns that "isolated" that component. In about a dozen cases, no one column of those listed above could yield a peak free of contaminants. In each such case one could calculate the appropriate area by correcting for the known area percentages attributable to the contaminants, from columns capable of "isolating" them. None of the columns were able to provide sufficient resolution to preclude the possible occurrence of traces of five isomers (indicated in Table I) under the tails of other peaks. All final area percentages were corrected for relative molar response of the hydrogen flame-ionization detector as described previously¹⁰.

In order to provide further confirmation of the identifications, the Aroclors were fractionated by reversed-phase high-performance chromatography (HPLC) on Bondapak C₁₈ (Waters Assoc., Milford, Mass., U.S.A.) with 85% aq. methanol as

TABLE I

PCB COMPOSITIONS OF AROCLOR 1242 AND 1016

Possible trace components whose presence or absence could not be confirmed: 3,5,3'; 2,4,6,3'; 2,3,6,4'; 2,4,5,2,3'; 2,4,6,2',6'.

PCB	Mol.% in		PCB	Mol.% in		PCB	Mol.% in	
	1242	1016		1242	1016		1242	1016
BP	0.01	0.50	2,6,2',6'	0.17	0.19	2,3,4,3',5'	0.46	0.16
2	0.68	0.80	2,3,6,2'	0.90	1.00	2,3,4,2',4'	0.40	—
3	0.04	0.10	2,5,2',6'	0.97	1.07	2,3,4,2',5'	0.09	—
4	0.22	1.00	2,5,2',5'	4.08	4.35	2,3,4,3',4'	0.25	—
2,6	0.13	0.20	2,4,6,4'	2.18	2.40	2,3,5,2',5'	0.12	—
2,2'	3.99	4.36	2,3,5,2'	0.44	0.47	2,4,5,2',4'	0.55	—
2,5	0.31	0.34	2,3,2',6'	0.31	0.33	2,4,5,2',5'	0.27	—
2,4	1.04	1.16	2,4,5,2'	1.33	1.41	2,4,5,3',5'	0.31	—
2,3'	1.24	1.37	2,4,2',5'	3.28	3.48	3,4,5,2',4'	0.36	—
2,4'	8.97	10.30	2,3,2',5'	1.06	1.14	3,4,5,3',5'	0.05	—
3,5	0.35	0.37	2,3,4,2'	1.67	2.00	3,4,5,3',4'	0.03	—
3,4	0.09	0.11	2,3,2',3'	0.15	0.18	2,3,4,5,2',6'	0.07	—
3,4'	0.12	0.12	2,3,3',4'	0.60	—	2,3,4,2',4',5'	0.08	—
4,4'	0.99	1.07	2,4,2',4'	1.65	1.81	2,4,5,2',4',5'	0.02	—
2,6,2'	0.97	1.08	2,4,5,4'	2.02	1.35			
2,5,2'	9.36	10.87	2,5,3',4'	1.11	—	Monochloro (%)	0.94	2.40
2,4,2'	2.92	3.14	3,4,5,2'	trace	—	Dichloro (%)	17.23	19.40
2,3,2'	3.25	3.50	3,4,5,3'	0.52	—	Trichloro (%)	51.67	56.31
2,6,3'	0.54	0.58	3,4,5,4'	0.28	—	Tetrachloro (%)	24.65	21.32
2,6,4'	2.15	2.31	3,4,3',4'	0.34	—	Pentachloro (%)	5.24	0.40
2,5,3'	0.55	0.62	2,5,3',5'	0.33	—	Hexachloro (%)	0.17	—
2,5,4'	4.53	4.72	2,4,3',4'	0.81	0.14			
2,4,3'	1.68	1.79	3,4,3',5'	0.24	—			
2,4,4'	13.30	14.48	2,3,4,4'	0.21	—			
2,3,3'	3.64	3.99	2,4,6,3',5'	0.92	—			
2,3,4'	2.64	2.80	2,4,6,2',3'	0.13	0.04			
3,4,2'	2.83	3.08	2,3,6,2',5'	0.53	0.18			
3,4,3'	0.66	0.38	2,3,6,3',5'	0.39	0.01			
3,4,4'	1.62	1.89	2,3,6,2',4'	trace	—			
3,5,4'	1.03	1.08	2,3,6,2',3'	0.38	0.01			

solvent. The fractionation was found to be roughly according to the degree of chlorination. No new components were seen when these HPLC fractions were subjected to gas-liquid chromatography (GLC) that were not seen on GLC of the original Aroclor. Finally, GLC-electron-impact mass spectrometry (MS) was used to confirm the number of chlorine atoms assigned to each peak.

Samples were introduced into a Finnigan 3300 mass spectrometer, equipped with a Finnigan/Incos 2300 data system. The Finnigan 9500 gas chromatograph was fitted with a 1.52 m × 2 mm glass column containing 3% OV-1 on 100-120 mesh Gas-Chrom Q, or a 2 m × 2 mm column of 3% Dexil 410 on 90-100 mesh Anakrom AS, and was programmed from 100 to 280° at 10°/min. Throughout the GLC-MS runs, 4-sec scans over the mass range m/e 40-800 were obtained. Individual PCB (and polychlorinated naphthalene, PCN) peaks were assigned chlorine numbers from reconstructed single ion chromatograms. The m/e values used for PCBs were 154, 188, 190, 222, 224, 256, 258, 290, 292, 324, 326, 358, 360, 390, 392, 426, 428, 460, 462,

494 and 496 (parent ion clusters for biphenyl through decachlorobiphenyl). For PCNs, the m/e values were 128, 160, 162, 196, 198, 230, 232, 264, 266, 298, 300, 332, 334, 366, 368, 400 and 402 (naphthalene through octachloronaphthalene). The ratios of the peaks from each cluster enabled evaluation of the presence of different chlorine numbers in each peak.

The PCNs were quantitated from the areas of the reconstructed single ion chromatograms. In the cases where the peak ratios in the parent cluster suggested some interference with one of the ions from a PCB fragment ion, that cluster ion indicating the lowest amount of PCN was used. Halowax 1099 (a mixture of PCNs) was used to calibrate the instrument for total PCN response. Potential interference by PCB fragment ions was further investigated by running a variety of synthetic PCBs (free of naphthalenes) to measure the relative abundance of the M-26 ion.

The chlorinated dibenzofuran fraction was isolated as follows: 2 g of Aroclor were run on a 100-g, dry-packed column of 100-200 mesh Florisil PR. PCBs and PCNs were eluted with 1 l of 3% dichloromethanol in *n*-hexane, after which the furans were eluted with 800 ml of 20% (v/v) dichloromethane in hexane. The residue from the 20% dichloromethane fraction was chromatographed sequentially on three 3-g columns of Fisher A-540 alumina as described previously¹¹. The final dibenzofuran fraction was analyzed by GLC with a ⁶³Ni electron-capture detector on a Hewlett-Packard Model 5750 instrument. Quantitation was from standard curves made using the appropriate chlorinated dibenzofuran standards. In addition, the furans were examined by methane-supported negative chemical-ionization MS. The isomers were identified on the basis of their negative ion mass spectra, as well as their retention times relative to dieldrin on GLC columns packed with 10% OV-210 and 3% Dexil 410 on 100-120 mesh Gas-Chrom Q (ref. 9).

RESULTS AND DISCUSSION

The compositions of the PCB mixtures comprising Aroclors 1242 and 1016 are shown in Table I. The total number of components seen is in agreement with that seen during chromatography of Clophen A40 on 27-m glass capillaries coated with OV-101 (ref. 12) and is much larger than that seen on stainless-steel capillaries coated with either OV-101 or Apiezon L (ref. 13). Thus, the qualitative information obtained using a sequence of packed columns, none of which exceeded 6000 theoretical plates, was similar to what could be obtained on a single capillary column providing 200,000 theoretical plates¹². As has been pointed out previously¹³, even a 60-m glass capillary column does not provide sufficient resolution for separate quantitation of all of the components of Aroclor 1242, and the use of a variety of liquid phases can not be avoided.

As can be seen from Table I, Aroclors 1242 and 1016 have similar PCB compositions up to tetrachloro isomers. Aroclor 1016 lacks the more polar tetrachloro, most of the pentachloro, and essentially all of the hexachloro isomers present in Aroclor 1242. Nothing can be said at this point about the possible effects of lot-to-lot variations on these analytical results.

The synthetic PCBs tested showed an M-26 ion cluster in their spectra amounting in relative abundance to approximately 0.5-0.6% of the relative abundance of the molecular ions. Thus, chloronaphthalenes could only be measured when they

amounted to $>1\%$ of a coeluting PCB, or about 0.1% of the Aroclor if their peaks were not obscured by PCB peaks. In general, PCBs and PCNs were not well distinguished on OV-1, but several peaks in the chromatograms of the Halowaxes were separated from PCB peaks on Dexil 410. Analysis of mixtures of Aroclor 1242 and Halowax 1099 confirmed that a total PCN content of 0.1% relative to PCBs could indeed be detected.

The amounts of PCNs in Aroclor 1242 and 1016 were found to be indeterminate under these conditions. Although the reconstructed single ion chromatograms indicated contents of about 0.04% PCN in 1242 and 0.06% in 1016, all of the apparent PCN peaks coincided exactly with PCB peaks on both GLC columns, indicating that what was being measured was M-26 fragments from the PCBs. Therefore, the true levels of PCNs must be less than $0.04\text{--}0.06\%$ for both Aroclors. Eastman Practical Grade biphenyl was examined for the presence of naphthalene, and was found to contain less than 0.008% .

Table II lists the chlorinated dibenzofurans that were detected in Aroclor 1242. These compounds were not seen in Aroclor 1016 (less than 5 ppb). 2,3,7,8-Tetrachlorodibenzofuran and the 2,3,4,7,8-pentachloro isomer have been previously identified in Aroclors 1248 and 1254, Kaneclor 200 and Kaneclor 500 (ref. 8). The 1,3,6,7-tetrachloro isomer has been very tentatively identified in these PCB preparations also⁸. Aroclor 1254 has been reported to contain at least nine chlorodibenzofuran isomers, but only those mentioned above have been identified¹⁴. To our knowledge, the present report is the first to quantitate and identify the dibenzofurans in Aroclor 1242.

TABLE II
DIBENZOFURANS FROM AROCLOR 1242*

Isomer**	1242 (ng/g)	Relative retention time***	
		OV-210	Dexil 410
2,3,6-Trichloro	47	0.71	0.91
1,3,6,7-Tetrachloro	7	0.90	1.31
2,3,7,8-Tetrachloro	64	1.30	1.82
2,3,4,7,8-Pentachloro	28	2.40	3.84
1,2,3,6,7,8-Hexachloro	<3	3.16	5.68

* Lot No. KA 491.

** The pentachloro isomers 1,2,3,7,8- and/or 2,3,4,6,7- could not be confirmed present or absent for lack of standards.

*** OV-210 and Dexil 410 both at 200° isothermal. Retention times relative to dieldrin = 1.000.

This study indicates the presence of two presumably toxic PCB isomers^{15,16}, 3,4,3',4'-tetrachlorobiphenyl and 2,3,4,3',4'-pentachlorobiphenyl, and of a series of chlorinated dibenzofurans including the extremely toxic 2,3,7,8-tetrachloro isomer¹⁷ in Aroclor 1242 but absent or in greatly reduced concentrations in Aroclor 1016.

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