

CHROM. 12,218

## ANALYSIS OF ALKYLATED MIXTURES OF POLYCHLORINATED BIPHENYLS BY CAPILLARY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

J. KRUPČÍK

*Department of Analytical Chemistry, Chemical Faculty, Slovak Technical University, Jáňská 1, 88037 Bratislava (Czechoslovakia)*

P. A. LECLERCQ

*Laboratory of Instrumental Analysis, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven (The Netherlands)*

and

J. GARAJ and A. ŠÍMOVÁ

*Department of Analytical Chemistry, Chemical Faculty, Slovak Technical University, Jáňská 1, 88037 Bratislava (Czechoslovakia)*

---

### SUMMARY

Gas chromatographic separations of chlorobiphenyls, alkylbiphenyls and alkylchlorobiphenyls were carried out at 200° on glass capillary columns coated with OV-101, Carbowax 20M and Apiezon L as stationary phases. Apiezon L was the most suitable phase for this purpose, in terms of separation, reproducibility of retention indices and reliability of structure-retention correlations for the prediction of indices. Compounds in the mixtures were identified by comparison with reference materials analyzed under similar conditions, by structure-retention correlations and by combined gas chromatography-mass spectrometry. Quantitative analysis of a mixture of polychlorinated biphenyls was performed by using the internal standard method, taking into account experimentally determined flame ionization detector response factors. The results, obtained on stationary phases with different polarities, can be used as an additional tool for qualitative analysis.

---

### INTRODUCTION

Polychlorinated biphenyls (PCBs) are very persistent and accumulative environmental pollutants. Alkylated PCBs have been suggested as possible substitutes, because biodegradation is facilitated by the presence of the alkyl groups. This has been verified for both the metabolic<sup>1</sup> and the photolytic<sup>2</sup> degradation. The isopropyl group is the most suitable alkyl substituent for this purpose. Mixtures of isopropylchlorobiphenyls (IPCBs) are produced by catalytic isopropylation of PCBs.

Sundström *et al.*<sup>3</sup> analyzed a mixture of IPCBs (Chloralkylene 12, Prodelec, Paris, France), using proton magnetic resonance spectroscopy, gas-liquid chro-

matography (GC) and mass spectrometry (MS). It was shown that this mixture is very complex, containing also PCBs and isopropylbiphenyls (IPBs). Packed columns, with Apiezon L and Carbowax 20M as stationary phases, were used for GC analyses. Combined GC-MS has shown, however, that several peaks in the chromatograms of Chloralkylene 12 were not resolved.

The present report shows the possibilities of glass capillary columns for the analysis of mixtures of PCBs, IPCBs and IPBs, by GC and GC-MS.

## MATERIALS AND METHODS

Mixtures of alkylated PCBs were prepared by catalytic isopropylation of a 42% chlorine-containing PCB mixture (Aroclor 1242)<sup>4</sup>. IPBs were prepared by isopropylation of biphenyl<sup>5</sup>. Pure 2-, 3- and 4-isopropylbiphenyl, as well as 3,5-, 3,3'-, 3,4'- and 4,4'-diisopropylbiphenyl were obtained from Dr. J. Kříž. The origin of individual PCBs and commercial mixtures has been described<sup>6</sup>.

### *Gas chromatography*

A Carlo Erba (Milan, Italy) Model 2300 gas chromatograph, equipped with a flame ionization detector (FID) and inlet sample splitter, was used. Glass capillary columns were made of soft glass. Column etching, coating and testing procedures were described earlier<sup>7</sup>. The columns (50 m × 0.25 mm I.D.) were coated with OV-101, Carbowax 20M or Apiezon L as stationary phase. Nitrogen was used as carrier gas at inlet pressures of 100–250 kPa. Samples were dissolved in acetone before injection. Separations were carried out isothermally at 200°. Retention times were measured with stop-watches. Peak areas were obtained from a Spectrophysics Autolab (Mountain View, Calif., U.S.A.) Model 6300 digital integrator.

### *Combined gas chromatography-mass spectrometry*

Combined GC-MS analyses were carried out using the capillary columns as mentioned above. Helium was used as carrier gas, with inlet pressures of 50–150 kPa. Two GC-MS systems were applied: a Finnigan 4000 (Sunnyvale, Calif., U.S.A.) quadrupole mass spectrometer interfaced via a Pt-Ir capillary (60 cm × 0.1 mm I.D.); an AEI (Manchester, England) MS-12 single-focussing magnetic sector instrument, coupled directly via an all-glass interface<sup>8</sup>. Both mass spectrometers were operated in electron impact mode, under the following conditions: electron energy, 70 eV; electron current, 0.20 mA; source temperature, 250°. The MS-12 was operated at 4 kV ion accelerating voltage. Mass spectra were recorded at scan speeds of 1 sec per scan and 2 sec per decade, respectively. Data were acquired and handled by a home-made hard- and software system, based on a DCC (Fairfield, N.J., U.S.A.) D-116E mini-computer.

## RESULTS AND DISCUSSION

### *Qualitative analysis*

Isopropylated mixtures of PCBs are complex. They contain isopropylbiphenyls (IPBs), isopropylchlorobiphenyls (IPCBs), chlorinated biphenyls (PCBs) and by-products of the isopropylation. The number of isomers present in these mixtures

depends on the number of substituents as is seen from Table I. The total number of compounds with up to four substituents, which could be expected in a mixture, is more than 785 (Table I). Therefore, the mixtures were analyzed on capillary columns. To minimize the number of components in the mixture, samples with a limited number of isopropyl groups were used. Model mixtures of PCBs and IPBs, as well as samples of IPCBs, were analyzed on glass capillary columns coated with OV-101, SE-30, Apiezon L and Carbowax 20M as stationary phases.

TABLE I

NUMBER OF POSSIBLE ISOMERS OF ISOPROPYL (IPBs), CHLORO (PCBs) AND ISOPROPYLCHLORO (IPCBs) DERIVATIVES OF BIPHENYL, CONTAINING ONE TO FOUR SUBSTITUENTS

No. of substituents			No. of isomers			
Total	Chlorine	Isopropyl	PCBs	IPBs	IPCBs	Total
1	1	0	3	—	—	6
	0	1	—	3	—	
2	2	0	12	—	—	43
	1	1	—	—	19	
	0	2	—	12	—	
3	3	0	24	—	—	176
	2	1	—	—	64	
	1	2	—	—	64	
	0	3	—	24	—	
4	4	0	42	—	—	560
	3	1	—	—	136	
	2	2	—	—	204	
	1	3	—	—	136	
	0	4	—	42	—	

Recently we have shown that glass capillary columns, coated with OV-101, can be used for the separation of a standard Aroclor 1242 mixture of PCBs<sup>6</sup>. However, some compounds coelute as overlapping peaks on such columns (Fig. 1). Separation problems could not satisfactorily be solved by changing the temperature, even if high efficiency columns were used. The reproducibility of Kováts' retention indices of PCBs, obtained on glass capillary columns coated with this phase, was within a few units only after standardization of the column preparation procedure<sup>7</sup>. Contrary to published results<sup>9</sup>, we have found that the prediction of Kováts' indices, using structural increments, is inadequate for all trichlorobiphenyl and tetrachlorobiphenyl derivatives. The largest differences between predicted and measured Kováts' indices were found for compounds having chlorine atoms at *para* positions with respect to the phenyl-phenyl bond.

Differences between predicted and measured Kováts' indices were even larger on Carbowax 20M columns, although the separation of some overlapping peaks of PCBs on this phase is better than on OV-101 (Fig. 2). Some overlapping peaks on Carbowax 20M can be resolved by decreasing the separation temperature (*e.g.*, peaks 10 and 15 are each resolved into two peaks). Analysis of PCBs on Carbowax 20M capillary columns is rather complicated, as the elution order of the peaks depends even on the film thickness of the stationary phase. The reproducibility of such analy-

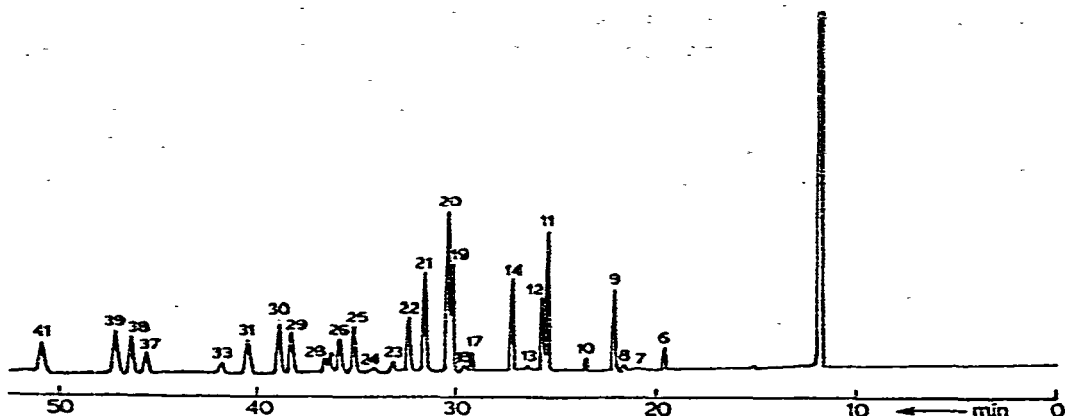


Fig. 1. Separation of Aroclor 1242 by capillary gas chromatography on OV-101 as stationary phase at 200°. Peaks of PCBs: 6 = 2,2'; 7 = 2,4; 8 = 2,3'; 9 = 2,4'; 10 = 2,6,2'; 11 = 2,5,2'; 12 = 4,4' + 2,4,2'; 13 = 2,6,3'; 14 = 2,3,2' + 2,6,4'; 17 = 2,5,3'; 18 = 2,4,3'; 19 = 2,5,4'; 20 = 2,4,4'; 21 = 2,3,3' + 2,5,2',6' + 3,4,2'; 22 = 2,3,4'; 23 = 3,5,3'; 24 = 3,5,4' + 2,3,3',6'; 25 = 2,5,2',5'; 26 = 2,4,2',5'; 27 = 2,4,2',4'; 28 = 2,4,6,4'; 29 = 2,3,2',5'; 30 = 2,3,2',4' + 3,4,3'; 31 = 2,3,4,2' + 2,3,6,4' + 2,6,3',4'; 33 = 2,3,2',3'; 37 = 2,3,2',5' + 2,3,3',5'; 38 = 2,5,3',4'; 39 = 2,4,3',4' + 2,3,6,2',5'; 41 = 2,3,3',4'.

ses is not satisfactory and can be improved only by standardization of the column preparation procedure.

The best separation of the Aroclor 1242 mixture was achieved on Apiezon L glass capillary columns (Fig. 3). Since the predicted and measured Kováts' indices of PCBs with three and four chlorine atoms also agreed within a few index units on these columns, most further analyses of PCBs, IPBs and IPCBs were carried out on this

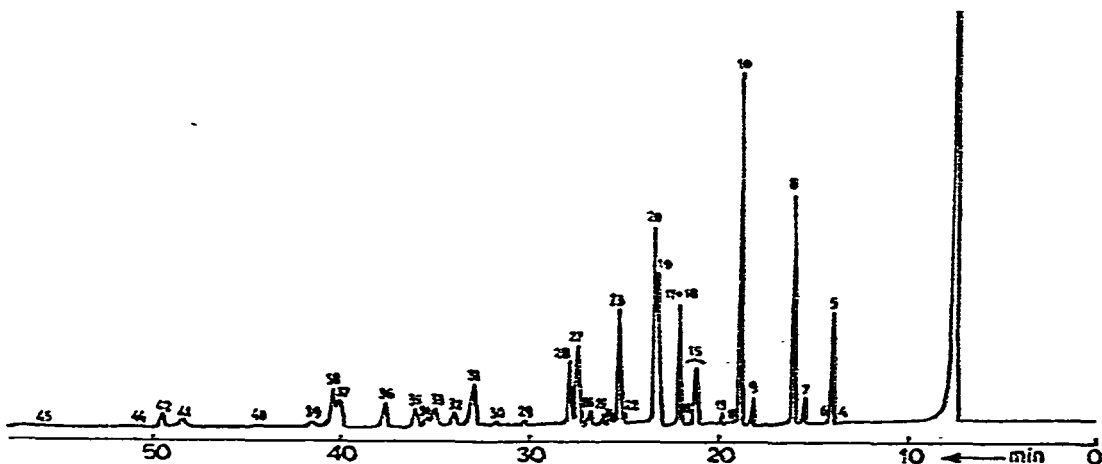


Fig. 2. Separation of Aroclor 1242 by capillary gas chromatography on Carbowax 20M as stationary phase at 200°. Peaks of PCBs: 5 = 2,2'; 7 = 2,3'; 8 = 2,4'; 9 = 2,6,2'; 10 = 2,4,2' + 2,5,2'; 13 = 2,6,3'; 15 = 4,4' + 2,6,4'; 17 = 2,3,2'; 18 = 2,5,3'; 19 = 2,4,4'; 20 = 2,5,4'; 23 = 3,4,2' + unknown; 26 = 2,4,2',4'; 27 = 2,4,2',5' + 2,5,2',5'; 28 = 3,4,3'; 31 = 2,3,2',5' + unknown; 36 = 2,3,2',4'; 37 = 2,5,3',4'; 38 = 2,4,5,2',5'.

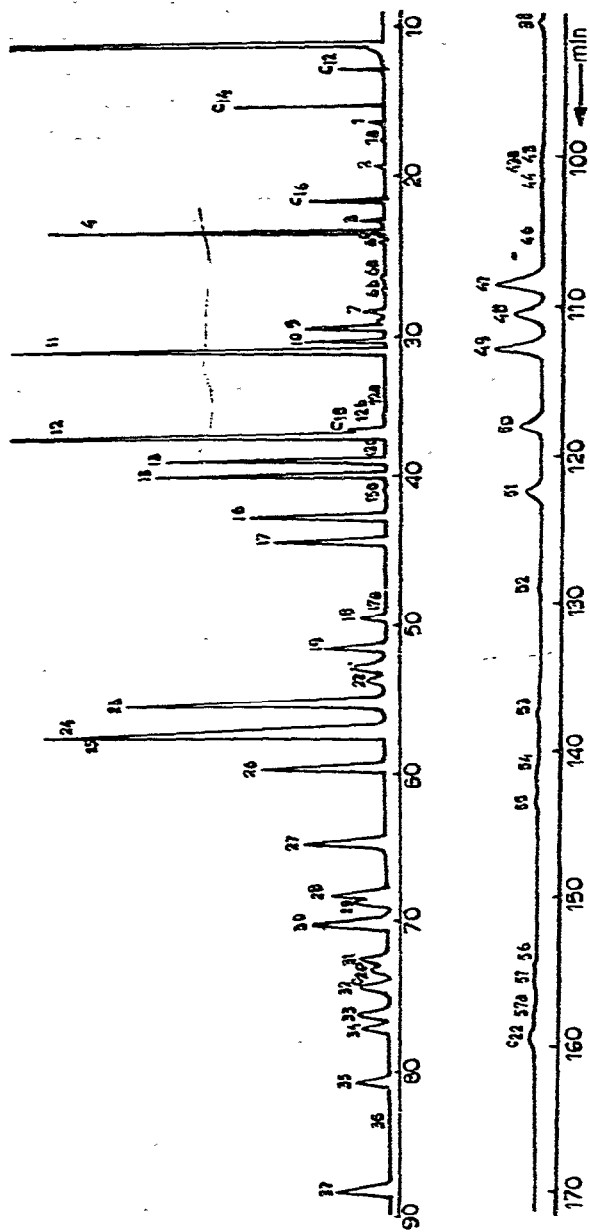


Fig. 3. Separation of Aroclor 1242 by capillary gas chromatography on Apiezon L, as stationary phase at 200°, *n*-Alkanes are marked as C<sub>*i*</sub>, with *i* = number of carbon atoms. The PCB peaks are numbered as in Table II.

phase. Fig. 4 shows the separation at 200° of a mixture of PCBs, IPBs and IPCBs, and added *n*-alkanes, on a glass capillary column coated with Apiezon L. The peaks were characterized by analyzing model mixtures of PCBs and IPBs, using structure-retention correlations and quantitative information, as well as by combined GC-MS.

To model mixtures of PCBs and Aroclor 1242, *n*-alkanes were added as internal standards. These mixtures were separated on Apiezon L capillary columns, and retention indices were determined (Table II). The indices for known compounds were used to predict retention indices for unidentified compounds. Structural increments<sup>10,11</sup> were calculated as follows.

From symmetrically substituted PCBs, the structural increment is simply half of the retention index. For instance, the increment *H* for 2,6-dichlorophenyl was calculated from the Kováts' index of 2,6,2',6'-tetrachlorobiphenyl:

$$H_{2,6} = 1826.2/2 = 913.1$$

From asymmetrically substituted PCBs, the structural increment for one substituted phenyl group can be calculated by subtraction of the increment of the other group from the retention index. For instance,  $H_{2,3,4}$  of trichlorophenyl was calculated by subtracting the increment of 2,5-dichlorophenyl ( $H_{2,5} = 981.9$ ) from the retention index of 2,3,4,2',5'-pentachlorobiphenyl ( $I = 2173.9$ ):

$$H_{2,3,4} = 2173.9 - 981.9 = 1192.0$$

TABLE II

KOVÁTS' RETENTION INDICES OF PCBs ON A GLASS CAPILLARY APIEZON L COLUMN AT 200°

The chromatogram is shown in Fig. 3.

Peak No.	Aroclor 1242	Pure compounds	Calculated	PCB derivative
1	1452.2	1452.3	1452.2	Biphenyl
2	1545.4	1545.5	1545.8	2
4	1638.6	1640.0	1639.2	2,6
4	1638.6		1639.8	2,2'
5	1645.2	1646.5	1643.3	3
6	1652.0		1653.9	4
		1708.8	1708.0	2,5
8	1725.8		1723.8	2,4
9	1730.1		1730.3	2,3
			1733.0	2,6,2'
10	1740.2		1737.1	2,3'
11	1747.4		1747.7	2,4'
12	1802.6	1802.2	1801.8	2,5,2'
12a	1808.6	1808.2	1808.7	3,5
13	1817.3		1817.6	2,4,2'
14	1819.1		1824.1	2,3,2'
15	1825.3	1826.2	1826.2	2,6,2',6'
			1830.3	2,6,3'
15a	1833.7	1834.5	1834.4	3,3'
16	1840.0		1840.9	2,6,4'
		1843.4	1844.5	3,4
			1845.0	3,4'

TABLE II (continued)

Peak No.	Aroclor 1242	Pure compounds	Calculated	PCB derivative
17	1858.4	1857.9	1855.6	4,4'
18a	1895.5		1895.0	2,5,2',6'
		1902.4	1899.1	2,5,3'
19	1902.9		1902.5	3,5,2'
20	1909.3		1909.7	2,5,4'
21	1910.6		1910.8	2,4,2',6'
22	1914.6		1914.9	2,4,3'
			1917.3	2,3,2',6'
			1918.1	2,3,4
23	1922.2		1921.4	2,3,3'
			1925.5	2,4,4'
24	1931.9	1929.1	1932.0	2,3,4'
25	1933.2		1938.3	3,4,2'
26	1944.1			
27	1966.9	1965.7	1963.8	2,5,2',5'
28	1979.3	1980.6	1979.6	2,4,2',5'
30	1989.0	1988.0	1986.1	2,3,2',5'
31	1997.8	1997.1	1995.4	2,4,2',4'
			1995.7	2,6,3',5'
			1999.8	3,5,3'
32	2004.6		2001.9	2,3,2',4'
33	2011.0	2010.8	2008.4	2,3,2',3'
33	2011.0		2010.4	3,5,4'
			2011.9	2,3,4,2'
			2031.5	2,6,3',4'
36	2034.9		2035.6	3,4,3'
37	2049.5		2046.2	3,4,4'
			2064.5	2,5,3',5'
43	2082.3		2080.3	2,4,3',5'
44	2084.4		2086.8	2,3,3',5'
47	2103.6	2102.3	2100.3	2,5,3',4'
48	2108.2		2109.2	2,3,4,3'
49	2114.1		2116.1	2,3,3',4'
			2119.8	2,3,4,4'
50	2124.9		2122.6	2,3,3',4'
			2165.2	3,5,3',5'
			2201.0	3,4,3',5'
			2236.8	3,4,3',4'

In Table III structural increments of mono-, di- and trichlorophenyl groups are given, from which Kováts' retention indices of mono-, di-, tri- and tetrachlorobiphenyls were calculated (fourth column in Table II).

Structural increments of monoisopropyl- and diisopropylphenyl groups were calculated similarly (Table IV). The calculated Kováts' indices of isopropylbiphenyls are given in Table V. Kováts' indices of chloroisopropylbiphenyls (Table VI) were calculated from the increments given in Tables III and IV.

As the number of compounds expected in the IPCB mixtures exceeds the separation power of the column used (the separation number is lower than the expected number of peaks), Kováts' indices were used for characterization of the peaks only in

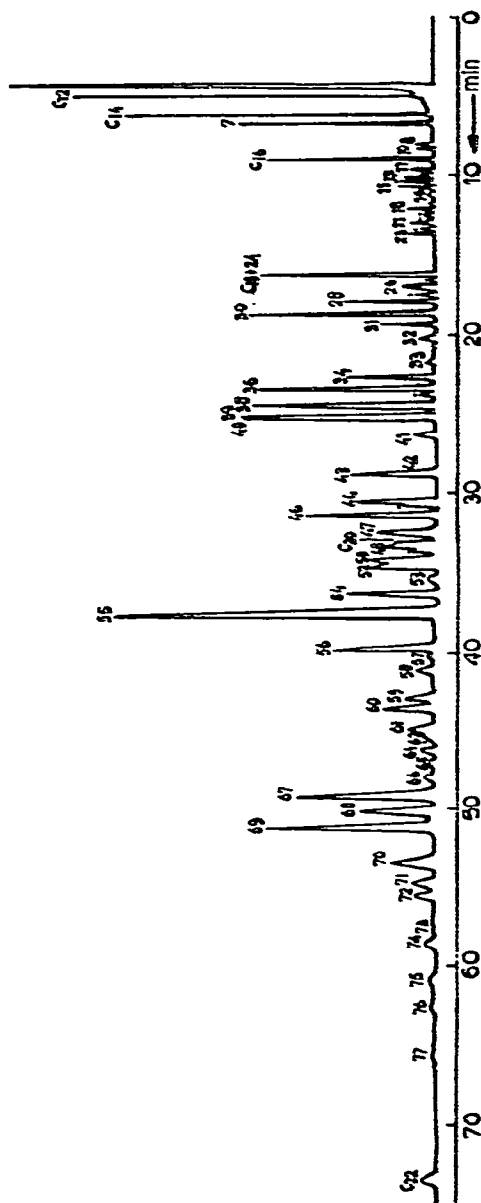


Fig. 4. Separation of a mixture of PCBs, IPBs, IPCBs and *n*-alkanes at 200° on a glass capillary column coated with Apiczon L. *n*-Alkanes as in Fig. 3. The numbers of the other peaks correspond with the peak numbers in Table VII.



TABLE III

## STRUCTURAL INCREMENTS OF CHLORINATED PHENYL GROUPS

Calculated from retention indices of PCBs on a glass capillary Apiezon L column at 200°.

<i>Substructure</i>	<i>Increment</i>
Phenyl	726.1
2	819.9
3	917.2
4	927.8
2,3	1004.2
2,4	997.7
2,5	981.9
2,6	913.1
3,4	1118.4
3,5	1082.6
2,3,4	1192.0

TABLE IV

## STRUCTURAL INCREMENTS OF ISOPROPYLATED PHENYL GROUPS

Calculated from retention indices of IPBs on a glass capillary Apiezon L column at 200°.

<i>Substructure</i>	<i>Increment</i>
Phenyl	727.2
2	775.8
3	934.6
4	981.9
3,5	1090.6

TABLE V

## KOVÁTS' RETENTION INDICES OF ISOPROPYLATED BIPHENYLS

Calculated from increments given in Table IV (Apiezon L, 200°).

<i>Biphenyl derivative</i>	<i>Index</i>
2	1503.0
3	1661.8
4	1709.1
2,2'	1551.6
2,3'	1710.4
2,4'	1757.7
3,3'	1869.2
3,4'	1916.5
4,4'	1963.8
3,5,2'	1866.4
3,5,3'	2025.2
3,5,4'	2072.5
3,5,3',5'	2181.2

cases, where the structure agreed with that suggested by mass spectral data. In Table VII proposed structures, Kováts' indices and data from GC-MS for the peaks in Fig. 4 are given.

While interpreting the mass spectra obtained on the Finnigan 4000 quadrupole

TABLE VI

## KOVÁTS' RETENTION INDICES OF SOME ISOPROPYLCHLOROBIPHENYLS

Calculated from increments listed in Tables III and IV (Apiezon L, 200°). iPr = Isopropyl; Cl = chloro.

<i>Biphenyl derivative</i>	<i>Index</i>
2-Cl-2'-iPr	1595.7
2-Cl-3'-iPr	1754.5
2-Cl-4'-iPr	1801.8
2-Cl-3',5'-diPr	1910.5
4-Cl-3',5'-diPr	2018.4
2,3-diCl-2'-iPr	1780.0
2,3-diCl-3'-iPr	1938.8
2,3-diCl-4'-iPr	1986.1
2,4-diCl-2'-iPr	1773.5
2,4-diCl-3'-iPr	1932.3
2,4-diCl-4'-iPr	1979.6
2,5-diCl-2'-iPr	1757.7
2,5-diCl-3'-iPr	1916.5
2,5-diCl-4'-iPr	1963.8
2,6-diCl-2'-iPr	1688.9
2,6-diCl-3'-iPr	1847.7
2,6-diCl-4'-iPr	1895.0
3,4-diCl-2'-iPr	1894.2
3,4-diCl-3'-iPr	2053.0
3,4-diCl-4'-iPr	2100.3
3,5-diCl-2'-iPr	1858.4
3,5-diCl-3'-iPr	2017.2
3,5-diCl-4'-iPr	2064.5

instrument, it became clear that catalytic dechlorination had occurred to some extent. This is probably caused by the Pt-Ir GC-MS interface. Mass spectra obtained on the AEI MS-12, with an all-glass interface, did not show this effect. Moreover, the spectra from both mass spectrometers showed different ratios in the abundances of molecular

TABLE VII

## MEASURED KOVÁTS' INDICES AND MASS SPECTROMETRIC CHARACTERIZATION OF ALKYLBIPIHENYLS, ALKYLCHLOROBIPHENYLS AND CHLOROBIPHENYLS

iPr = Isopropyl; Cl = chloro. The corresponding chromatogram is given in Fig. 4 (Apiezon L, 200°).

<i>Peak No.</i>	<i>Biphenyl derivative</i>	<i>Index</i>	<i>GC-MS characterization</i>
7	Biphenyl	1452.6	biphenyl
8	2-Cl	1546.4	monoCl
9	3-Methyl (+ 4-Cl)	1551.6	methyl (+ monoCl)
10	4-Methyl	1565.3	methyl
11	3-Ethyl	1628.1	
12	2,2'-diCl and/or 2,6-diCl	1639.0	alcohol (MW 145)
13	3,3'-Dimethyl	1642.6	dimethyl
14	4-Cl	1652.4	monoCl
15	3-iPr	1666.1	iPr
18	4-iPr	1709.0	iPr
19	2,5-diCl	1718.5	diCl

TABLE VII (continued)

Peak No.	Biphenyl derivative	Index	GC-MS characterization
20	2,4-diCl	1725.8	diCl
21	2,3-diCl	1730.1	diCl
22	2,6,2'-triCl	1739.6	triCl
23	2,4'-diCl	1747.2	diCl
24	2,5,2'-triCl	1802.8	triCl
26	3,5-diiPr + 2,4,2'-triCl	1816.7	diiPr + triCl
27	2,3,2'-triCl	1825.0	triCl
28	3,3'-diCl	1833.8	diCl
29	2,6,4'-triCl	1843.3	triCl
30	3,4'-diCl + 3,4-diCl	1846.1	diCl
31	4,4'-diCl	1857.9	diCl
32	3,3'-diiPr	1868.4	diiPr
33a		1887.2	diCl + triCl
33b	2,5,2',6'-tetraCl	1890.4	tetraCl
34	3,5,2'-triCl	1902.6	triCl
36	2,5,4'-triCl	1911.0	triCl
37	2,4,3'-triCl (+ 2,3,2',6'-tetraCl)	1914.4	triCl (+ tetraCl)
38	2,3,3'-triCl + 3,4'-diiPr	1921.4	triCl + diiPr
38a	2,4,4'-triCl	1923.0	triCl
39		1930.9	triCl
40	2,3,4'-triCl	1931.9	triCl
41	3,4,2'-triCl + 2,3-diCl-3-iPr	1942.8	triCl + iPr-diCl
42	4,4'-diiPr	1963.2	diiPr
43	2,5,2',5'-tetraCl	1966.4	tetraCl
44	2,4,2',5'-tetraCl	1981.0	tetraCl
45		1983.1	tetraCl
46	2,3,2',5'-tetraCl	1988.9	tetraCl
47	2,4,2',4'-tetraCl	1997.8	tetraCl
48		2004.8	triiPr
51	3,5,4'-triCl + 2,3,4,2'-tetraCl	2011.9	triCl + tetraCl
52		2014.7	tetraCl
53	3,5-diCl-3'-iPr	2019.3	iPr-diCl
54		2026.9	tetraCl + iPr-triCl
55	3,4,3'-triCl	2037.3	triCl
56	3,4,4'-triCl	2051.8	triCl
57	3,4-diCl-3'-iPr	2053.0	iPr-diCl
58		2058.7	tetraCl + pentaCl
59	3,5-diCl-4'-iPr	2068.6	iPr-diCl
60	3,5,4'-triiPr	2071.5	triiPr + tetraCl
61		2079.3	iPr-diCl
62		2082.6	iPr-diCl + iPr-triCl
64	2,3,3',5'-tetraCl	2087.0	tetraCl
65		2090.8	iPr-triCl
66		2096.0	tetraCl
67	2,5,3',4'-tetraCl	2103.9	tetraCl
68	2,3,4,3'-tetraCl	2108.4	tetraCl + triiPr
69	2,4,3',4'-tetraCl	2114.1	tetraCl
70	2,3,3',4'-tetraCl	2122.0	tetraCl + tetraiPr
71		2129.3	iPr-triCl + pentaCl
72		2134.4	tetraCl + hexaCl
73		2143.4	iPr-triCl
74		2146.8	pentaCl
76		2163.0	pentaCl

TABLE VIII

## FID RESPONSE FACTORS FOR PCBs

Measured on glass capillary columns coated with OV-101 at 200°. Anthracene was used as standard ( $f_i = 1.00$ ).  $f_i$  = Mean value of the response factors from three measurements;  $s$  = standard deviation.

Compound	$f_i$	$s$	Compound	$f_i$	$s$
3	1.14	0.07	2,5,4'	1.40	0.04
2,2'	1.26	0.01	2,4,4'	1.82	0.05
2,3'	1.49	0.06	2,3,4'	1.45	0.04
2,5	1.33	0.01	2,6,2',6'	1.52	0.05
2,4'	1.27	0.01	2,4,2',4'	1.57	0.05
2,6	1.18	0.06	2,5,2',5'	1.59	0.04
4,4'	1.26	0.03	2,4,2',5'	1.61	0.05
2,4	1.24	0.06	2,3,2',3'	1.61	0.05
3,5	1.22	0.06	2,3,2',5'	1.59	0.04
3,3'	1.33	0.01	2,5,3',4'	1.61	0.05
3,4'	1.30	0.01	3,4,3',4'	1.84	0.02
2,5,2'	1.32	0.04	2,3,4,2',5'	1.85	0.02
3,5,3'	1.42	0.05			

ions ( $M^+$ ) and fragment ions ( $[M - Cl]^+$ ,  $[M - 2Cl]^+$ , etc.) This indicates that the metal interface also causes a catalytic redistribution of the chlorine substituents. Dechlorination and redistribution phenomena have previously been observed in metal capillary columns<sup>6</sup>.

*Quantitative analysis*

Knowledge of the quantitative composition of the studied mixtures can be applied as an additional tool in the identification of gas chromatographic peaks. Results of quantitative analysis, obtained on columns with stationary phases of different polarity, can be used for the detection of overlapping peaks.

An FID was used for the analyses of PCBs and IPCBs. Its response depends *inter alia* on the number of chlorine atoms. This effect in the analysis of commercial mixtures of PCBs was studied using the internal standard method<sup>12</sup>. Anthracene was chosen as internal standard. From analyses of model mixtures, prepared from standard PCBs and anthracene, flame response factors ( $f_i$ ) were estimated according to

$$f_i = \frac{n_i}{n_s} \cdot \frac{A_s}{A_i}$$

where  $n$  is the amount in mg and  $A$  is the peak area. The subscript  $i$  denotes the respective PCB and  $s$  refers to anthracene.

The calculated flame response factors for standard PCBs are listed in Table VIII. It can be concluded that response factors increase with increasing number of chlorine atoms in the molecule. Mean values of the correction factors for dichlorobiphenyls ( $f_i = 1.29$ ), trichlorobiphenyls ( $f_i = 1.48$ ) and tetrachlorobiphenyls ( $f_i = 1.62$ ) were used for quantitative analysis of the compounds which were not available as standards. The concentration of a component in the mixture was calculated as

$$W_i = f_i \cdot \frac{A_i}{A_s} \cdot \frac{n_s}{n} \cdot 100\%$$

where  $n$  is the total amount of sample in mg. Table IX gives results obtained for the main components of Aroclor 1242, using internal normalization<sup>13</sup> and internal standard methods. The results obtained by the internal normalization method are *ca.* 20% higher than those obtained by the internal standard method. The FID response not only depends on the chlorine content, but also on the carbon content. Therefore the differences between the results of these two methods for the analysis of IPCBs can be as large as 50%.

Table X contains the quantitative results, obtained on three stationary phases, for the main components of Aroclor 1242. The internal normalization method was used in this case. From these results it can be seen which peaks are overlapped on OV-101, Apiezon L and Carbowax 20M. The conclusions agree with the results found by the methods of qualitative analysis, described before.

TABLE IX

## QUANTITATIVE ANALYSIS OF THE MAIN COMPONENTS OF AROCLOR 1242

Measured by internal normalization and internal standard methods on a glass capillary column coated with OV-101 at 200°.

Peak No. (Fig. 1)	Composition (%)	
	Internal normalization	Internal standard
6	3.19	2.52
7	0.33	0.26
8	1.04	0.98
9	8.08	6.45
10	1.06	0.99
11	12.11	10.05
12	5.15	4.79
13	0.65	0.61
14	6.95	7.36
17	1.51	1.30
18	0.52	0.39
19	10.30	9.95
20	8.53	10.06
21	7.92	7.66
22	3.90	3.93
23	0.75	0.73
24	0.29	0.31
25	2.80	3.03
26	2.42	2.46
27	0.93	0.80
28	0.88	0.78
29	2.85	3.34
30	3.96	3.76
31	3.10	3.08
33	0.63	0.58
37	1.55	1.42
38	2.87	2.87
39	3.18	3.42
41	2.53	2.54

TABLE X

## QUANTITATIVE ANALYSIS OF THE MAIN COMPONENTS OF AROCLOR 1242

Measured by the internal normalization method on glass capillary columns coated with OV-101, Apiezon L and Carbowax 20M at 200°.

PCB derivative	Composition (%)		
	OV-101	Apiezon L	Carbowax 20M
2,2'	3.19	3.07	3.15
2,3'	1.04	1.06	1.08
2,4'	8.08	8.07	8.07
2,6,2'	1.06	1.11	1.05
2,5,2'	12.11 + ?	10.74	14.90 + 2,4,2'
2,4,2'	5.15 + 4,4'	4.47	14.90 + 2,5,2'
4,4'	5.15 + 2,4,2'	2.41	5.19 + 2,6,4'
2,3,2'	6.95 + 2,6,4'	4.47	5.86 + 2,5,3'
2,6,4'	6.95 + 2,3,2'	2.78 + 3,4'	5.19 + 4,4'
2,5,3'	1.51	1.59	5.86 + 2,3,2'
2,4,3'	0.52	0.73	0.67
2,5,4'	10.30 + ?	9.42	9.05
2,4,4'	8.53	17.34 + 3,4,2'	10.44
3,4,2'	7.92	17.34 + 2,4,4'	7.38
3,4,3'	3.90		10.90 + 2,5,2',5' + 2,4,2',5'
2,5,2',5'	2.80	2.99	10.90 + 2,4,2',5' + 3,4,3'
3,4,4'		2.59	2.58
2,4,2',5'	2.42	2.32	10.90 + 3,4,3' + 2,5,2',5'
2,4,2',4'	0.93	1.08	1.00
2,3,2',5'	2.85	2.96	4.20 + ?
2,3,2',3'	0.63	0.83	3.78 + 2,5,3',4'
2,5,3',4'	2.87	2.65	3.78 + 2,3,2',3'

## ACKNOWLEDGEMENTS

Support by the Scientific Exchange Agreement is acknowledged. We thank Dr. J. Kříž, University of Technology, Prague, for supplying many pure PCBs and Mr. J. Smolders, Eindhoven University of Technology, for checking this manuscript.

## REFERENCES

- 1 S. Begum, J. P. Lay, W. Klein and F. Korte, *Chemosphere*, 4 (1975) 241.
- 2 L. O. Ruzo, G. Sundström, O. Hutzinger and S. Safe, *Chemosphere*, 5 (1976) 71.
- 3 G. Sundström, O. Hutzinger, F. W. Karasek and J. Michnowitz, *J. Ass. Offic. Anal. Chem.*, 59 (1976) 982.
- 4 Z. Červenka, unpublished results, 1978.
- 5 K. Hyška, *Chem. Prum.*, 21 (1971) 264.
- 6 J. Krupčík, P. A. Leclercq, A. Šimová, P. Suchánek, M. Čollák and J. Hrivňák, *J. Chromatogr.*, 119 (1976) 271.
- 7 J. Krupčík, M. Kristín, M. Valachovičová and Š. Janiga, *J. Chromatogr.*, 126 (1976) 147.
- 8 J. G. Leferink and P. A. Leclercq, *J. Chromatogr.*, 91 (1974) 385.
- 9 M. Zell, H. J. Neu and K. Ballschmitter, *Chemosphere*, 6 (1977) 69.
- 10 D. Sissons and D. Welti, *J. Chromatogr.*, 60 (1971) 15.
- 11 P. W. Albro, J. K. Haseman, T. A. Clemmer and B. J. Corbett, *J. Chromatogr.*, 136 (1977) 147.
- 12 M. Ugava, A. Nakamura and T. Kashimoto, *New Methods in Environmental Chemistry and Toxicology*, International Academic Printing Co., Totsuka, Tokio, 1973.
- 13 A. B. Littlewood, *Gas Chromatography*, Academic Press, New York, 1970.