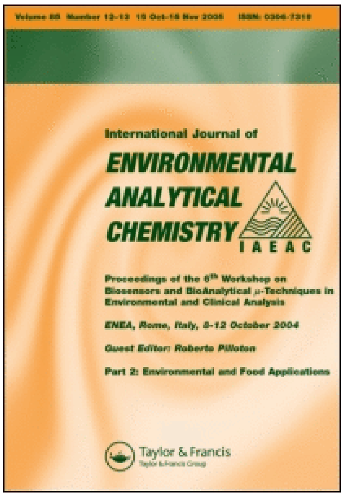

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CONGENER SPECIFIC ANALYSIS OF 140 CHLOROBIPHENYLS IN TECHNICAL MIXTURES ON FIVE NARROW-BORE GC COLUMNS

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The separation of 140 chlorobiphenyl (CB) congeners from technical polychlorinated biphenyl (PCB) mixtures was investigated on five narrow-bore (0.22–0.25 mm I.D.) gas chromatography (GC) columns with stationary phases representing a broad range of polarities: dimethylsiloxane (0.15 μm SIL-5, 50 m), 5% diphenyl dimethylsiloxane (0.26 μm SIL-8, 50 m), 14% cyanopropylphenyl 1% vinyl dimethylsiloxane (0.26 μm SIL-19, 50 m), bis-cyanopropyl phenylsiloxane (0.20 μm SIL-88, 50 m) and 1,2-dicarba-*closo*-dodecarborane dimethylsiloxane (0.1 μm HT-5, 25 m). Technical PCB mixtures (Aroclors) and authentic standards (totally 66 CBs) were injected on the narrow-bore columns and analyzed by GC-ECD and GC-MS. Peak assignments were based on experimental data together with published retention data and data on the quantitative composition of Aroclors.

Structural principles for retention of CBs on polar stationary GC phases were developed.

Surprisingly, the general performance of the classical column for PCB analysis, 5% diphenyl dimethylsiloxane, was slightly worse than of the other tested columns indicating that interest should be given to other columns for the analysis of PCBs as single congeners.

KEY WORDS: PCB congeners, GC-ECD, GL-stationary phases, Aroclors.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are among the environmental contaminants of highest concern. PCBs are widespread, persistent, and have the potential for harmful biological effects. There are 209 possible chlorobiphenyl (CB) configurations (congeners), but about 150 account for nearly all the environmental contamination attributable to PCBs. Still fewer congeners are both prevalent and toxic. Recently, 36 congeners have been indicated as most environmentally threatening based on their frequency of reported occurrence in environmental samples, their relative abundance in animal tissue, and their potential for toxicity[1]. The 36 priority CBs are the most potent mixed function oxidase (MFO) inducing CBs: 77, 126 and 169; the somewhat less potent CBs found in the environment at relatively high concentrations: 105, 118, 128, 138, 156 and 170; the relatively weak MFO inducing but highly abundant CBs: 87, 99, 101, 153, 180, 183 and 194; the weak or non-inducing CBs reported frequently in the environment or present in high concentrations in animal tissues relative to other CBs: 18, 44, 49, 52, 70, 74, 151, 177, 187 and 201; and finally the MFO inducing CBs present at very low tissue concentrations: 37, 81, 114, 119, 123, 157, 158, 167, 168 and 189. There is a strong need for unambiguous separations of these CBs.

Retention times of all 209 CBs on a SE-54 capillary gas chromatography (GC) column have been published[2] showing that not all CBs can be separated on this stationary phase. Some unresolved CBs have been separated on other phases of higher polarity[3,4]. Recently, the retention times of 51 CB congeners have been determined on seven narrow-bore GC columns[5]. Further investigations including a larger number of CBs are needed before CB analysis on other GC columns may be considered as unambiguous.

Multidimensional GC (MD-GC) is an excellent technique to improve the separation of co-eluting compounds. Examples of MD-GC separation of CBs which co-elute on a SE-54 column have been shown for a number of technical PCB mixtures[6,7] and environmental samples[7–9]. Investigations of CB separations on other GC column phases than SE-54 with MD-GC would be highly interesting. To date, no data have been published in this field. MD-GC is far from being a routine technique and most laboratories rely on parallel determination of PCBs on two different GC columns. Simultaneous dual-column, dual-detector GC analysis is a recent development of this approach[10,11]. This stresses the strong need for investigations of the chromatographic behavior of CBs on other columns than SE-54.

Early attempts have been made to determine the elution order of CBs on glass capillary columns coated with non- to moderately polar phases[12–16]. Only a limited number of CBs were available as reference compounds for these initial investigations and peak assignments had to be done simultaneously with the elucidation of the composition of technical PCB mixtures. Recently, the composition of a number of technical PCB mixtures has been analyzed by MD-GC with all 209 CBs available as reference compounds[7]. The acquisition of all 209 CBs is highly expensive and requires synthesis of commercially unavailable congeners. In place of single congeners, well characterized technical mixtures may serve as secondary standards for the determination of elution orders of CBs on various GC columns.

In the present investigation the GC retention on five different narrow-bore columns was determined for the 140 most abundant congeners in technical PCB mixtures. The stationary phases were selected to present a broad range of polarity from the non-polar dimethylsiloxane to the highly polar *bis*-cyanopropyl polysiloxane. This approach has facilitated the study of the relation between stationary phase polarity and selectivity in PCB retention, and allowed for the development of structural principles for the gas chromatographic behavior of CBs.

EXPERIMENTAL

Materials

All individual 209 CBs have been given a IUPAC number to replace their rather long chemical names. For three congeners (CBs 199–201) their original number[2] has been found to be in disagreement with the IUPAC numbering system[7]. However, the original numbers are widely used, and the numbers[2] will be used in the present paper. A total of 66 CBs were available for this study as either authentic reference standards or certified standard mixtures.

Individual CBs were obtained as neat crystals from the Community Bureau of Reference (BCR), Brussels, Belgium (CBs 18, 20, 28, 35, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180) or were synthesized as described previously[3,17] (77, 122, 126, 127, 163, 169). CB standard solutions were obtained from the National Research Council, Canada (CLB-1A: 18, 31, 40, 44, 49, 54, 77, 86, 87, 121, 153, 156, 159, 209; CLB-1B: 15, 52, 60, 103, 105, 128, 143, 154, 173, 182, 202, 205, 207, 208, 209; CLB-1C: 15, 114, 129, 137, 153, 171, 183, 185, 189, 191, 199, 201, 203, 206, 209; CLB-1D: 15, 101, 118, 138, 141, 153, 170, 180, 187, 194, 195, 196, 199, 209), from University of Kiel, Germany (PCB-I-IOC: 18, 26, 44, 49, 101, 118, 128, 138, 149, 151, 170, 180, 183, 187, 194) and from Supelco, Italy (DCMA: 1, 11, 29, 47, 121, 136, 185, 194, 206 and 209).

Technical PCB mixtures were obtained in iso-octane from Supelco as the Aroclor lots LA12790 (A1232), LA13646 (A1242), LA13657 (A1248), LA13614 (A1254), LA13576 (A1260), LA12791 (A1262) and a mixture of four Aroclors (A1016, A1232, A1248 and A1262, 1:1:1:1).

The GC columns were obtained from Scientific Glass Engineering (HT-5) and Chrompack (SIL-5 to SIL-88) as narrow-bore (0.22–0.25 mm I.D.) fused silica wall coated open tubular columns. The stationary phases were dimethylsiloxane (0.15 μm SIL-5), 5% diphenyl dimethylsiloxane (0.26 μm SIL-8), 14% cyanopropyl phenyl 1% vinyl dimethylsiloxane (0.26 μm SIL-19), bis-cyanopropyl phenylsiloxane (0.20 μms SIL-88) and 1,2-dicarba-*closo*-dodecaborane dimethylsiloxane (0.1 μm HT-5). The HT-5 column was only available in a length of 25 m, whereas the remaining columns were used in a length of 50 m.

Instrumental analysis

Gas chromatography-ECD. GC analyses were performed with a DANI 8520 gas chromatograph operated in the splitless mode (splitter closing time 2 min, 0.7 μl auto-injected on a programmed temperature vaporizer (PTV) at 90–280°C). The electron capture detector (ECD) was operated at 300°C, purged with 60 ml min^{-1} of 5% methane in argon. The helium carrier gas velocity was 23–24 cm s^{-1}. Detection limits were 2–10 pg depending on the column bleed. The Aroclors were injected in *iso*-octane at concentrations around 2–20 ng μl^{-1} (total PCB). The GC temperature programme was the following for the five columns: 2 min isothermal at 90°C, then at 20°C min^{-1} to 170°C (only 150°C for SIL-88), isothermal for 7.5 min, then at 3°C min^{-1} to 280°C (only 240°C for SIL-88), isothermal until the end. The given conditions were established after testing several temperature programs and represent the best overall separation conditions for the concerning columns. Optimizations for specific critical separations may still be possible. For instance, CB-84 which potentially interfere with CB-101[8] can be separated on the SIL-8 column by running a different temperature programme. However, in order to compare the chromatographic behavior of the stationary phases it was decided to keep the temperature programme as constant as possible.

Chromatographic data were acquired on a Chromstation/2 system (Spectra Physics).

Gas chromatography mass spectrometry

A Finnigan MAT ITS-40 ion trap mass spectrometer interfaced to a Varian 3400 gas chromatograph and a Compaq/386 computer was used for the mass spectrometric analyses of the technical PCB mixtures. Full scan spectra were run in the electron impact mode from 50 to 550 amu every second. Selected ion traces were software reconstructed as follows (m/z): Mono-CBs 186 + 188, di-CBs 222 + 224 + 226, tri-CBs 254 + 256 + 258, tetra-CBs 290 + 292 + 294, penta-CBs 324 + 326 + 238, hexa-CBs 358 + 360 + 362, hepta-CBs 394 + 396 + 398, octa-CBs 430 + 432 + 434, nona-CBs 464 + 466 + 468, and deca-CB 498 + 500 + 502. Injections were performed manually (2 μl) in the splitless mode (2 min closed) at 280°C. The detection limit of the ITS-40 varied from 25 to 50 pg (full spectrum of CB 77 at a signal to noise ratio around 10) depending on the GC column bleeding. The Aroclors were injected in *iso*-octane at concentrations around 1 $\mu g\ \mu l^{-1}$ (total PCB). The Varian 3400 gaschromatograph was equipped with the same columns as for GC-ECD analyses run under identical conditions.

Peak assignments

High resolution gas chromatograms (ECD) of the Aroclor mixture on the five investigated columns are shown in Figures 1–5. The peak assignments were made with the following data:

1) Electron impact mass spectrometric data derived from GC/ITS-40 analysis of an Aroclor mixture (A1016-A1260) and individual Aroclors (A1232, A1242, A1248, A1254, A1260 and A1262). Full scan chromatograms established the degree (or degrees) of chlorination of individual peaks. Confirmations of partial structures where *o,o'*-substitution was involved were based on the relative intensity of the $[M\text{-}Cl]^+$ fragment ion (the so-called *ortho*-effect).

2) Injections and co-injections of authentic reference compounds on each column phase (66 individual congeners).

3) Published chromatograms obtained by injections and co-injections of authentic reference compounds on narrow-bore columns. The following published data were used: Mullin *et al.* 1984[2] (SE-54: all 209 PCBs), deBoer and Dao, 1989[4] (SIL-8 and SIL-19: 27 congeners), Dubelbeis 1988[18] (DB-5: the 109 most abundant CBs in a mixture of Aroclors 1242, 1248, 1254 and 1260), Schulz *et al.* 1989[7] (SE-54: the 132 most abundant congeners in technical PCB mixtures), Durell and Sauer, 1990[10] (DB-5 and DB-17: 19 major PCBs in environmental samples), deBoer and Dao, 1991[5] (SIL-8, SIL-19 and SIL-88: 51 congeners, relevant for environmental analysis) and Storr–Hansen, 1991[11] (DB-5 and DB-1701: 32 congeners relevant for seal analysis).

4) Published data on the quantitative composition of Aroclors obtained with all 209 PCBs as authentic reference compounds[7].

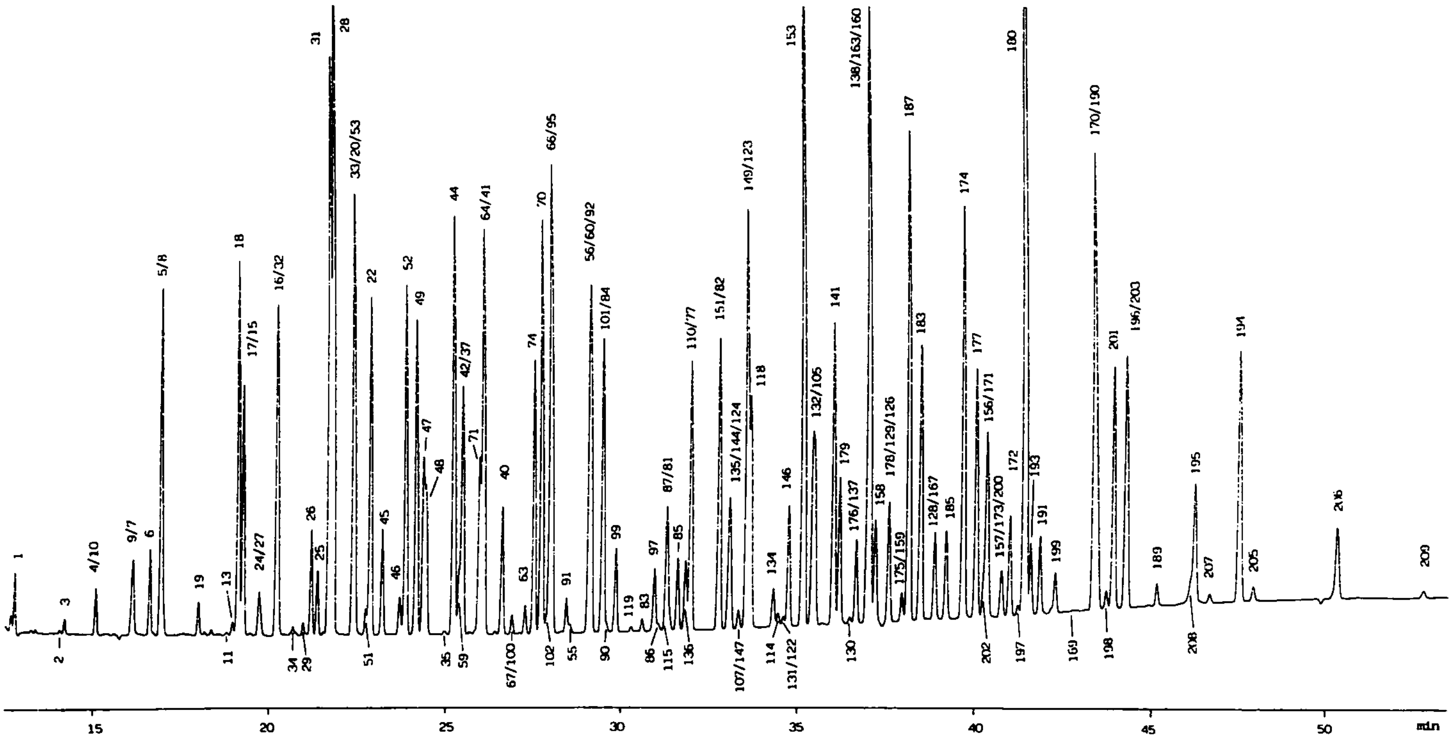

Figure 1 ECD-chromatogram of an Aroclor mixture (A1016, A1232 A1248, A1260 1:1:1:1) on the SIL-8 column.

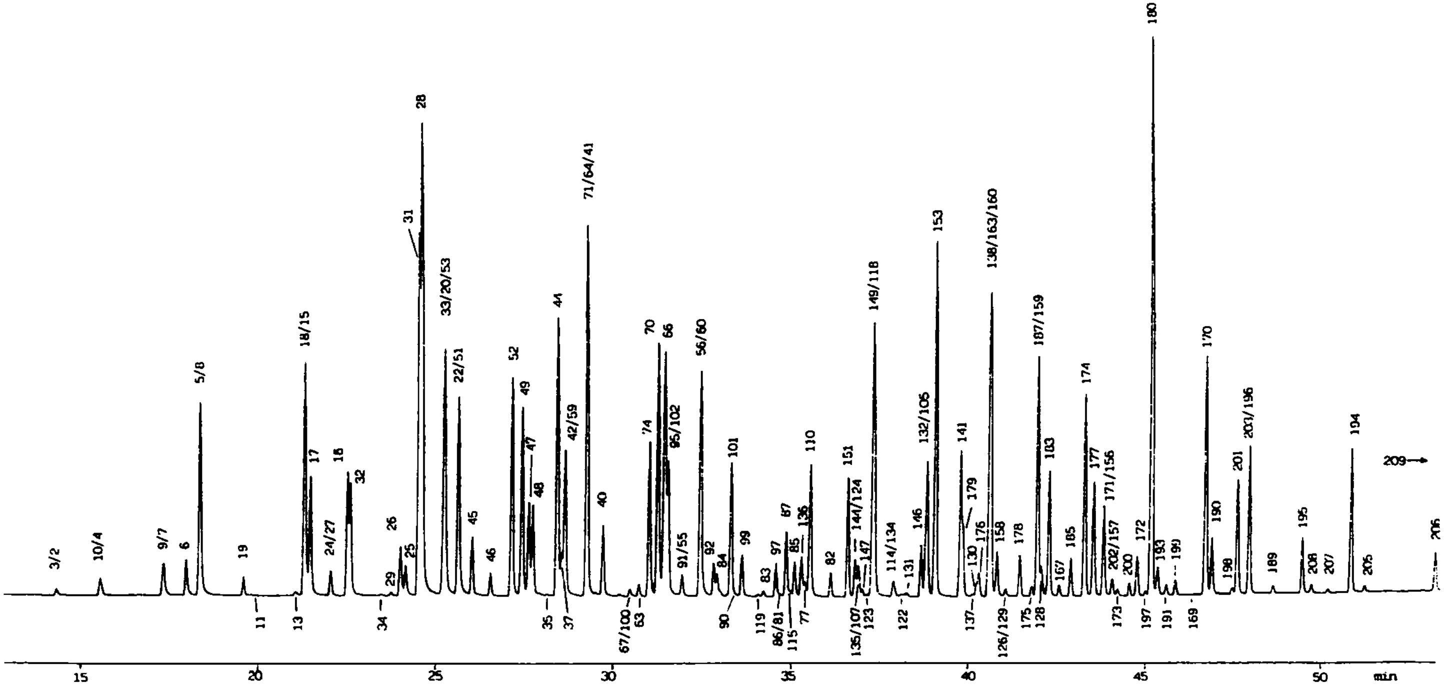

Figure 2 ECD-chromatogram of an Aroclor mixture (A1016, A1232 A1248, A1260 1:1:1:1) on the SIL-5 column.

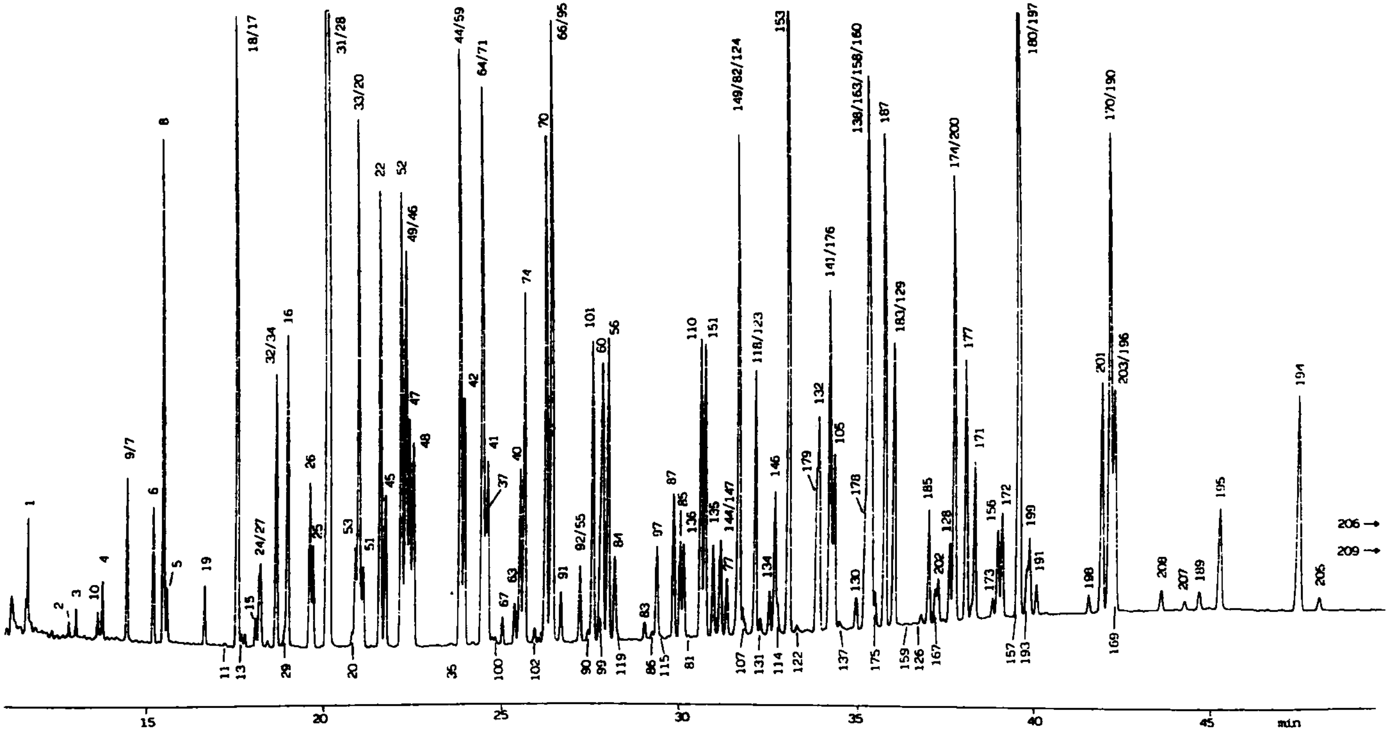

Figure 3 ECD-chromatogram of an Aroclor mixture (A1016, A1232 A1248, A1260 1:1:1:1) on the SIL-19 column.

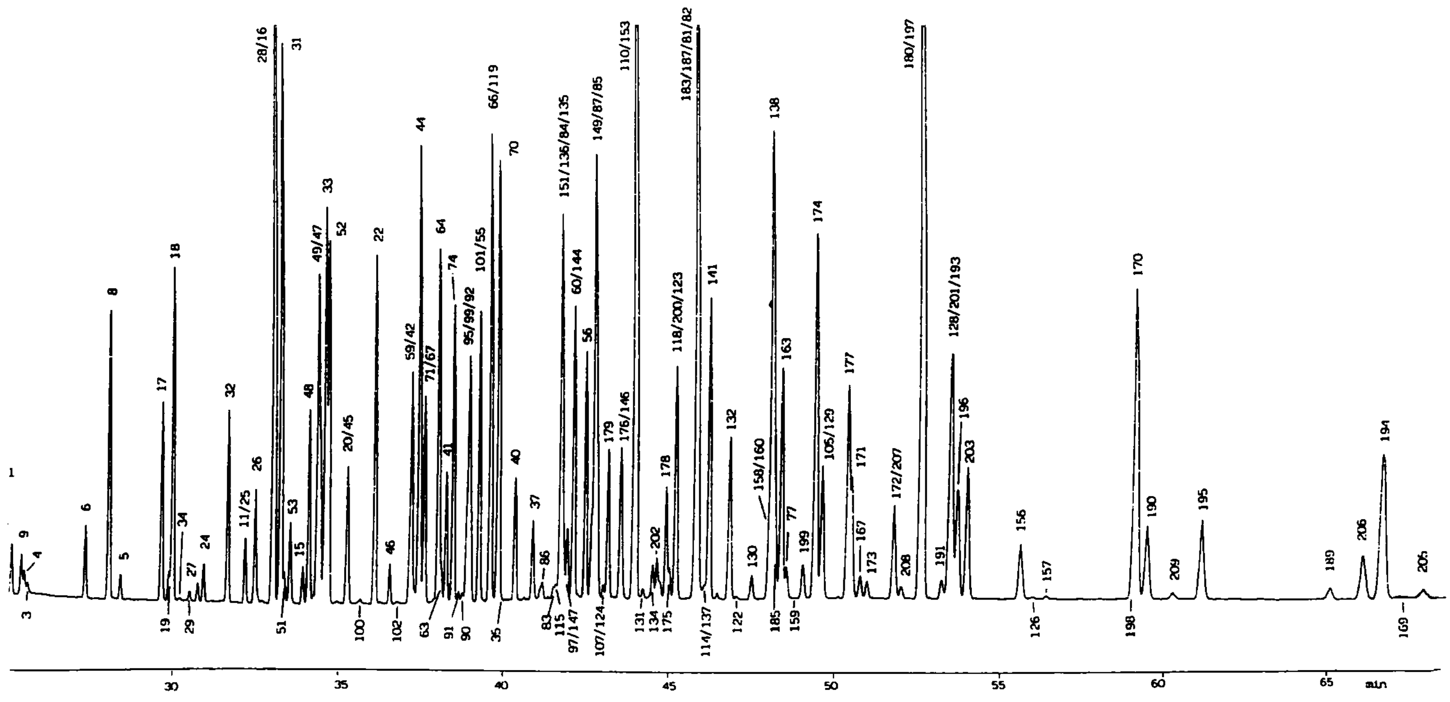

Figure 4 ECD-chromatogram of an Aroclor mixture (A1016, A1232 A1248, A1260 1:1:1:1) on the SIL-88 column.

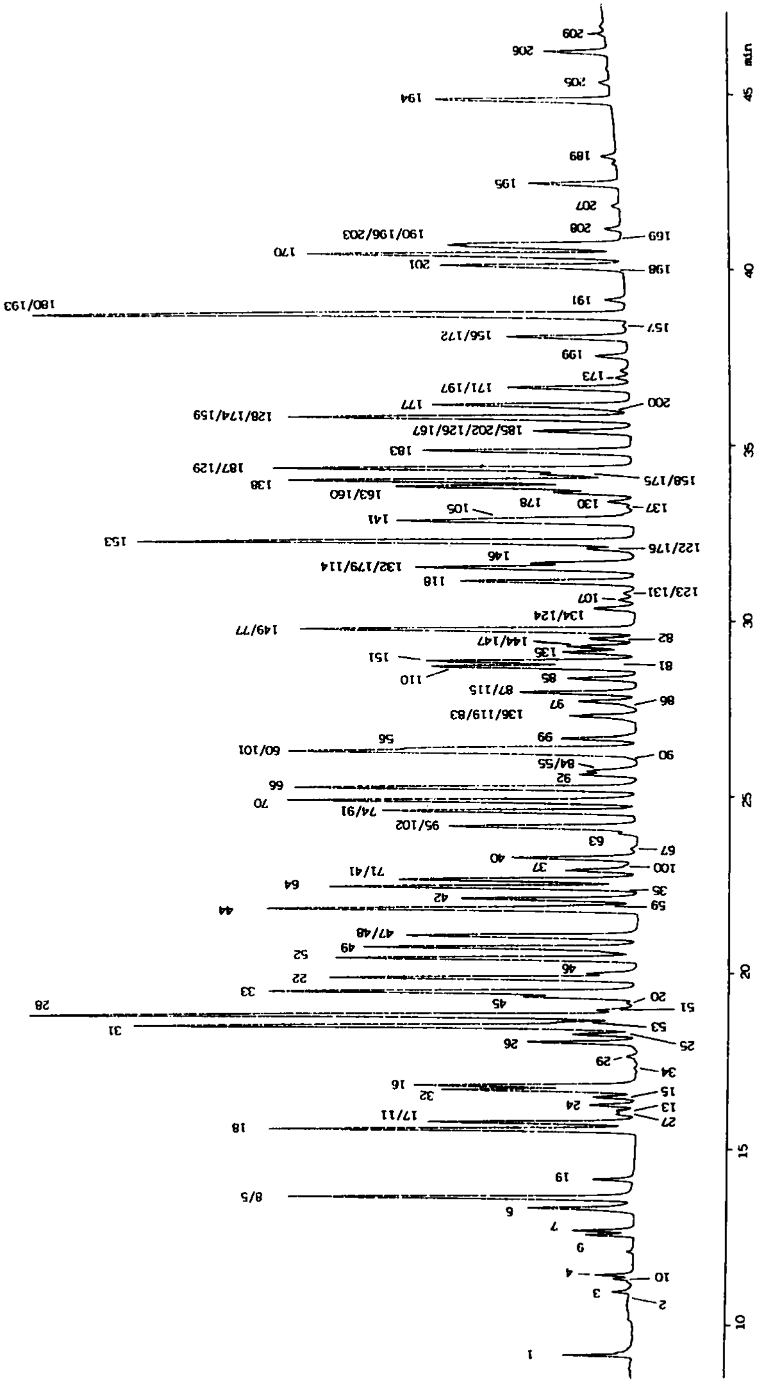

Figure 5 ECD-chromatogram of an Aroclor mixture (A1016, A1232 A1248, A1260 1:1:1:1) on the HT-5 column.

By combining data from (3) the elution order of all 209 congeners could be determined for SIL-8. Retention data for CBs not available for this study as reference standards was found for the CBs: 16, 33, 37, 53, 56, 66, 72, 81, 82, 84, 85, 92, 95, 110, 132, 140, 157, and 167 for SIL-88, plus a few more CBs for SIL-19: 3, 8, 42, 90, 91, 97, 99, 155, 158, 166 and 198.

The total number of CBs with retention data traceable to injections of authentic reference compounds (point (2) + (3)) make up to 209 for SIL-8, 105 for SIL-19, 95 for SIL-88 and 66 for SIL-5 and HT-5.

The procedure for the peak assignment was the following:

All Aroclors were analyzed by GC-MS on all five columns. Selected ion chromatograms were plotted for each chlorination class and arranged in the order of increasing column phase polarity. In order to minimize the mass spectrometric interference from higher chlorinated CBs co-eluting with lower chlorinated CBs the selected ion chromatograms obtained with A1232 were used for the study of mono-, di- and tri-CBs, A1242 for the study of tetra-CBs, A1248 for the study of penta-CBs, A1254 for the study of hexa-CBs, A1260 for the study of hepta- and octa-CBs and A1262 for the study of nona- and deca-CBs.

All peaks were assigned in the chromatograms of the SIL-8 column. A total of 140 congeners were found at a detection limit of 0.01% (w/w) compared to the 132 reported at a detection limit of 0.05% by Schulz *et al.* 1989[7].

All peaks traceable to authentic standards were assigned in the chromatograms of the four other columns with data from (1) to (3) and the remaining peaks were tentatively assigned with data from (4) by the following procedure:

a) For the lower (mono- to tri-CBs) and the higher (hepta-, to deca-CBs) chlorination classes, where the selected ion chromatograms were simple due to the presence of only few peaks, each congener was traced by gradually moving from the SIL-8 column towards higher or lower polarity (see examples in Figures 6 and 8).

b) In order to determine structural retention principles the isomers were arranged in subgroups within each chlorination class and the effect of increased GC column polarity on retention was examined. The discovered principles are discussed in details later.

c) For the medium (tetra- to hexa-CBs) chlorination classes, where the selected ion chromatograms were complicated by the presence of a high number of peaks, the structural retention principles were applied and again each congener was traced by gradually moving away from the SIL-8 column (see examples in Figure 7).

d) For each column, the selected ion chromatograms of all chlorination classes were merged and the retention data of all traceable chlorobiphenyls was shown on the total ion chromatogram.

e) For control, the mass spectrum of all peaks were carefully investigated with respect to the *ortho*-effect and finally, the retention profiles of each column were copied to the GC-ECD chromatograms of the Aroclor mixture (A1016-A1260) (Figure 1–5).

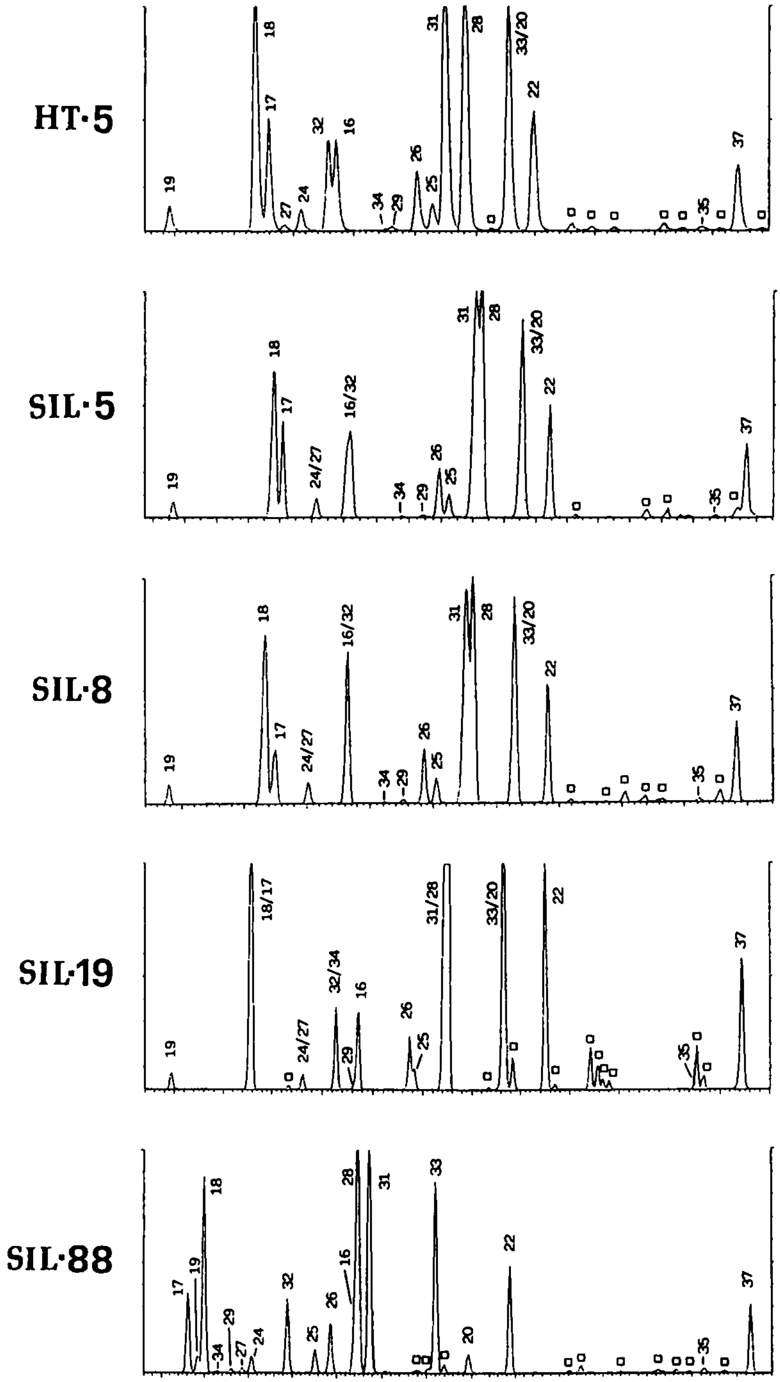

Figure 6 Selected ion chromatograms (254 + 256 + 258 m/z) of trichlorobiphenyls in technical PCB mixtures on five narrow-bore columns.

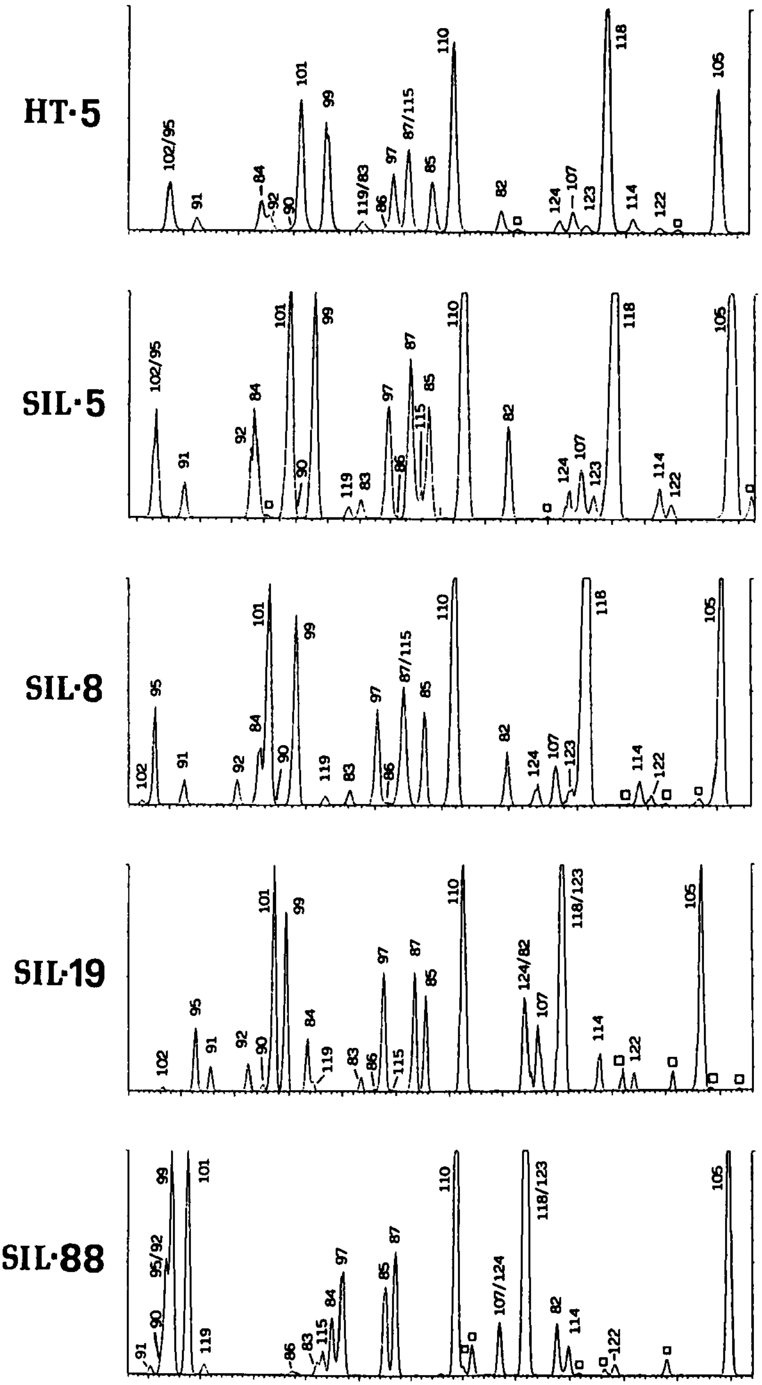

Figure 7 Selected ion chromatograms (324 + 263 + 238 m/z) of pentachlorobiphenyls in technical PCB mixtures on five narrow-bore columns.

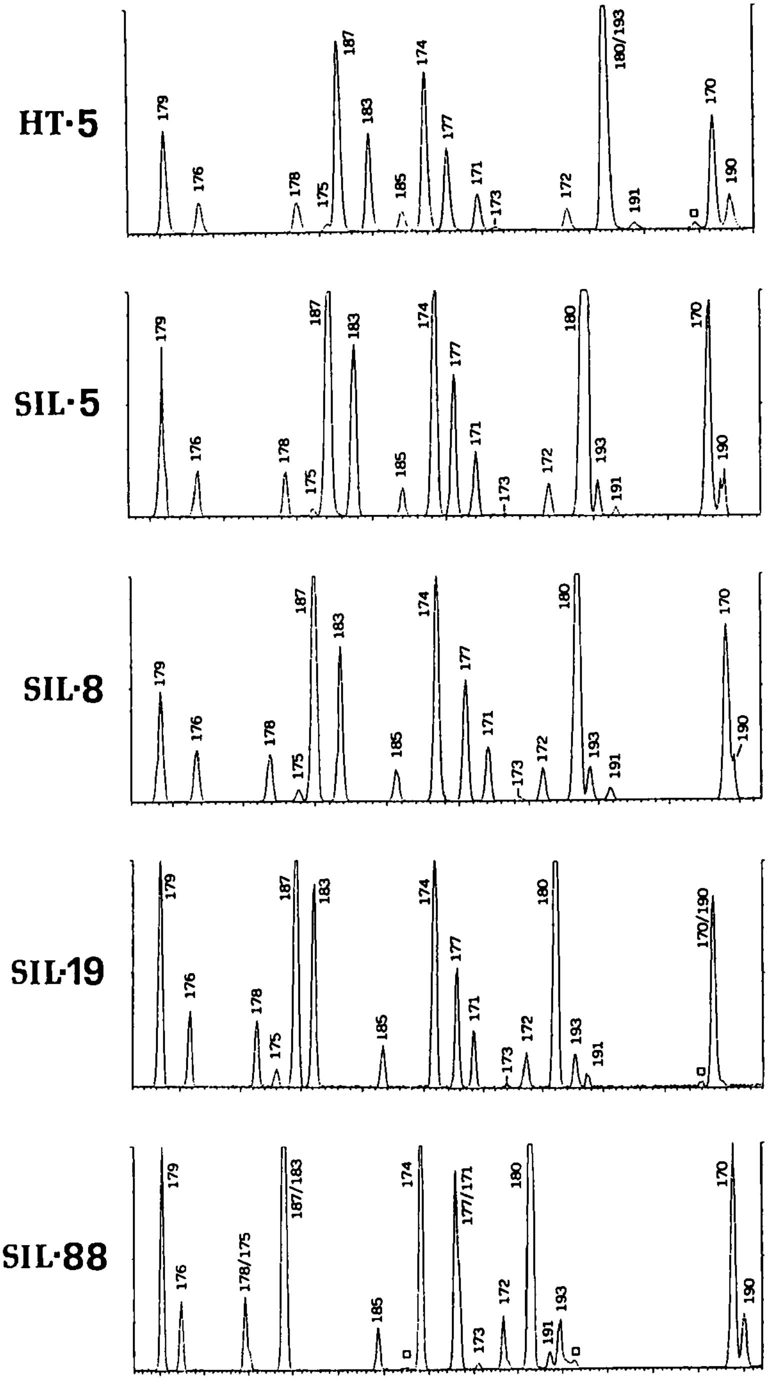

Figure 8 Selected ion chromatograms (394 + 396 + 398 m/z) of heptachlorobiphenyls in technical PCB mixtures on five narrow-bore columns.

RESULTS AND DISCUSSION

For all chlorination classes the selected ion chromatograms of the column SIL-5 were extremely similar to the reference chromatograms of SIL-8, and no problems in peak assignments were encountered. Therefore, the tentative peak assignments on this column have a very high level of confidence. The columns HT-5 and SIL-19 produced selected ion chromatograms rather similar to SIL-8 and tentative peak assignments on these columns are also of a high level of confidence. SIL-88, however produced rather different selected ion chromatograms and tentative peak assignments of the low intensity peaks (which sometimes co-elute with higher chlorinated congeners and therefore have some MS interference) may not be so certain as the assignments of the high-intensity peaks.

Structural principles for retention

On all columns the retention time generally increased with increasing CB chlorine content. This is consistent with basic gas chromatography theory, saying that the boiling point is a major retention factor for compounds which only interact weakly with the stationary phase. With increasing polarity of the stationary phase this picture was gradually distorting and for the highly polar phase SIL-88 several lower chlorinated CBs were retained stronger than higher chlorinated CBs.

One determining factor was the degree of *ortho*-substitution; i.e. increasing polarity of the stationary phase increased the retention time more for compounds with none or few *ortho*-substituents than for compounds with many *ortho*-substituents.

Another determining factor was the substitution pattern in the two rings. For isomeric homologs increasing polarity of the stationary phase increased the retention time in the following order (2-, 3-, and 4- represent the *ortho*-, *meta*-, and *para*-position, respectively):

mono-CBs: 4- > 3- > 2-

(see e.g. CBs 3/2/1, 15/13/8, 60/55/41 and 64/59/45).

di-CBs: 3,4- > 2,3- > 2,5- > 2,4- > 2,6-

(see e.g. CBs (12)/5/9/7/10, 33/16/18/17/19 and 35/20/26/25/27).

This principle is slightly modified when the other phenyl ring is not *ortho*-substituted: 3,4- > 2,3- > 2,6- > 2,5- > 2,4- (see e.g. CBs 37/22/32/31/28).

tri-CBs: 2,3,4- ≥ 3,4,5- > 2,3,6- > 2,3,5- > 2,3,4- > 2,4,5-

(see e.g. CBs 81/60/64/63/75/74 and 55/(78)/59/57/69/67).

tetra-CBs: 2,3,4,5- > 2,3,5,6- > 2,3,4,6-

(see e.g. CBs 141/151/144 and 180/187/183).

The special HT-5 phase, differing from the other stationary phases by its carborane-siloxane co-polymer, exhibited a dual nature. For CBs with two or more *ortho*-chlorines the structural retention principles described above were valid and this phase acted as non-polar. However, retention time increased considerably for non- and mono-*ortho* substituted CBs which is characteristic for the polar phases. The degree of rotational freedom for non- and mono-*ortho* chlorinated CBs is high compared to di-, tri-, and tetra-*ortho* chlorinated CBs which allows for a co-planar conformation of the former CBs. The high affinity of the HT-5 phase towards co-planar CBs may be explained by a π-electron interaction between the CB moiety and 1,2-dicarba-*closo*-dedecacarborane.

Performance of GC columns

The performance of the five GC columns is summarized in Table 1. No single column was able to separate all 140 congeners from technical mixtures. However, with the exception of six congeners (CBs: 60, 81, 124, 144, 149 and 160) each individual CB could be analyzed separately on at least one column.

A reasonable criterion for sufficient separation is less than 10% interference from a co-eluting congener. It is well-known that this criterion is met for symmetric peaks when the separation is just visible and peak heights are used for quantification[19]. Interfering CBs by HRGC-ECD analysis according to this criterion are listed in the table. Although MS detection may deteriorate GC separations due to dead volumes in the ion source, CBs with different numbers of chlorine substituents may be resolved better by selecting ion monitoring MS analysis than HRGC-ECD analysis. Critical separations for which the interference can be reduced to less than 10% by HRGC-MS are listed in brackets in the table.

All columns showed a number of non-separated priority CBs (highlighted in the table), and it is clear that for unambiguous determination of all 32 priority CBs parallel analysis on at least two columns is essential.

SIL-8

The SE-54 type columns (in this case SIL-8) are believed to offer the best overall PCB separations. As seen in Figure 1, there is a total of 31 peaks in the ECD-chromatogram of this column containing one or more co-eluting CBs. A total of 65 congeners elute from this column as well resolved single peaks. This number is higher than published recently for SE-54 columns[7], although the present investigation comprises 140 congeners compared to 132 congeners, and we believe that the criterion used in the previous publication[7] of baseline separation for accurate analysis is too conservative. By GC-MS a total number of 81 congeners can be analyzed accurately with this column. Of the 36 priority congeners 22 can be accurately analyzed by GC-ECD and 24 by GC-MS.

SIL-5

The SE-30 type columns (in this case SIL-5) were among the first columns used in routine PCB analysis but were replaced in popularity by SE-54. As seen in Figure 2 there is a number of 24 unresolved peaks in the ECD chromatogram on this column.

Table 1 Co-eluting CB congeners on five GC narrow-bore columns with different stationary phases

PCB #	*HT-5*	*SIL-5*	*SIL-5*	*SIL-19*	*SIL-88*
mono-CBs					
1	—[a]	—	—	—	—
2	—	3	—	—	7
3	—	2	—	—	—
di-CBs					
4	—	10	10	—	—
5	8	8	8	—	—
6	—	—	—	—	—
7	—	9	9	9	(2)[b]
8	5	5	5	—	—
9	—	7	7	7	—
10	—	(4)	(4)	—	—
11	17	—	—	—	25
13	—	—	—	—	—
15	—	18	17	—	—
tri-CBs					
16	—	—	32	—	28
17	(11)	—	(15)	18	—
18[c]	—	(15)	—	17	—
19	—	—	—	—	—
20	33	33, 53	33, 53	33	45
22	—	51	—	—	—
24	—	27	27	27	—
25	—	—	—	—	(11)
26	—	—	—	—	—
27	—	24	24	24	—
28	—	—	—	—	16
29	—	—	—	16	—
31	—	—	—	—	—
32	—	—	16	—	—
33	20	20, 53	20, 53	20	—
34	—	—	—	32	—
35	64	—	—	—	70
37	—	—	42	(41, 64, 71)	—
tetra-CBs					
40	—	—	—	—	—
41	71	64, 71	64	(37)	—
42	—	59	(37)	—	59
44	—	—	—	59	—
45	—	—	—	—	(20)
46	(22)	—	—	49	—
47	48	—	48	—	49
48	47	—	47	—	—
49	—	—	—	—	47
51	(28)	(22)	—	46	(31)
52	—	—	—	—	—
53	(31)	(33, 20)	(33, 20)	—	—
55	84	91	—	92	101
56	84, 101	60	60, 92	—	—
59	44	42	—	44	42
60	101	56	56, 92	99	144
63	—	—	—	—	64

(*continued*)

Table 1 (*continued*)

PCB #	*HT-5*	*SIL-5*	*SIL-5*	*SIL-19*	*SIL-88*
64	—	71, 41	41	71	—
66	—	—	95	95	—
67	—	—	100	—	71
70	—	—	—	—	—
71	41	64, 41	—	64	67
74	91	—	—	—	—
77	149	—	110	—	—
81	110, 151	86	87, 115	87, 115	82, 183, 187
penta-CBs					
82	—	—	151	149	(81), 183, 187
83	119, 136	—	—	—	115
84	(55)	—	101	—	135, 136, 151
85	—	—	—	—	(149), 87
86	—	(81)	—	—	—
87	115	—	(81), 115	—	(149), 85
90	101, 60	101	101	—	—
91	(74)	(55)	—	—	—
92	—	—	(56, 60)	(55)	95, 99
95	102	102	(66)	(66)	92, 99
97	—	—	—	—	147
99	—	—	—	(60)	95, 92
100	(37)	(67)	(67)	—	—
101	(60)	—	84	—	(55)
102	95	95	—	—	—
105	141	132	132	—	129
107	—	—	147	123	124
110	—	—	(77)	—	153
114	—	—	—	(146)	137
115	87	—	(81), 87	97	83, 84
118	—	—	149, 118	—	200, 123
119	83, 136	—	—	84	(66)
122	176	—	131	—	—
123	131	—	149	107	118, 200
124	134	144	135, 144	82, 149	107
126	167, 185, 202	129	129, 178	—	—
hexa-CBs					
128	159, 174	—	167	—	193, 201
129	187	—	178	183	(105)
130	—	—	—	—	—
131	(123)	—	122	—	—
132	(114), 179	(105)	(105)	179	—
134	124	(114)	—	—	—
135	—	(107)	(124), 144	—	151, 136, (84)
136	(83, 119)	—	—	—	(84), 151, 135
137	—	—	176	—	(114)
138	—	160, 163	160, 163	160, 163, 158	—
141	(105)	—	—	176	—
144	147	(124)	(124), 135	147	(60)
146	—	—	—	—	176
147	144	—	(107)	144	(97)
149	(77)	(118)	(123)	(82, 124)	(85, 87)
151	—	—	(82)	—	(84), 136
153	—	—	—	—	(110)

(*continued*)

Table 1 (*continued*)

PCB #	*HT-5*	*SIL-5*	*SIL-5*	*SIL-19*	*SIL-88*
156	172	171	202, 171	—	—
157	—	202	173, 200	180, 197	—
158	175, 178	—	—	163, 138	138, 160
159	(128), 174	187	175	—	—
160	163	138, 163	163, 138	163, 138, 158	138, 158
163	160	138, 160	160, 138	160, 138, 158	—
167	185, 202	—	128	—	—
169	—	—	—	203, 196	—
hepta-CBs					
170	—	—	190	190	—
171	197	(156)	(156)	—	—
172	(156)	—	—	—	207
173	—	—	(157), 200	—	—
174	(128, 159)	—	—	200	—
175	(158)	—	(159)	—	—
176	(122)	—	(137)	(141)	(146)
177	—	—	—	—	—
178	—	—	(129)	(138, 163, 158, 160)	—
179	(114, 132)	(141)	—	(132)	—
180	(193)	—	—	(197)	(197)
183	—	—	—	(129)	187
185	202, (167)	—	—	—	(138)
187	129	(159)	—	—	183
189	—	—	—	—	—
190	196, 203	—	170	170	—
191	—	—	—	—	—
193	(180)	—	—	—	201, (128)
octa-CBs					
194	—	—	—	—	—
195	—	—	—	—	—
196	190, 203	203	203	203	—
197	(171)	—	—	(180)	(180)
198	201	—	—	—	(170)
199	—	—	—	—	—
200	(177)	—	(157, 173)	(174)	(118, 123)
201	—	—	—	—	(128, 193)
202	(185, 167)	(157)	(156, 171)	—	—
203	(190), 196	196	196	196	—
205	—	—	—	—	—
nona-CBs					
206	—	—	—	—	—
207	—	—	—	—	(172)
208	—	—	—	—	—
deca-CBs					
209	—	—	—	—	—

[a] Well resolved CBs (less than 10% interference from any co-elutant on the peak height) are marked in the table with a hyphen.

[b] Critical separations for which interference can be reduced to less than 10% by GC-MS are listed in brackets.

[c] CBs which have been indicated as priority CBs due to their potential for toxicity and their prevalance in the environment[1] are highlighted in the table.

Compared to SIL-8 separation of 15 congeners are lost but other 34 congeners are gained, which gives a total of 84 well resolved CBs by GC-ECD and 102 by GC-MS on SIL-5. Of the 36 priority congeners 27 can be accurately analyzed by GC-ECD and 29 by GC-MS. It appears that SIL-5 is overall superior to SIL-8 and it is an interesting single column alternative for analysis of priority CBs.

SIL-19

Only with the 1980's development of thermo-stabile chemically bounded phases has it become feasible to perform routine analysis of PCBs on polar columns. Their background noise (bleed) is higher than for non-polar columns (especially by MS detection), but this is only interfering with ultra trace analysis. The OV-1701 type of columns (in this case SIL-19) has been the classical main choice for confirmation of PCB analysis on SE-54. The number of CBs which can be accurately analyzed by GC-ECD on either SIL-19 or SIL-8 is 103 (114 by GC-MS). However, the number of CBs which can be accurately analyzed on both SIL-8 and SIL-19 (the criterion for true confirmation) is only 64 (GC-MS). It is clear that more than two columns are needed for true confirmation of the major part of the CBs. As a single column, SIL-19 offers accurate analysis of 84 congeners by GC-ECD (Figure 3) and 100 congeners by GC-MS. Of the priority CBs 20 can be accurately analyzed by GC-ECD and 25 by GC-MS.

SIL-88

The highly polar *bis*-cyanopropyl columns (in this case SIL-88) commonly used in dioxin analysis have only recently been introduced in PCB analysis[3,5]. Although chemically stabilized, this phase puts extreme requirements on sample clean-up and carrier gas purity due to its sensitivity towards oxidation and it cannot be characterized as suitable for routine PCB analysis. During the three month period for the completion of the present study the elution profile of technical mixtures changed significantly on the SIL-88 column. The lifetime of this phase may be prolonged considerably by the use of hydrogen as carrier gas. A drawback of this strongly polar phase is its low maximum temperature 240°C which increases the time of analysis. When intact, this phase offers good separations of the most toxic CBs (77, 126 and 169) and it is the only of the five investigated columns capable of separating CBs: 8, 33, 24, 27, and 196 from co-elutants. A total of 74 congeners can be accurately analyzed by GC-ECD (Figure 4) and 99 congeners by GC-MS. Of the priority CBs 18 can be accurately analyzed by GC-ECD and 24 by GC-MS. Due to its great separation power, this phase may be an excellent choice as second column for MD-GC. By this technique only a small fraction of the main chromatogram is transferred to the second column which is thereby protected from chemical reactions with bulk matrix compounds resulting in a prolonged lifetime.

HT-5

The carborane-siloxane co-polymers are characterized by their high thermal stability and the HT-5 phase has been developed for analysis of heavy oils. To the authors best knowledge, exhaustive CB elution profiles have not yet been published for this phase. Due to its extremely high temperature limit of >400°C this phase allows for fast temperature programing and potentially fast analysis. In our first application of this column for rapid PCB analysis of earthworms[20] it was noticed that this phase exhibited strong retention for congeners with a low degree of *ortho*-substitution, and it was decided to thoroughly examine the retention of CBs on this phase. As a single column HT-5 may not be as efficient as most of the other investigated columns. It offers accurate anaysis of 69 congeners (21 priority CBs) by GC-ECD and 92 congeners (23 priority CBs) by GC-MS. However, its high temperature stability and strong retention of co-planar PCBs makes it an interesting column for coupling with other columns either in MD-GC or in one-dimensional GC. A recent study of HT-5 coupled in series with SIL-8 for analysis of toxic CBs has indicated the potential of this new type of column[21] and work is in progress for a complete characterization of the PCB retention on the SIL-8/HT-5 combination column[22]. For rapid chromatographic screening of CB congeners the HT-5 column seems very well suited. By the use of hydrogen as carrier gas at high linear velocity and ballistic temperature programming the total analysis time on this column can be reduced to less than 10 min practically without losing its separation power[23]

CONCLUSIONS

The majority of peaks in the chromatograms of technical PCB mixtures have been assigned from data traceable to authentic reference CB congener standards on five narrow-bore columns representing a broad range of GC phase polarities. The remaining peaks in the chromatograms have been tentatively assigned from GC-MS data on technical PCB mixtures of a known[7] composition and from structural principles for retention of CBs on polar stationary GC phases.

A number of co-eluting congeners have been identified on all GC columns. However, the authors acknowledge that GC conditions may be optimized for the separation of specific co-eluting pairs e.g. by the use of smaller column diameters, hydrogen as carrier gas and different temperature programs. The conditions used in the present investigation were selected in order to represent routine conditions practiced in most laboratories.

The best overall performing GC-phase was found to be the non-polar dimethyl siloxane (SIL-5) followed by the medium polar 14% cyanopropylphenyl, 1% vinyldimethylsiloxane (SIL-19) which allowed for the interference-free analysis of around eighty congeners by GC-ECD and around hundred by GC-MS. The highly polar bis-cyanopropyl phenylsiloxane (SIL-88) displayed an equally good separation power. However, this phase is not as chemically and thermally stable as the other tested phases and the CB elution profile changed significantly over a three-month period. As such, SIL-88 is not recommended for routine PCB analysis. The non- to slightly polar phases 1,2-dicarba-*closo*-dodecaborane dimethylsiloxane (HT-5) and 5% diphenyl dimethyl siloxane (SIL-8) showed a slightly worse general performance and allowed for the interference-free analysis of around half the 140 congeners present in technical mixtures. The fact that 5% diphenyl dimethyl siloxane showed the weakest overall performance is surprising since this phase and its equivalents (SE-54, DB-5 etc.) are widely used in PCB analysis.

The elution profiles were very different on the various columns and it was not the same congeners that co-eluted on all columns. Parallel analysis of PCBs on two (or more) columns will therefore increase the number of congeners that can be analyzed free of interference. The best two-column combinations seem to be HT-5 with SIL-5 or with SIL-19, which allow for the accurate GC-ECD analysis of 117 congeners (129 by GC-MS) and 114 congeners (127 by GC-MS), respectively.

For the analysis of the 36 priority CBs[1] SIL-5 seems to be the best single column alternative (27 congeners by GC-ECD and 29 by GC-MS) and in parallel with SIL-19 the best two-column combination (30 congeners by GC-ECD and 32 by GC-MS).

The performance of the columns is important also for another set of CB congeners; i.e. CBs: 28, 52, 101, 118, 138, 153, 180 which appear in PCB legislations of some countries and international organizations. HT-5 seems to be the best single column alternative for this set of CBs (it allows for the interference-free analysis of all seven congeners by GC-MS) and the best two-column combination in parallel with SIL-5 (all seven congeners by GC-ECD).

Summarizing, the present results indicate that more emphasis should be given in PCB analysis to other GC phases than the traditional 5% diphenyl dimethyl siloxane. The choice of GC column should be based on the congeners to be analyzed. The present investigation may assist in the correct choice.

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