Fresenius Z. Anal. Chem. 302, 20–31 (1980)

Fresenius Zeitschrift für Analytische Chemie

Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography

Composition of Technical Aroclor- and Clophen-PCB Mixtures

K. Ballschmiter and M. Zell

Abteilung Analytische Chemie, Universität Ulm, D-7900 Ulm/Donau, Federal Republic of Germany

Analyse der polychlorierten Biphenyle (PCB) durch Glas-Capillar-Gas-Chromatographie

Zusammensetzung der technischen Aroclor- und Clophen-PCB Mischungen

Zusammenfassung. Die Zusammensetzung sieben technischer Gemische polychlorierter Biphenyle (PCB) mit unterschiedlichem Chlorierungsgrad (Aroclor- [Monsanto, USA] und Clophen A- [Bayer, Bundesrepublik Deutschland] -Typen) wurde mit hochauflösender Gas-Chromatographie mit Elektroneneinfang-Detektion in Dünnfilm-Glascapillaren mit Methylpolysiloxan (SE 30) und gereinigtem Apiezon L als flüssiger Phase untersucht. Die Identifizierung der Einzelkomponenten erfolgte durch chromatographischen Vergleich mit definierten Referenzsubstanzen oder Vergleich der aus Inkrementen berechneten Retentionsindices. Für die Kennzeichnung der Einzelkomponenten wird eine systematische Numerierung entsprechend der Substituentenbezifferung verwendet.

Summary. The composition of seven technical PCB-mixtures (Aroclor [Monsanto, USA] und Clophen A [Bayer, FRG]) has been investigated by high-resolution thin-film glass capillary gas chromatography with electron-capture detector. Methylpolysiloxane (SE 30) and purified Apiezon L have been used as liquid phases. Identification of the single PCB components has been performed by comparison of their retention indices with those of polychlorinated biphenyls defined by synthesis or with values calculated from retention index increments. For marking the individual PCB compounds a systematic numbering has been used.

Key words: Analyse von Polychlorbiphenylen, Aroclor, Clophen; Chromatographie, Gas; Glascapillaren, Electron capture

Herrn Prof. Dr. R. Bock zum 65. Geburtstag gewidmet

1. Introduction

The chemistry of the polychlorinated biphenyls (PCB) has been reviewed recently [14]. The world wide occurrence of PCB seems to be well established [11, 23, 25, 33, 34]. The overall world production since 1929 is guessed to be close to $2 \cdot 10^9$ kg [3, 14, 20, 23]. Though the production of PCB will eventually slow down in the global scale, the input of PCB into the environment will continue. The problems associated with the manufacture, use and disposal of PCB have been summarized in a conference report compiled by the U.S. Environmental Protection Agency [20].

For a thorough analysis of PCB in environmental samples the composition of the underlying technical mixtures has to be known [4, 5, 19, 27, 28, 38]. The quantitation of PCB requires single component identification as well as a discussion of the structural aspects of their degradation or toxicology [12, 34, 38]. The task of identifying single components in technical PCB mixtures by capillary gas chromatography has been undertaken by several authors [1, 2, 15, 18, 30, 36]. A detailed analysis of all Clophen trademark PCB has been published recently [37]. Table 1 summarizes the main technical PCB mixtures produced in the USA and West Germany.

Table 1. Trade names and chlorine contents of major technical PCB mixtures (for further brands see [14])

% Chlorine	Cl/Mol	Trade names	
		Bayer, FRG	Monsanto, USA
41	3.0	–	Aroclor 1016[a]
42	3.10	Clophen A 30	Aroclor 1242
54	4.96	Clophen A 50	Aroclor 1254
60	6.30	Clophen A 60	Aroclor 1260
68	8.70	–	Aroclor 1268

[a] Reduced content of pentachlorobiphenyls and hexachlorobiphenyls compared to Aroclor 1242, see Fig. 1

0016-1152/80/0302/0020/$02.40

Table 2. Systematic numbering of PCB compounds. The number is used as a synonym for the corresponding PCB compound in tables and figures

No.	Structure
	Monochlorobiphenyls
1	2
2	3
3	4
	Dichlorobiphenyls
4	2,2′
5	2,3
6	2,3′
7	2,4
8	2,4′
9	2,5
10	2,6
11	3,3′
12	3,4
13	3,4′
14	3,5
15	4,4′
	Trichlorobiphenyls
16	2,2′,3
17	2,2′,4
18	2,2′,5
19	2,2′,6
20	2,3,3′
21	2,3,4
22	2,3,4′
23	2,3,5
24	2,3,6
25	2,3′,4
26	2,3′,5
27	2,3′,6
28	2,4,4′
29	2,4,5
30	2,4,6
31	2,4′,5
32	2,4′,6
33	2′,3,4
34	2′,3,5
35	3,3′,4
36	3,3′,5
37	3,4,4′
38	3,4,5
39	3,4′,5
	Tetrachlorobiphenyls
40	2,2′,3,3′
41	2,2′,3,4
42	2,2′,3,4′
43	2,2′,3,5
44	2,2′,3,5′
45	2,2′,3,6
46	2,2′,3,6′
47	2,2′,4,4′
48	2,2′,4,5
49	2,2′,4,5′
50	2,2′,4,6
51	2,2′,4,6′
	Tetrachlorobiphenyls
52	2,2′,5,5′
53	2,2′,5,6′
54	2,2′,6,6′
55	2,3,3′,4
56	2,3,3′,4′
57	2,3,3′,5
58	2,3,3′,5′
59	2,3,3′,6
60	2,3,4,4′
61	2,3,4,5
62	2,3,4,6
63	2,3,4′,5
64	2,3,4′,6
65	2,3,5,6
66	2,3′,4,4′
67	2,3′,4,5
68	2,3′,4,5′
69	2,3′,4,6
70	2,3′,4′,5
71	2,3′,4′,6
72	2,3′,5,5′
73	2,3′,5′,6
74	2,4,4′,5
75	2,4,4′,6
76	2′,3,4,5
77	3,3′,4,4′
78	3,3′,4,5
79	3,3′,4,5′
80	3,3′,5,5′
81	3,4,4′,5
	Pentachlorobiphenyls
82	2,2′,3,3′,4
83	2,2′,3,3′,5
84	2,2′,3,3′,6
85	2,2′,3,4,4′
86	2,2′,3,4,5
87	2,2′,3,4,5′
88	2,2′,3,4,6
89	2,2′,3,4,6′
90	2,2′,3,4′,5
91	2,2′,3,4′,6
92	2,2′,3,5,5′
93	2,2′,3,5,6
94	2,2′,3,5,6′
95	2,2′,3,5′,6
96	2,2′,3,6,6′
97	2,2′,3′,4,5
98	2,2′,3′,4,6
99	2,2′,4,4′,5
100	2,2′,4,4′,6
101	2,2′,4,5,5′
102	2,2′,4,5,6′
103	2,2′,4,5′,6
104	2,2′,4,6,6′
	Pentachlorobiphenyls
105	2,3,3′,4,4′
106	2,3,3′,4,5
107	2,3,3′,4′,5
108	2,3,3′,4,5′
109	2,3,3′,4,6
110	2,3,3′,4′,6
111	2,3,3′,5,5′
112	2,3,3′,5,6
113	2,3,3′,5′,6
114	2,3,4,4′,5
115	2,3,4,4′,6
116	2,3,4,5,6
117	2,3,4′,5,6
118	2,3′,4,4′,5
119	2,3′,4,4′,6
120	2,3′,4,5,5′
121	2,3′,4,5′,6
122	2′,3,3′,4,5
123	2′,3,4,4′,5
124	2′,3,4,5,5′
125	2′,3,4,5,6′
126	3,3′,4,4′,5
127	3,3′,4,5,5′
	Hexachlorobiphenyls
128	2,2′,3,3′,4,4′
129	2,2′,3,3′,4,5
130	2,2′,3,3′,4,5′
131	2,2′,3,3′,4,6
132	2,2′,3,3′,4,6′
133	2,2′,3,3′,5,5′
134	2,2′,3,3′,5,6
135	2,2′,3,3′,5,6′
136	2,2′,3,3′,6,6′
137	2,2′,3,4,4′,5
138	2,2′,3,4,4′,5′
139	2,2′,3,4,4′,6
140	2,2′,3,4,4′,6′
141	2,2′,3,4,5,5′
142	2,2′,3,4,5,6
143	2,2′,3,4,5,6′
144	2,2′,3,4,5′,6
145	2,2′,3,4,6,6′
146	2,2′,3,4′,5,5′
147	2,2′,3,4′,5,6
148	2,2′,3,4′,5,6′
149	2,2′,3,4′,5′,6
150	2,2′,3,4′,6,6′
151	2,2′,3,5,5′,6
152	2,2′,3,5,6,6′
153	2,2′,4,4′,5,5′
154	2,2′,4,4′,5,6′
155	2,2′,4,4′,6,6′
156	2,3,3′,4,4′,5
157	2,3,3′,4,4′,5′
158	2,3,3′,4,4′,6
159	2,3,3′,4,5,5′
160	2,3,3′,4,5,6
	Hexachlorobiphenyls
161	2,3,3′,4,5′,6
162	2,3,3′,4′,5,5′
163	2,3,3′,4′,5,6
164	2,3,3′,4′,5′,6
165	2,3,3′,5,5′,6
166	2,3,4,4′,5,6
167	2,3′,4,4′,5,5′
168	2,3′,4,4′,5′,6
169	3,3′,4,4′,5,5′
	Heptachlorobiphenyls
170	2,2′,3,3′,4,4′,5
171	2,2′,3,3′,4,4′,6
172	2,2′,3,3′,4,5,5′
173	2,2′,3,3′,4,5,6
174	2,2′,3,3′,4,5,6′
175	2,2′,3,3′,4,5′,6
176	2,2′,3,3′,4,6,6′
177	2,2′,3,3′,4′,5,6
178	2,2′,3,3′,5,5′,6
179	2,2′,3,3′,5,6,6′
180	2,2′,3,4,4′,5,5′
181	2,2′,3,4,4′,5,6
182	2,2′,3,4,4′,5,6′
183	2,2′,3,4,4′,5′,6
184	2,2′,3,4,4′,6,6′
185	2,2′,3,4,5,5′,6
186	2,2′,3,4,5,6,6′
187	2,2′,3,4′,5,5′,6
188	2,2′,3,4′,5,6,6′
189	2,3,3′,4,4′,5,5′
190	2,3,3′,4,4′,5,6
191	2,3,3′,4,4′,5′,6
192	2,3,3′,4,5,5′,6
193	2,3,3′,4′,5,5′,6
	Octachlorobiphenyls
194	2,2′,3,3′,4,4′,5,5′
195	2,2′,3,3′,4,4′,5,6
196	2,2′,3,3′,4,4′,5′,6
197	2,2′,3,3′,4,4′,6,6′
198	2,2′,3,3′,4,5,5′,6
199	2,2′,3,3′,4,5,6,6′
200	2,2′,3,3′,4,5′,6,6′
201	2,2′,3,3′,4′,5,5′,6
202	2,2′,3,3′,5,5′,6,6′
203	2,2′,3,4,4′,5,5′,6
204	2,2′,3,4,4′,5,6,6′
205	2,3,3′,4,4′,5,5′,6
	Nonachlorobiphenyls
206	2,2′,3,3′,4,4′,5,5′,6
207	2,2′,3,3′,4,4′,5,6,6′
208	2,2′,3,3′,4,5,5′,6,6′
	Decachlorobiphenyl
209	2,2′,3,3′,4,4′,5,5′,6,6′

2. Materials and Instruments

Reference Compounds. The reference compounds were partly a gift from Bayer AG (Leverkusen, FRG) and were partly obtained from NEN Chemicals, Dreieichenhain, FRG; Analabs, North Haven, Conn., USA; RFR Corp., Hope, R. I., USA, and Aldrich Europe, Beerse, Belgium.

Solvents. All solvents were pesticide analysis grade.

Adsorbents. Florisil, 60 – 100 mesh ASTM; Merck, Darmstadt, FRG.

Glass Capillaries. Own preparation; soda lime glass; HCl gas phase etching; carbowax high temperature desactivation; static coating; phase ratio 1,000; i.d. 0.3 mm; length 40 m.

Liquid Phase. a) Methylpolysiloxane SE 30, GC grade; b) Alicyclic hydrocarbon Apiezon L, purified.

Fractionation of Apiezon L. 0.5 g of Apiezon L are dissolved in 5 ml of n-hexane. This solution is transferred onto a solvent packed Florisil column (1% H_2O) (10 g). 200 ml of n-hexane will elute a slightly yellow product. This fraction is being used for coating glass capillaries. Fractionated Apiezon L brings the temperature stability of the GC capillaries up to 240° C.

Instruments. a) Gas chromatograph Varian 3700. Electron capture detector: constant current mode. Conditions of gas chromatography: carrier gas: hydrogen; splitless on-column injection; temperature program: injection at 40° C; 2 min at 40° C; 40 – 140° C temperature program 50° C/min; 3 min at 140° C; 140 – 190° C temperature program 1.6° C/min; 190° C isothermal.

Instruments. b) Gas chromatograph Carlo Erba Fractovap 2150; Flame ionization detector; isothermal operation.

3. Systematic Numbering of PCB Compounds

Isolation and synthesis of PCB compounds of defined chlorination patterns have made available only about one third of the 209 PCB as reference compounds [14]. Retention index addition is therefore the only other way to identify those not available as reference compounds [2, 30, 36]. It is also the only way to check the bias of any matching of unknown and reference compound.

To rationalize the identification of defined PCB components in figures and tables, we have developed a scheme of numbering the PCB that follows the IUPAC rules of substituent characterization in biphenyls [14]. The number of position according to this arrangement is taken as an abbreviation for the PCB structure. Table 2 summarizes this correlation of "PCB number" and PCB structure. The PCB numbers are used throughout this paper to characterize any individual PCB component.

4. Composition of Technical PCB Mixtures

Though the production of PCB largely follows the same scheme world-wide [16, 32], minor differences in composition of technical mixtures are encountered. Figures 1 – 3 compare the most widely used technical PCB mixtures Clophen (Bayer, FRG) and Aroclor (Monsanto, USA) (Table 1) on a methylpolysiloxane phase SE 30 glass capillary column. Details of chromatographic conditions are reported in the section gas chromatography.

Depending on the chemistry of the glass surface, methyl-silicon phases like OV 1 or SE 30 do not or only partly resolve the PCB with the 2,4- and 2,5-patterns. The separation of the 2,4- and 2,5-moiety is best achieved by more polar liquid silicon phases or by Apiezon L. The 2,4-substitution belongs to the environmentally recalcitrant patterns and therefore is enhanced in environmental samples [27, 38].

Figures 4 and 5 present the elution pattern of technical Clophen and Aroclor mixtures on an Apiezon L glass capillary column. The PCB eluate from this complex alicyclic hydrocarbon stationary phase in a different order than from SE 30. Using the relative intensities and the different elution pattern, the PCB identification can be counterchecked.

5. Calculation of Retention Indices

Identification of PCB components, that are not available as reference compounds, can be performed by calculation of their retention indices. Sissons and Welti extensively used the method of increment addition in their early report of identification of single PCB components in technical mixtures [30]. The retention index increments for defined substitution pattern are measured on unpolar phases and are added for new combinations of substitution [2, 38]. The rationale for this method is the linear additivity of dispersion forces [17]. Any extended polar interaction will require a vectorial addition. The precision of retention index measurements has been increased substantially since that time [21, 22]. Table 3 summarizes the retention indices (Apiezon L, 180° C) of the different PCB compounds present in Clophen type PCB mixtures. The values are based on index measurements using the n-alkanes as reference homologues. Retention indices of the PCB can be measured by electron capture detector using n-alkyltrichloroacetates as reference homologues [21].

The numerical value of the retention index of a single PCB component strongly depends on the separation characteristics of the individual glass capillary. Glass type and surface, its chemical modification, the type of desactivation and the liquid phase together form the "stationary phase" involved in separation. No standard retention indices of PCB components can be indexed so far. Despite this drawback the identification of PCB components can be done by retention index matching of unknowns with reference compounds

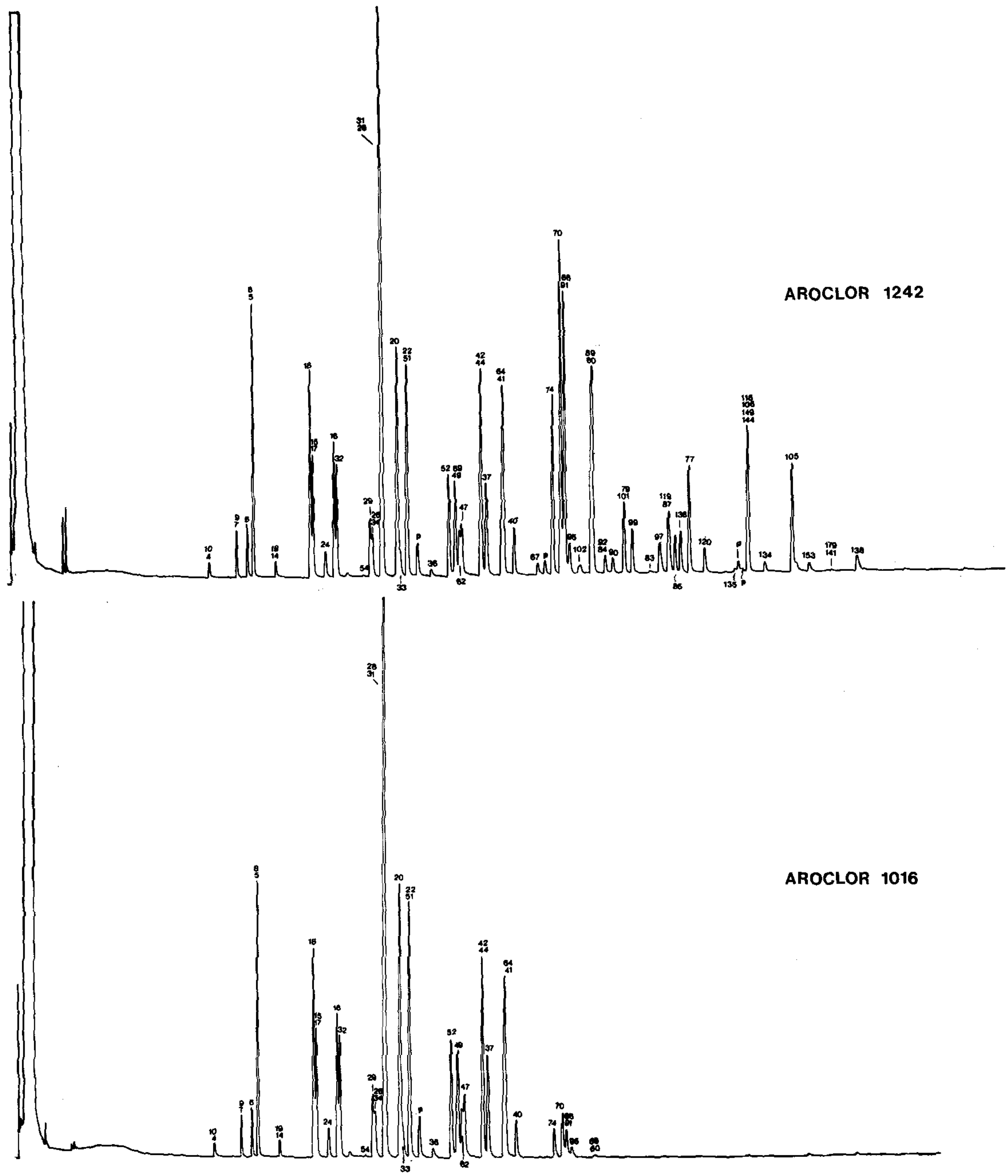

Fig. 1. Glass capillary gas chromatogram with electron capture detection (*ECD*) of technical polychlorinated biphenyl (*PCB*) mixtures. Aroclor 1242 = 42 % chlorine; Aroclor 1016 = 41 % chlorine (Monsanto, USA). Liquid phase: Methylpolysiloxan: SE 30, GC. Condition of gas chromatography see experimental section. Numbering correlates to PCB structure, see Table 2

Fig. 2. Glass capillary gas chromatogram with electron capture detection (*ECD*) of technical polychlorinated biphenyl (*PCB*) mixtures. Aroclor 1260 = 60 % chlorine; Aroclor 1254 = 54 % chlorine (Monsanto, USA). Liquid phase: Methylpolysiloxan: SE 30, GC. Conditions of gas chromatography see experimental section. Numbering correlates to PCB structure, see Table 2

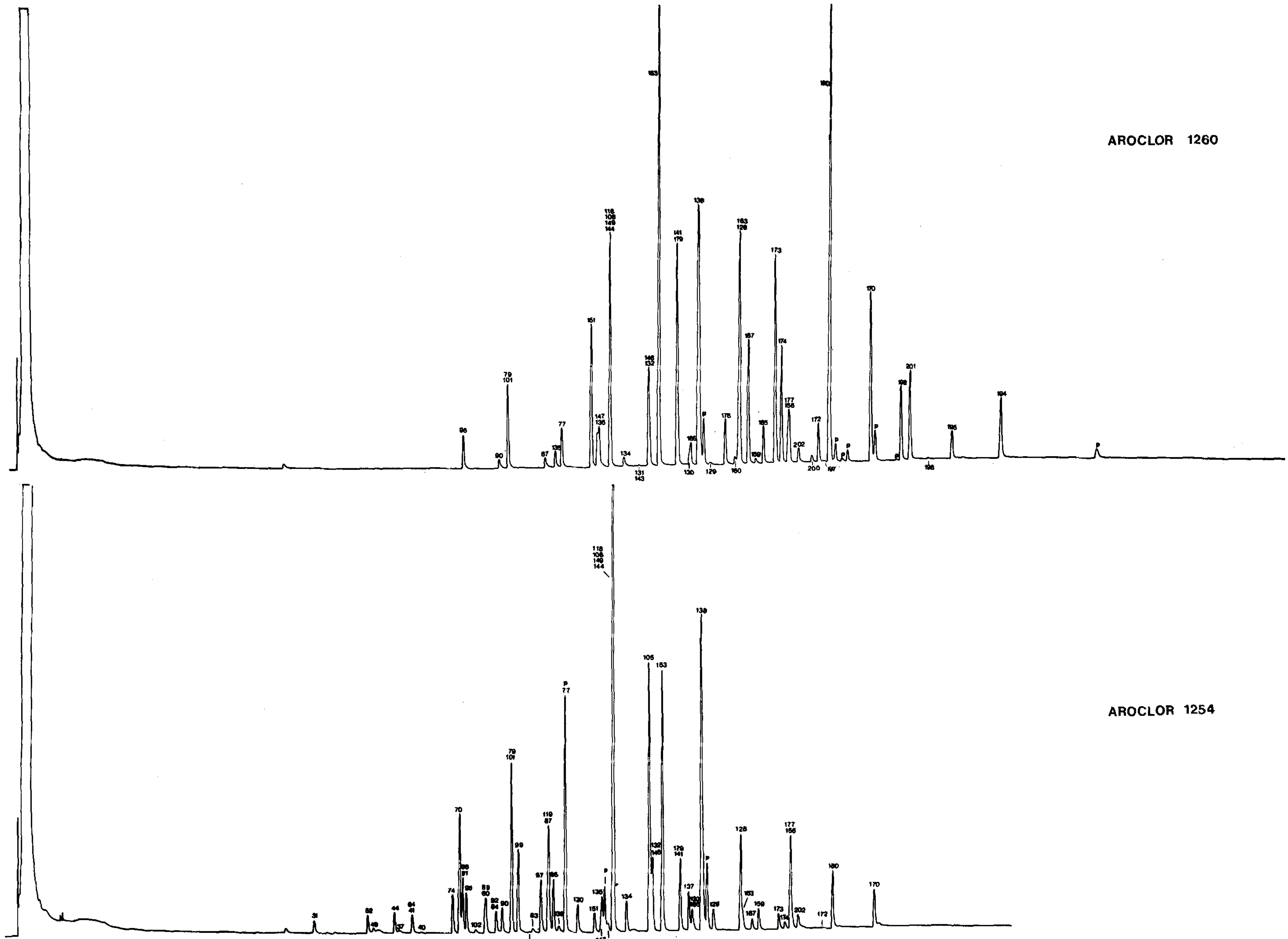

Fig. 2 (Legend see page 23)

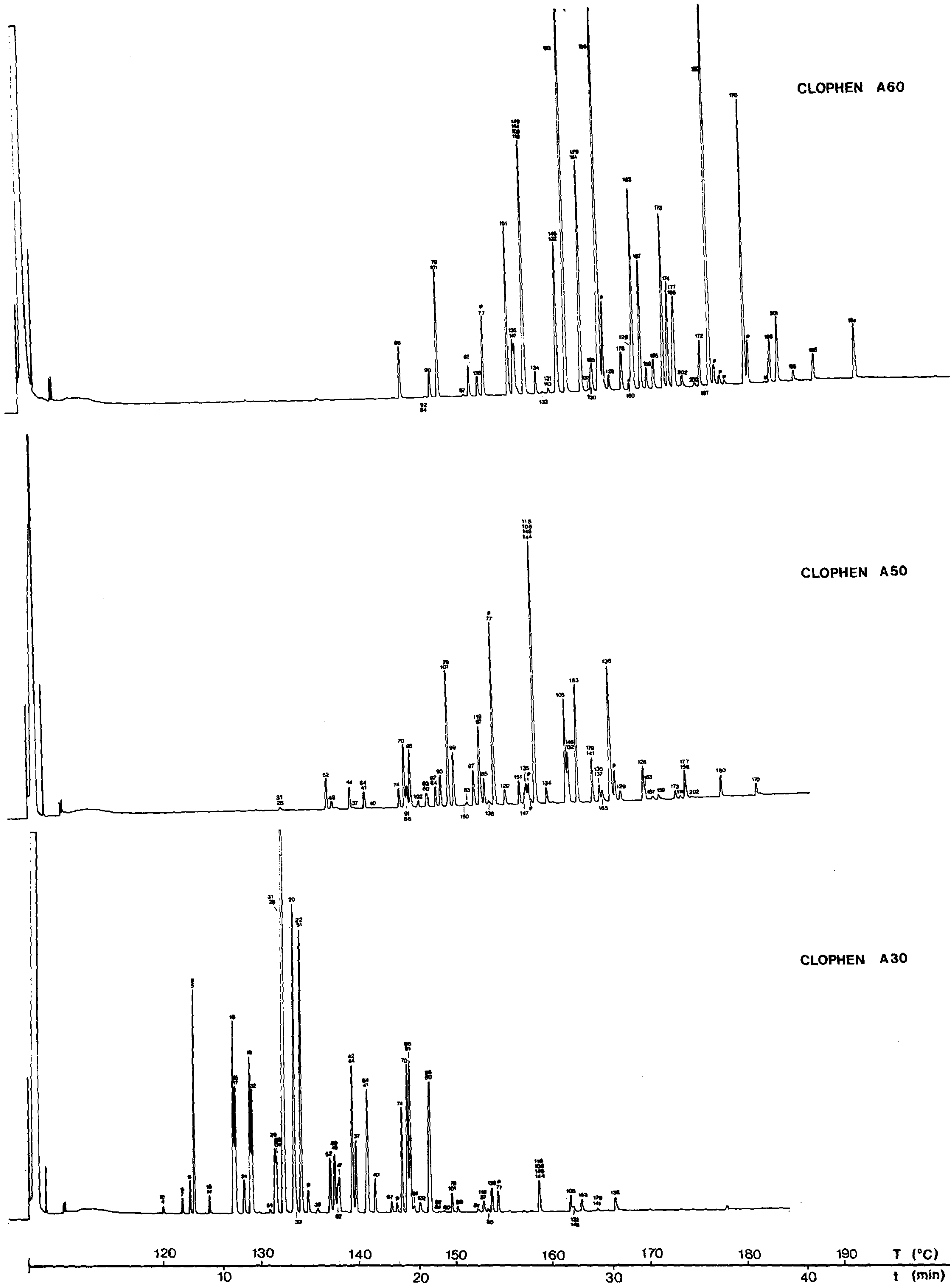

Fig. 3 (Legend see page 26)

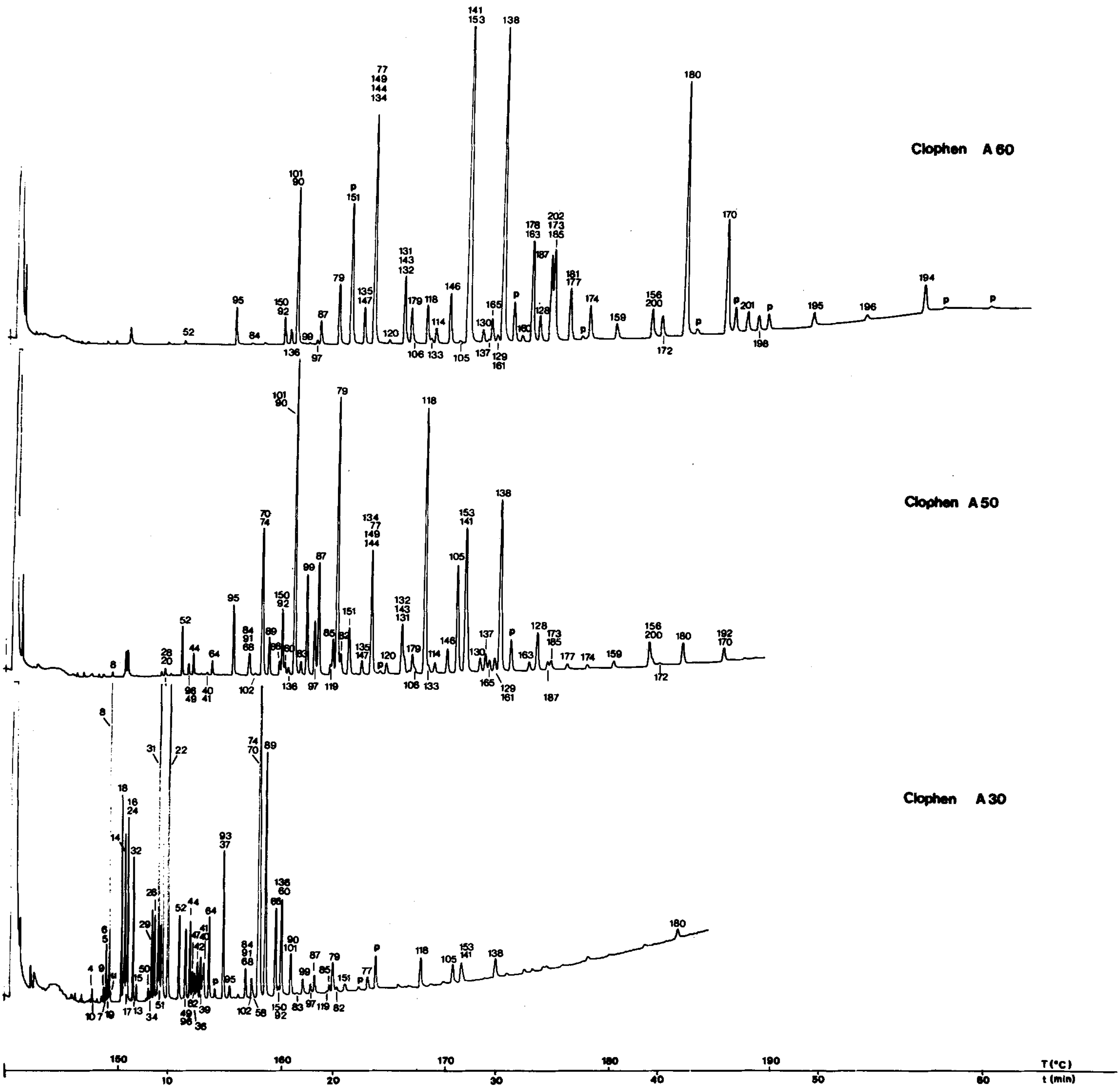

Fig. 4

Fig. 3. Glass capillary gas chromatogram with electron capture detection (*ECD*) of technical polychlorinated biphenyl (*PCB*) mixtures. Clophen A 60 = 60% chlorine; Clophen A 50 = 54% chlorine; Clophen A 30 = 42% chlorine (Bayer, FRG). Liquid phase: Methylpolysiloxan: SE 30, GC. Conditions of gas chromatography see experimental section. Numbering correlates to PCB structure, see Table 2

Fig. 4. Glass capillary gas chromatogram with electron capture detection (*ECD*) of technical polychlorinated biphenyl (*PCB*) mixtures. Clophen A 60 = 60% chlorine; Clophen A 50 = 54% chlorine; Clophen A 30 = 42% chlorine; (Bayer, FRG). Liquid phase: Apiezon L (yellow fraction). Conditions of gas chromatography see experimental section. Numbering correlates to PCB structure see Table 2

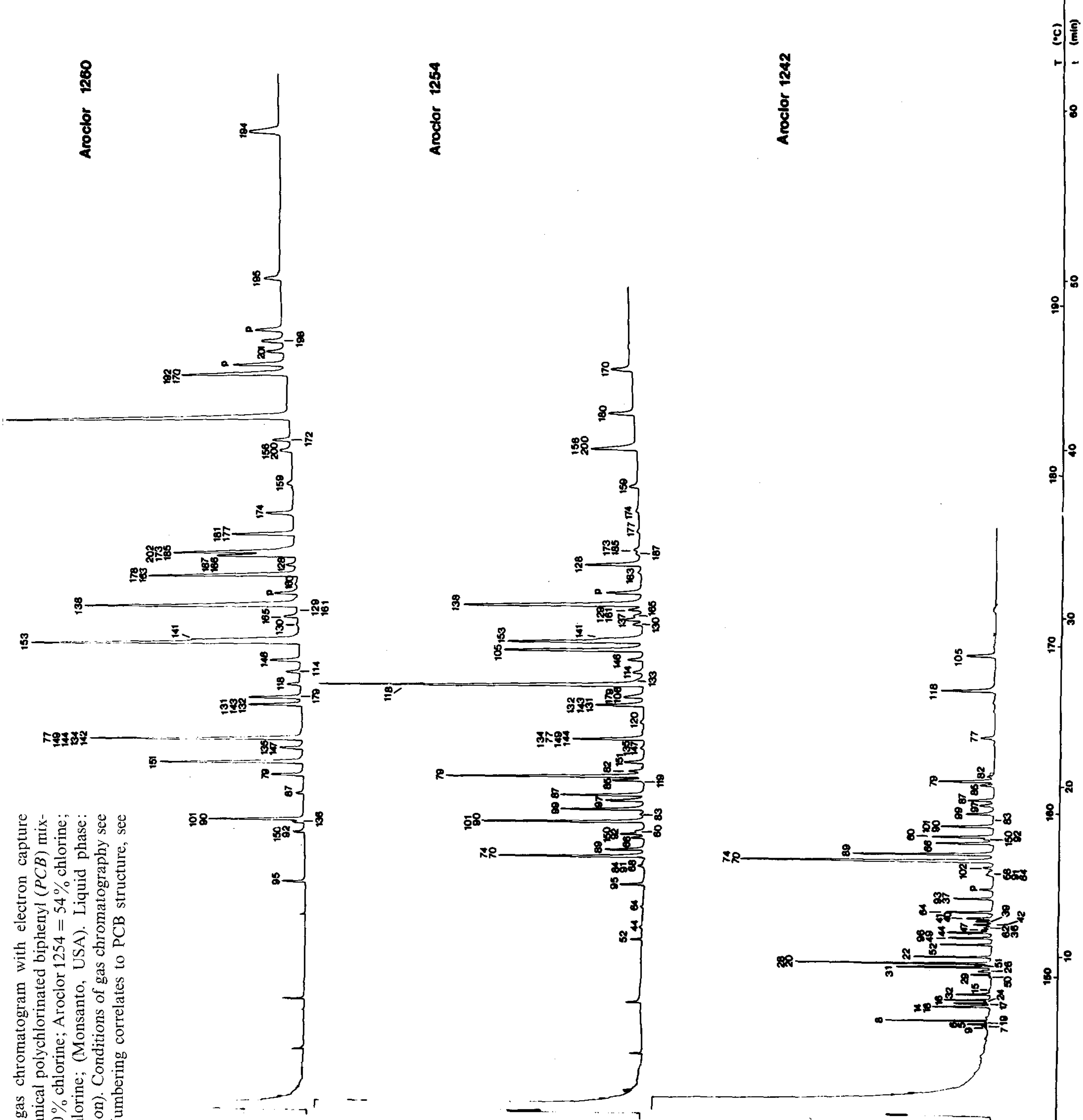

Fig. 5. Glass capillary gas chromatogram with electron capture detection (*ECD*) of technical polychlorinated biphenyl (*PCB*) mixtures. Aroclor 1260 = 60% chlorine; Aroclor 1254 = 54% chlorine; Aroclor 1242 = 42% chlorine; (Monsanto, USA). Liquid phase: Apiezon L (yellow fraction). Conditions of gas chromatography see experimental section. Numbering correlates to PCB structure, see Table 2

Table 3. Measured and calculated retention indices of PCB compounds present in Clophen type PCB mixtures; liquid phase: Apiezon L; temperature: 180° C; detector: FID; homologues: n-alkanes. The PCB compounds given with measured retention indices were available as reference substances. Their structures have been characterized either by synthesis and/or by NMR-spectroscopy and MS

PCB peak no.	PCB structure	Retention index measured	Retention index calculated	PCB components present in:		
				Clophen A 30	Clophen A 50	Clophen A 60
0	bp	1,445.8		1,446.3		
				1,526.0		
1	2	1,538.5		1,538.5		
4	2,2′	1,630.6		1,630.9		
10	2,6	1,637.9		1,637.5		
9	2,5	1,709.2	–	1,709.0		
7	2,4	1,716.5		1,720.6	–	1,720.3
5	2,3	1,729.8		1,730.6	–	1,730.7
6	2,3′		1,727.02	–	–	–
19	2,2′,6	1,731.1	–	1,731.1	–	–
8	2,4′	1,738.2	–	1,738.3	1,738.1	1,738.1
				1,768.3	–	–
18	2,2′,5	1,793.2	–	1,793.3	1,792.7	1,793.0
14	3,5	1,797.6	–	1,800.0	–	–
17	2,2′,4	–	1,807.7	1,807.3	1,806.9	1,806.9
16	2,2′,3	1,815.3	–	–	1,815.2	1,815.3
24	2,3,6	1,815.8	–	1,815.8	–	–
13	3,4′	–	1,833.4	1,833.9	–	–
32	2,4′,6	–	1,837.1	1,836.0	1,835.5	1,835.6
15	4,4′	1,848.8	–	1,849.0	–	1,849.0
50	2,2′,4,6	–	1,872.3	1,872.7	–	–
				1,881.1	1,880.6	–
29	2,4,5	1,891.0	–	1,892.2	1,891.3	–
34	2′,3,5	–	1,890.4	1,892.2	1,891.3	–
26	2,3′,5	–	1,897.6	1,900.0	1,899.8	–
25	2,3′,4	–	1,904.9	1,905.0	–	–
51	2,2′,4,6′	–	1,908.16	–	–	–
31	2,4′,5	–	1,910.7	1,911.1	1,910.7	1,910.6
28	2,4,4′	1,920.5	–	1,920.0	1,919.6	1,919.5
20	2,3,3′	–	1,918.6	1,920.0	1,919.6	1,919.5
22	2,3,4′	–	1,929.0	1,932.5	1,931.8	–
52	2,2′,5,5′	1,955.4	–	1,956.1	1,955.8	1,955.6
96	2,2′,3,6,6′	–	1,970.7	–	1,970.2	–
49	2,2′,4,5′	–	1,971.9	1,970.7	–	–
44	2,2′,3,5′	1,977.6	–	1,977.8	1,977.5	–
47	2,2′,4,4′	1,986.1	–	1,986.5	1,985.8	–
62	2,3,4,6	–	1,986.1	1,986.5	1,985.8	–
36	3,3′,5	–	1,986.4	1,986.5	1,985.8	–
42	2,2′,3,4′	–	–	1,993.4	1,992.7	–
39	3,4′,5	–	1,996.8	1,998.7	1,998.9	–
41	2,2′,3,4	1,999.9	–	2,000.0	–	–
40	2,2′,3,3′	2,000.1	–	2,000.0	–	–
59	2,3,3′,6	–	2,004.6	–	2,002.6	–
64	2,3,4′,6	–	2,015.0	2,015.3	2,015.0	–
93	2,2′,3,5,6	–	2,035.1	–	2,032.7	–
37	3,4,4′	2,038.4	–	2,038.4	2,037.8	–
95	2,2′,3,5′,6	2,047.9	–	–	2,047.5	2,047.8
91	2,2′,3,4′,6	–	2,066.5	–	–	–
68	2,3′,4,5′	–	2,068.2	2,070.8	2,070.8	2,070.7
84	2,2′,3,3′,6	–	2,070.0	2,070.8	2,070.8	2,070.7
102	2,2′,4,5,6′	–	2,072.3	2,073.5	–	–
58	2,3,3′,5′	–	2,081.6	2,083.9	2,082.2	–
70	2,3′,4′,5	2,091.0	–	2,091.0	2,090.7	2,091.0
74	2,4,4′,5	–	2,092.5	2,094.9	2,094.4	–
89	2,2′,3,4,6′	–	2,099.8	2,100.9	–	2,100.2
135	2,2′,3,3′,5,6′	–	2,110.5	2,112.4	2,112.3	–
66	2,3′,4,4′	–	2,110.0	2,112.4	2,112.3	–
92	2,2′,3,5,5′	–	2,118.4	–	2,118.3	2,218.5

Table 3. (continued)

PCB peak no.	PCB structure	Retention index measured	Retention index calculated	PCB components present in:		
				Clophen A 30	Clophen A 50	Clophen A 60
150	2,2′,3,4′,6,6′	–	2,119.5	–	2,118.3	2,118.5
60	2,3,4,4′	2,122.5	–	2,122.4	–	–
136	2,2′,3,3′,6,6′	2,124.9	–	–	2,124.3	2,124.9
101	2,2′,4,5,5′	2,134.5	–	2,134.6	2,134.4	2,134.5
90	2,2′,3,4′,5	–	2,133.5	2,134.6	2,134.4	2,134.5
83	2,2′,3,3′,5	–	2,140.5	–	2,139.0	–
99	2,2′,4,4′,5	2,150.1	–	2,150.5	2,150.1	2,150.1
97	2,2′,3′,4,5	2,157.2	–	2,157.2	2,157.5	2,157.5
87	2,2′,3,4,5′	2,162.0	–	2,161.6	2,161.7	2,161.7
85	2,2′,3,4,4′	–	2,179.1	–	2,179.3	–
82	2,2′,3,3′,4	–	2,184.6	2,182.1	2,181.9	2,181.8
79	3,3′,4,5′	–	2,184.2	2,182.1	2,181.9	2,181.8
119	2,3′,4,4′,6	–	2,184.6	2,182.1	2,181.9	2,181.8
151	2,2′,3,5,5′,6	2,197.7	–	–	2,197.2	2,197.2
135	2,2′,3,3′,5,6′	–	2,210.5	–	2,212.5	2,212.4
147	2,2′,3,4′,5,6	–	2,212.8	–	2,212.5	2,212.4
134	2,2′,3,3′,5,6	–	2,218.8	–	2,220.6	2,220.6
149	2,2′,3,4′,5′,6	–	2,227.2	–	2,227.2	–
144	2,2′,3,4,5′,6	–	2,226.8	–	2,227.2	–
77	3,3′,4,4′	2,227.6	–	2,227.8	–	–
120	2,3′,4,5,5′	–	2,238.1	–	2,237.9	2,237.7
131	2,2′,3,3′,4,6	–	2,248.9	–	2,250.0	2,249.8
143	2,2′,3,4,5,6′	–	2,252.2	–	2,250.0	2,249.8
132	2,2′,3,3′,4,6′	–	2,254.1	–	2,254.9	–
179	2,2′,3,3′,5,6,6′	–	2,258.2	–	–	2,259.4
106	2,3,3′,4,5	2,264.3	–	–	2,263.7	–
118	2,3′,4,4′,5	–	2,277.2	–	2,275.6	2,275.2
133	2,2′,3,3′,5,5′	–	2,280.9	–	–	2,283.1
114	2,3,4,4′,5	2,286.2	–	–	2,286.5	2,286.4
146	2,2′,3,4′,5,5′	–	2,297.0	–	2,297.5	2,297.8
105	2,3,3′,4,4′	2,302.3	–	–	2,302.6	–
153	2,2′,4,4′,5,5′	2,314.1	–	–	2,314.3	2,314.1
141	2,2′,3,4,5,5′	2,314.6	–	–	2,314.3	2,314.1
130	2,2′,3,3′,4,5′	–	2,324.5	–	2,325.1	2,324.9
165	2,3,3′,5,5′,6	–	2,330.8	–	2,331.6	2,331.3
137	2,2′,3,4,4′,5	2,331.3	–	–	2,331.6	2,331.3
161	2,3,3′,4,5′,6	–	2,337.9	–	2,237.0	2,336.3
129	2,2′,3,3′,4,5	2,336.7	–	–	2,337.0	2,336.3
138	2,2′,3,4,4′,5′	2,342.7	–	–	2,343.3	2,343.2
–	–	–	–	–	2,354.6	2,353.7
178	2,2′,3,3′,5,5′,6	–	2,359.4	–	–	2,361.4
160	2,3,3′,4,5,6	–	2,362.0	–	–	2,361.4
163	(2,3,3′,4′,5,6)	–	2,367.3	–	–	2,370.3
128	2,2′,3,3′,4,4′	2,372.0	–	–	2,372.1	–
166	2,3,4,4′,5,6	–	2,374.7	–	–	–
187	2,2′,3,4′,5,5′,6	–	2,375.37	–	–	–
185	2,2′,3,4,5,5′,6	2,385.6	–	–	–	2,385.7
173	2,2′,3,3′,4,5,6	–	2,385.57	–	–	2,385.7
202	2,2′,3,3′,5,5′,6,6′	–	2,391.40	–	–	–
177	2,2′,3,3′,4′,5,6	–	2,402.8	–	–	2,400.4
159	2,3,3′,4,5,5′	–	–	–	–	2,416.8
174	2,2′,3,3′,4,5,6′	–	–	–	–	2,439.4
156	2,3,3′,4,4′,5	2,466.7	–	–	–	2,466.4
172	2,2′,3,3′,4,5,5′	–	2,477.0	–	–	2,475.9
180	2,2′,3,4,4′,5,5′	–	2,494.1	–	–	2,494.4
192	2,3,3′,4,5,5′,6	–	2,524.9	–	–	2,523.0
170	2,2′,3,3′,4,4′,5	–	2,524.3	–	–	2,523.0
–	–	–	–	–	–	2,532.6
–	–	–	–	–	–	2,540.6
–	–	–	–	–	–	2,550.4
201	2,2′,3,3′,4′,5,5′,6	–	2,556.5	–	–	2,558.0

measured in two consecutive runs, Table 3. The precision of this measurement is best when no overlapping of peaks occurs [22]. Preseparation of the PCB as a group by liquid chromatography further supports an unambiguous identification of unknowns as PCB [4, 6, 20, 24, 26, 31].

It should be noted, that any substitution forcing the two phenyl rings into a preferable position requires adjusted increments for predicting unknown structures. This is the reason why the 2,6-substitution increment has different values, depending on whether it is derived from 2,6-dichlorobiphenyl ($I_{2,6}$ = 915.0) or from 2,2′,6,6′-tetrachlorobiphenyl ($I_{2,6}$ = 908.3). A further irregularity is observed, when a strongly increased dipole moment is the result of a substitution pattern, as in 2,3-dichlorobiphenyl ($I_{2,3}$ = 1,006.9) compared to 2,2′,3,3′-tetrachlorobiphenyl ($I_{2,3}$ = 1,000.0). The limitations of index additivity on polar liquid phases and defined structural irregularities have been studied in detail for polybromobiphenyls [13]. Using the correct pattern increments, the elution behaviour of all 209 PCB can be predicted. The agreement with the values measured is in the range of ± 2 retention index units for the same chromatographic system.

6. Simulation of the Mixing Ratios of Complex PCB Patterns

As long as only a PCB mixture of a defined degree of chlorination has to be determined, the preparation of a reference solution is easy. Environmental samples very seldom will give such a single mixture pattern, though a certain type of chlorination might predominate [3, 5, 9, 19, 37].

Complex mixing patterns can be simulated by using the ratios of diagnostic PCB components that are only or predominantly present in PCB mixtures of a defined degree of chlorination. These diagnostic PCB components should be recalcitrant as an additional requirement. This will minimize the problems of fitting degraded PCB mixtures as found e.g. in warm blooded species [27]. Table 4 summarizes such diagnostic peaks for the various PCB mixtures. Particularly important are the PCB components indicative of 54% and 60% chlorine content PCB mixtures. These so called penta- and hexachlorobiphenyl mixtures are found in most of the environmental PCB patterns [5, 25, 37].

Additionally, we have developed a computing program, that on the basis of the internal ratios of all PCB components in the various technical PCB mixtures looks for the closest fit to a given PCB pattern in a sample [39]. The decision-making is regulated by PCB components that are known to be recalcitrant. Otherwise, PCB patterns that show a significant degree of degradation cannot be realistically fitted. Fitting of mixing ratios by a computing program has been done previously for low resolution gas chromatography of PCB [10, 41].

Table 4. Diagnostic peaks for technical PCB products

GC-phase	PCB-No.	Structure
a) with 42% chlorine content		
SE 30	28/31	2,4,4′/2,4′,5
	37	3,4,4′
	66	2,3′,4,4′
Apiezon L	28	2,4,4′
	37	3,4,4′
	66	2,3′,4,4′
b) with 54% chlorine content		
SE 30	85	2,2′,3,4,4′
	99	2,2′,4,4′,5
	137	2,2′,3,4,4′,5
Apiezon L	99	2,2′,4,4′,5
	105	2,3,3′,4,4′
	118	2,3′,4,4′,5
	137	2,2′,3,4,4′,5
c) with 60% chlorine content		
SE 30	170	2,2′,3,3′,4,4′,5
	180	2,2′,3,4,4′,5,5′
	194	2,2′,3,3′,4,4′,5,5′
	195	2,2′,3,3′,4,4′,5,6
	198	2,2′,3,3′,4,5,5′,6
	201	2,2′,3,3′,4′,5,5′,6
Apiezon L	180	2,2′,3,4,4′,5,5′
	194	2,2′,3,3′,4,4′,5,5′
	198	2,2′,3,3′,4,5,5′,6

7. Quantitation of PCB Mixtures

The quantitation of PCB is straightforward when a defined mixture only and no interfering pesticides are present. An interlaboratory study of the determination of PCB (Aroclor 1242) in paper mill effluent using packed columns has been published. In the 2.36–3.36 μg/l range a relative standard deviation of 14.4% was obtained [9].

The aspects of estimation of PCB as a sum after perchlorination to decachlorobiphenyl or reductive dechlorination to biphenyl have been discussed recently [29]. Such an integration method would be most appropriate for quantitation of PCB mixtures, as the PCB pattern will vary in environmental samples collected off any local input and no single standard mixture can be used.

Separation of all PCB components and a simulation of the pattern by a best-fit mixture will allow a quantitation by taking a few diagnostic peaks and a standard solution of the best-fix mixture. Inherent in this method is a systematic error corresponding to the extent of degradation.

The least systematic error will be given by the summation of all or at least nearly all areas of PCB peaks corrected by their individual ECD-response factor and their biphenyl content. Relative molar responses of the electron capture detector to chlorobiphenyls have been published [7, 8, 40]. This method would give a direct measure of the content of chlorinated biphenyl and would require only one PCB compound for a calibration curve. Still one has to decide how to calculate this area sum, either as tetra-, penta- or hexachlorobiphenyl or even only as biphenyl (PCB) as it would seem most appropriate. Modern computing integrators can easily run such a program.

Acknowledgement. This work has been supported by a grant from Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, FRG.

References

1. Albro, P. W., Fishbein, L.: J. Chromatogr. **69**, 273 (1972)
2. Albro, P. W., Hasemann, J. K., Clemmer, T. A., Corbett, B. J.: J. Chromatogr. **135**, 147 (1977)
3. Ballschmiter, K.: Nachr. Chem. Lab. Techn. **27**, 542 (1979)
4. Ballschmiter, K., Zell, M.: Int. J. Environ. Anal. Chem. 1980 (to be published)
5. Ballschmiter, K., Zell, M., Neu, H. J.: Chemosphere **7**, 173 (1978)
6. Brinkmann, U. A. Th., Seetz, J. W. F. L., Reymer, H. G. M.: J. Chromatogr. **116**, 353 (1976)
7. Bush, B., Baker, F., Dellacqua, P., Houck, C. L., Lo, F. C.: J. Chromatogr. **109**, 287 (1975)
8. Chau, A. S. Y., Sampson, R. C. Y.: Environ. Lett. **8**, 89 (1975)
9. Delfino, J. J., Easty, D. B.: Anal. Chem. **51**, 2235 (1979)
10. Eder, G.: Chemosphere **5**, 101 (1976)
11. Fishbein, L.: J. Chromatogr. **68**, 345 (1972)
12. Fishbein, L.: Potential Industrial Carcinogens and Mutagens, pp. 286–294. Amsterdam: Elsevier 1979
13. Heeg, F.: Diplomarbeit, Univ. Ulm 1978
14. Hutzinger, O., Safe, S., Zitko, V.: The Chemistry of PCB's, Cleveland, Ohio: CRC Press 1974
15. Jensen, S., Sundström, G.: Ambio **3**, 70 (1974)
16. Kirk-Othmer: Encyclopedia of Chemical Technology. 3rd ed., Vol. 5, p. 844. New York: Wiley 1979
17. Kovats, E.: Helv. Chim. Acta **41**, 1915 (1958)
18. Krupcik, J., Leclerc, P., Simova, A., Suchanek, P., Collak, M., Hrivuak, J.: J. Chromatogr. **119**, 271 (1976)
19. Mattsson, P. E., Nygren, S.: J. Chromatogr. **124**, 265 (1976)
20. National Conference on Polychlorinated Biphenyls, Nov. 19–21, 1975, Chicago, Ill.: Conference Proceedings EPA-560/6-75-004, U.S. Dept. Commerce, Springfield, Va. 1976
21. Neu, H. J., Zell, M., Ballschmiter, K.: Fresenius Z. Anal. Chem. **293**, 193 (1978)
22. Neu, H. J., Zinburg, R.: HRC and CC **2**, 395 (1979)
23. Nisbet, I. C. T., Sarofin, A. F.: Environ. Health Persp. **1**, 21 (1972)
24. Picer, M., Ahel, M.: J. Chromatogr. **150**, 119 (1978)
25. Risebrough, R. W., de Lappe, B. W., Walker II, W.: In: Marine pollutant transfer, H. L. Windom, E. A. Duce, eds., pp. 261–322. Lexington, Mass.: Lexington Books D. C. Heath Comp. 1976
26. Rohleder, H., Staudacher, H., Summermann, W.: Fresenius Z. Anal. Chem. **279**, 152 (1976)
27. Schulte, E., Acker, L.: Fresenius Z. Anal. Chem. **268**, 260 (1974); Schulte, E., Thier, H. P., Acker, L.: Deut. Lebensm.-Rdsch. **7**, 229 (1976)
28. Schulte, E., Acker, L.: Naturwissenschaften **61**, 79 (1974)
29. Seidl, G., Ballschmiter, K.: Fresenius Z. Anal. Chem. **296**, 281 (1979)
30. Sissons, D., Welti, D.: J. Chromatogr. **60**, 15 (1971)
31. Stalling, D. L., Huckins, J. N., Petty, J. D., Johnson, J. L., Sanders, H. O.: Ann. N. Y. Acad. Sci. **320**, 48 (1979)
32. Ullmanns Enzyklopädie der technischen Chemie, Vol. 9, p. 499, 4th ed. Weinheim: Verlag Chemie 1975
33. Versar Inc.: Final Report, PCBs in the United States: Industrial Use and Environmental Distribution, Report to U.S. EPA, Contract No. 68-01-3259 (1976)
34. Wassermann, M., Wassermann, D., Cucos, S., Miller, H. J.: Ann. N. Y. Acad. Sci. **320**, 69 (1979)
35. Weil, L., Duré, G., Quentin, K. E.: Wasser- u. Abwasserforsch. **7**, 169 (1974)
36. Zell, M., Ballschmiter, K.: Fresenius Z. Anal. Chem. 1980 (to be published)
37. Zell, M., Neu, H. J., Ballschmiter, K.: Chemosphere **6**, 69 (1977)
38. Zell, M., Neu, H. J., Ballschmiter, K.: Fresenius Z. Anal. Chem. **292**, 97 (1978)
39. Zinburg, R., Zell, M., Ballschmiter, K.: Computing program, available on request
40. Zitko, V., Hutzinger, O., Safe, S.: Bull. Environ. Contam. Toxicol. **6**, 160 (1971)
41. Zobel, M. G. R.: J. Assoc. Offic. Anal. Chemists **57**, 791 (1974)

Received February 12, 1980