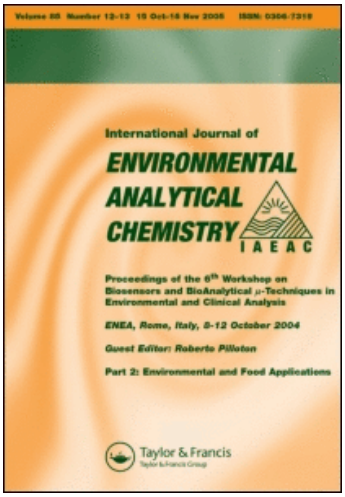

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SEPARATION OF TOXIC CONGENERS FROM PCB MIXTURES ON TWO SERIES COUPLED NARROW-BORE COLUMNS (50 m SIL-8 AND 25 m HT-5)

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The complete separation of the toxic non-*ortho*-substituted polychlorinated biphenyls (PCBs) PCB-77, PCB-126 and PCB-169 from the technical PCB mixtures Askarel and Aroclors (A1232, A1242, A1248, A1254, A1260 and A1262) was obtained on two series coupled narrow-bore columns: 50 m × 0.25 mm, 0.26 μm 5% diphenyldimethylsiloxane (CP-SIL-8) and 25 m × 0.2 mm, 0.1 μm 5% 1,2-dicarba-*closo*-dodecarborane dimethylsiloxane (HT-5).

The high upper temperature limit for these GC-phases (>300°C) allowed for fast temperature programming and short analysis time (60 min).

In addition to the non-*ortho*-substituted PCBs most of the toxic mono-*ortho*-substituted PCBs were completely separated from other PCBs (PCB-74, PCB-81, PCB-105, PCB-118, PCB-123, PCB-157 and PCB-189). Only four toxic PCBs were eluted with interference: PCB-60/PCB-56, PCB-114/PCB-134, PCB-167/PCB-128 and PCB-156/PCB-202. These could be analyzed satisfactorily on a CP-SIL-19 column i.e. 50 m × 0.25 mm, 0.20 μm 14% cyanopropylphenyl 1% vinyldimethylsiloxane.

The 2,3,7,8-TCDD toxicity equivalents (TEQ) of the technical mixtures, analyzed by GC-ECD and GC-MS (ITS-40), were determined from published toxicity equivalent factors (TEF). Aroclor A1254 was the most toxic PCB formulation (56–216 mg TEQ kg^{-1} depending on the TEF model used) and A1262 the least toxic formulation (4–11 mg TEQ kg^{-1}). PCB-74, PCB-77, PCB-105, PCB-118, PCB-126 and PCB-156 contributed with 80–99% of the total toxicity in all technical mixtures and it is suggested that future PCB legislation should be based on these six congeners.

KEY WORDS: PCBs, Askarel, Aroclor, congener analysis, coplanar congeners, gas chromatography, toxicity.

INTRODUCTION

Polychlorinated biphenyls (PCBs) are highly stable industrial chemical products. PCBs have been used as industrial fluids, flame retardants, diluents, hydraulic fluids and dielectric fluids for capacitors and transformers. Due to (former) careless disposal practices, environmental stability and bioaccumulation, PCBs have been widely identified in wildlife and human tissue[1]. A total of 209 theoretical PCB congeners exists and around 150 have been reported in the total environment. Each individual congener has been given a IUPAC number[2]. For simplicity, only the IUPAC numbers and not the full chemical name of each PCB congener will be used in the present paper.

With the synthesis of all 209 PCB congeners[2] and with the development of high resolution gas chromatography (HRGC), during the eighties, congener specific

analysis of PCBs has been largely improved. Since 1985, when the first complete congener specific characterization of a commercial PCB mixture (Aroclor 1260) and a human milk extract was reported[3], analysis of PCBs as single congeners has become an established alternative to the approximate analysis of PCBs as technical formulations.

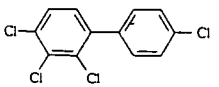
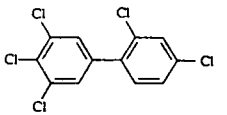
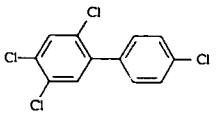
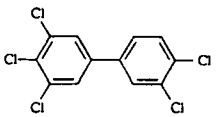
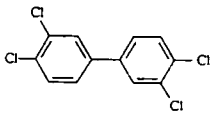
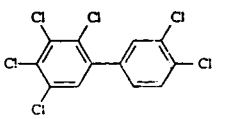
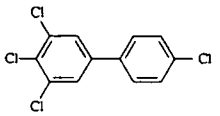
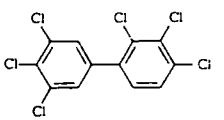
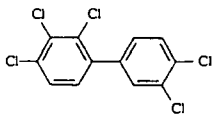
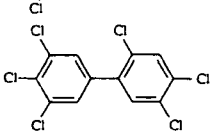
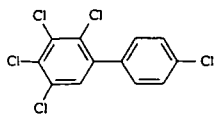
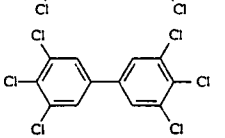
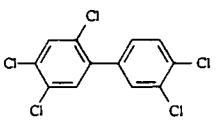
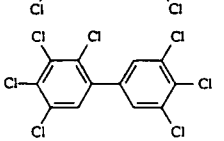
During the last years attention has been focused on the toxicity of PCBs, especially on the congeners which show the same type of toxicity as polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs)[4,5,6]. Certain PCBs, which lack chlorine substituents in the *ortho*-position, show particularly high "dioxin-like" toxicity, viz. PCB-77, PCB-126 and PCB-169. These are all approximate isomers of the highly toxic 2,3,7,8-substituted PCDDs and PCDFs. Certain mono-*ortho*-substituted PCBs have also displayed considerable "dioxin-like" toxicity[7]. These are shown in Table 1.

Based on toxic and biochemical potencies, the relative toxicity of PCB congeners compared to 2,3,7,8-TCDD may be expressed as toxicity equivalence factors (TEFs), and the total "dioxin-like" toxicity of a mixture of PCBs may be calculated as the summation of the concentration of individual toxic congeners times their TEF. Due to the simplicity of this method it has become a popular tool for environmental administrators. Two TEF models for PCBs have recently been proposed from toxicological expert groups (in the following called: USA[7] and NL[8]). These models are very different and TEF values for some PCBs disagree with several orders of magnitude. However, work is continued in this field (e.g. Hanberg *et al.* 1990[9]) and with more toxicity data being published a consensus for TEF models may be achieved. The USA and NL TEF models are shown in Table 1 for "dioxin-like" toxic PCB congeners together with their IUPAC numbers and chemical structure.

The analysis of these toxic PCBs may be complicated by two factors: (a) their presence in very low levels compared to the bulk of PCBs and (b) their co-elution with one or more interfering congeners on most GC columns. Several selective enrichment methods have been employed for the analysis of the three most toxic congeners (PCB-77, PCB-126 and PCB-169) with carbon chromatography being the most popular choice (reviewed by Voogt *et al.* 1991[10]). Most of the methods used activated charcoal to enrich these planar PCB congeners. Activated charcoal have some serious drawbacks such as low efficiency, severe tailing on elution profiles, irreversible adsorption and large batch-to-batch variations[11]. Some of these drawbacks may (partly) be overcome by the use of high pressure liquid chromatography (HPLC) with a porous graphite carbon column[12] or an "electron-donor acceptor" column phase[13]. However, if the problem of co-elution in the final GC determination step remains unresolved extreme selectivity of these enrichments procedures is required. This is demonstrated by the following examples.

The most widely used GC-column phase for the final determination of PCB-77, PCB-126 and PCB-169 is SE-54 and its equivalents (e.g. CP SIL-8)[15–22]. On this phase PCB-169 is resolved from any interference, but PCB-77 is co-eluting with PCB-110 and PCB-126 is co-eluting with PCB 129 and PCB-178. These interfering congeners are present in technical PCB mixtures at high levels e.g. in A1254 at concentrations of 58.5, 2.3 and 13.5 mg g^{-1} for PCB-110, PCB-129 and PCB-178,

Table 1 IUPAC numbers[2], chemical structure and toxicity equivalent factors of toxic PCBs

IUPAC No.	*Structure*	*TEF: NL*[8]	*TEF: USA*[7]	*IUPAC No.*	*Structure*	*TRF: NL*[8]	*TEF: USA*[7]
PCB-60		0.00001	0.001	PCB-123		0.00005	0.001
PCB-74		0.0001	0.001	PCB-126		0.1	0.1
PCB-77		0.01	0.01	PCB-156		0.0005	0.001
PCB-81		0	0.001	PCB-157		0.0005	0.001
PCB-105		0.0001	0.001	PCB-167		0.00001	0.001
PCB-114		0.0005	0.001	PCB-169		0.005	0.005
PCB-118		0.00005	0.001	PCB-189		0.00001	0.001

respectively[23]. This should be compared with the concentration of PCB-77 at 0.62–2.5 mg g^{-1} [24,25] and the concentration of PCB-126 at 0.04–0.16 mg g^{-1} [24,25].

Another popular GC-column phase for analysis of these planar PCB congeners is the slightly polar OV-1701 and its equivalents (e.g. CP SIL-19)[24,26–32]. On this phase PCB-77 and PCB-126 are resolved from any interference[33,35], but PCB-169 is co-eluting with PCB-196 and PCB-203, both of which are present at high levels in technical PCB mixtures e.g. in A1260 at concentrations of 30.0 mg g^{-1} [3] compared with the concentration of PCB-169 of <0.01 mg g^{-1} [24].

Also for biological samples interference from co-eluting PCB congeners may occur. This is exemplified by the concentration of PCB congeners in human milk (pg g^{-1} lipid)[34]: PCB-77/PCB-110 at 27/2300, PCB-126/PCB-178 at 98/8000 and PCB-169/PCB-203 at 47/4400.

Similar problems of interference in the final GC determination step are encountered for the mono-*ortho*-substituted toxic PCBs. Since the analysis of these compounds most often is carried out on the PCB bulk extract without previous selective enrichment, great demands are put on the analytical GC column.

On the widely used column phase (SE-54) some clusters remain unresolved, even under optimal conditions (column length minimum 50 m, i.d. maximum 0.25 mm)[3,32,35], in particular PCB-92/PCB-60/PCB-56, PCB-81/PCB87, PCB-132/PCB-105, PCB-123/PCB-149, PCB-171/PCB-156/PCB-202, PCB-173/PCB-157 and PCB-128/PCB-167. When analysis is carried out under less than optimal conditions (e.g. with 25 m columns or with an i.d. of 0.32 mm) other unresolved clusters may occur[23,36]: PCB-149/PCB-118, PCB-153/PCB-105, PCB-114/PCB-131/PCB-122.

Recently, the retention of PCBs on a SB-Octyl-50 column (Lee Scientific) has been reported[37]. When this column is operated at mild temperature conditions (with long analysis times) most toxic PCBs are resolved with the exception of the clusters: PCB-70/PCB-74/PCB-76, PCB-110/PCB-81/PCB-115, PCB-123/PCB-137 and PCB-167/PCB-181. PCB-126 was not reported.

Other GC column phases have been investigated with a limited number of PCB standards (51). The most promising appeared to be the slightly polar CP-SIL-12 and the non-polar C18 (Chrompack)[35]. These phases deserves further investigations. The highly polar bis-cyanopropylphenyl phase (CP-SIL-88 or equivalent), commonly used in PCDD and PCDF analysis, also offered good separations of most of the toxic PCBs[33,35]. However, this phase suffers from a very low chemical stability, which only

Table 2 Comparison of detection techniques for PCB-77 (weight percentage % w/w)

PCB mixture	*ITS-40*	*ECD*
A1232	0.11%	0.121%
A1242	0.29%	0.250%
A1248	0.53%	0.403%
A1254	0.13%	0.125%
A1260	0.0043%	0.0038%
A1262	0.0075%	0.0081%
Askarel	0.016%	0.0140%

allows for optimal separations over a limited time period, typically in the order of months.

By the use of a mass spectrometer (MS) as detector in place of the electron capture detector (ECD) some extra selectivity is brought into PCB analysis[38,39,40]. PCB isomers have almost identical mass spectra varying only for fragment ions due to a different number of chlorine substituents in the *ortho*-positions[41,42]. Therefore, a real benefit from MS is obtained only for co-eluting congeners belonging to different classes of chlorination. Even in such cases interference from higher chlorinated PCBs with lower chlorinated PCBs cannot be eliminated due to the production of lower chlorinated fragments in the electron impact ion source of the mass spectrometer. The non-*ortho* and mono-*ortho* substituted toxic PCBs are eluted as the lastest congeners from each chlorination class on most columns. So unfortunately, the interfering PCBs for the non-*ortho* and mono-*ortho* substituted toxic PCBs are all of a higher degree of chlorination. The use of a chemical ionization source in the spectrometer will minimize the formation of mass fragments and improve selectivity in the analysis of PCBs by GC-MS[10].

Most recently, multi-dimensional GC (MDGC) has been applied to congener specific PCB analysis[23,25,36,43,44]. This method is elegant and works properly, when the second GC column is sufficiently different from the main GC column. A combination of SE-54 as main column phase and OV-210 as second column phase has been proven useful in the analysis of toxic PCBs[23,36,43]. MDGC is far from being a simple technique and major drawbacks are the long analysis time and the difficulties in incorporating internal standards for quality assurance. Although, MDGC certainly has demonstrated its value as confirmational tool in PCB analysis (like MS) it is still not a routine technique.

Parallel coupling of two columns in a single gas chromatograph with two detectors has been used recently in congener specific PCB analysis[37,47], but surprisingly little work has been published on the series coupling of GC columns in a single gas chromatograph. Recently, this subject has been described from a theoretical point of view[49]. Whereas the series combination of two or more columns is unlikely to facilitate separation of all 209 PCBs, it should be possible to find combinations which allow for the complete separation of a limited number of congeners. In the present work we have aimed for the complete separation of the three most toxic congeners (PCB-77, PCB-126 and PCB-169).

The best studied GC column phase for PCB analysis is the SE-54 type[2,23]. Only recently, serious interest has been given to other phases, leading to the publication of PCB retention mechanisms together with relative retention times for the most abundant of the 209 PCBs[33,35,38]. Referring to these results, we have tried to modify an SE-54 type column (CP-SIL-8) by coupling it in series with a shorter column of a different phase. Based on its high temperature stability and its strong retention of non-*ortho*-substituted PCBs (possibly due to a π-electron interaction between the PCB moiety and carborane[33]) the HT-5 phase (1,2-dicarba-*closo*-dodecarborane dimethylsiloxane) was chosen.

The present paper reports on the performance of this combination column for analysis of toxic congeners in technical PCB mixtures.

EXPERIMENTAL

Apparatus

HRGC-ECD analysis was performed with a DANI 8520 gas chromatograph operated in the splitless mode. The technical PCB mixtures and calibration standards (in *iso*-octane) were automatically injected (0.7 μl) on a 75 m fused silica capillary column consisting of a 50 m × 0.25 mm (0.26 μm film of 5% diphenyl dimethylsiloxane) CP-SIL-8 column (Chrompack) coupled in series (via a Chrompack quick-seal glass tube) with a 25 m × 0.2 mm (0.1 μm film of 5% 1,2-dicarba-*closo*-dodecarborane dimethylsiloxane) HT-5 column (Scientific Glass Engineering). The following GC conditions were used: injector temperature 90–280°C ballistically; linear helium gas velocity 23 cm s^{-1}; temperature programme 2 min isothermal at 90°C, then at 20°C min^{-1} to 200°C, isothermal for 7.5 min, then at 3°C min^{-1} to 280°C, isothermal for 20 min; detector 310°C, ECD make-up gas 5% methane in argon at 60 ml min^{-1}. For comparison injections were repeated on a 50 m × 0.25 mm (0.20 μm film of 14% cyanopropylphenyl 1% vinyldimethyl siloxane) CP-SIL-19 column (Chrompack), on a 50 m × 0.25 mm (0.26 μm film of 5% diphenyl dimethylsiloxane) CP-SIL-8 column (Chrompack) and on a 50 m × 0.25 mm (0.20 μm film of bis-cyanopropylphenylsiloxane) CP-SIL-88 column (Chrompack). The GC temperature programme was identical for all four columns with the exception of the intermediate and final oven temperature which were 200/270°C for SIL-8 and SIL-19 and 150/240°C for SIL-88.

Data were acquired and processed on a Chromstation/2 system (Spectra Physics, Italy).

HRGC-MS analyses were conducted on an ion trap mass spectrometer, ITS-40 (Finnigan). Full scan spectra were run from 150 to 500 amu every second. Selected ion traces were software reconstructed as follows (m/z): Tetrachlorobiphenyls 290 + 292 + 294, pentachlorobiphenyls 324 + 326 + 238, hexachlorobiphenyls 358 + 360 + 362 and heptachlorobiphenyls 394 + 396 + 398. Injections were performed manually (1–2 μl) in the splitless mode at 290°C with the "empty needle" technique. The GC-ITS-40 was equipped with the same columns as for GC-ECD analysis run under identical conditions.

The lower linear range for quantification with HRGC-ECD was around 25 pg and the detection limit around 2–3 pg (PCB-77). The limit for quantitative work for the ITS-40 was around 25 pg (PCB-77) with a signal to noise ratio < 10. Full scan mass spectra could easily be obtained at this level using software background subtraction. Down to around 8 pg (distorted) mass spectra could still be obtained. The reproducibility for repeated injections was around 3–4% for the HRGC-ECD system and around 18–21% for the HRGC-MS system.

Materials

Glassware, solvents and chemicals were pesticide grade or cleaned as usual for trace analysis. Blanks were run on a routine basis for quality assurance. PCB calibrants were obtained as neat crystals from the Community Bureau of Reference (EEC,

Brussels) and from Promochem (Wesel, Germany) or were synthesized as described elsewhere[46]. Identity and purity of the calibrants were controlled by NMR and HRGC-MS analysis and for quality control the prepared mother solutions were submitted to interlaboratory tests. At the time of the study PCB-60, PCB-74, PCB-81, PCB-114, PCB-157, PCB-167 and PCB-189 were unavailable as neat crystals and were obtained only in standard mixtures. For their quantification published response factors[2] were used in the HRGC-ECD analysis. In the HRGC-MS analysis the nearest eluting PCB from the same chlorination class was used as a surrogate standard. Due to the combination of small TEFs and low concentrations of these congeners in technical PCB mixtures a minor systematic error from this approach, if any, will not influence the final toxicological evaluation. The quantitative results from the two methods were in agreement within the analytical reproducibility. Repeated analysis of selected samples at a late stage based upon neat crystals of PCB-60, PCB-81, PCB-114, PCB-157, PCB-167 has confirmed the validity of this quantification approach.

From the available technical PCB mixtures four of them (Aroclors A1242, A1248, A1254 and A1260) were selected for comparison with previous data[23–25] and three others (A1232, A1262 and Askarel, the widely used mixture in Italy and France) for completion of a toxicological evaluation. The Aroclor mixtures were obtained in solution (1 $\mu g\ \mu l^{-1}$ in *iso*-octane) from Supelco, lots: LA12790 (A1232), LA13646 (A1242), LA13647 (A1248), LA13614 (A1254), LA13576 (A1260) and LA12791 (A1262). The Askarel mixture was obtained as a pure liquid from a local stock previously used to refill transformers. The lot number was not identifiable.

Dilutions of the technical mixtures were in the 0.5–5 ng μl^{-1} (total PCB) range for HRGC-ECD analysis and in the 1–5 $\mu g\ \mu l^{-1}$ range (total PCB) for HRGC-MS analysis.

RESULTS AND DISCUSSION

Chromatography

The 75 m SIL8-HT5 combination column facilitated the separation of the three toxic non-*ortho*-substituted PCBs and most of the toxic mono-*ortho*-substituted PCBs from any interference (Figures 1–8). The analysis time was short, around 60 min (Figures 2–8). The background signal (bleeding) was minimal and did not interfere in the HRGC-MS analysis (Figure 1). The chemical stability at high temperatures of the two column phases allowed for routine baking overnight at 280°C in order to improve blanks. Only small variations in retention times were observed over a two-month time period.

In order to evaluate the chromatographic performances of the combination column a mixture of four Aroclors (A1016, A1232, A1248 and A1260, 1:1:1:1) was analyzed by HRGC-MS. The critical separations for the toxic congeners are enlarged from the reconstructed selected ion traces in Figure 1 together with a mass spectrum of the toxic PCB taken at the top of the peak. From the absence of masses higher than

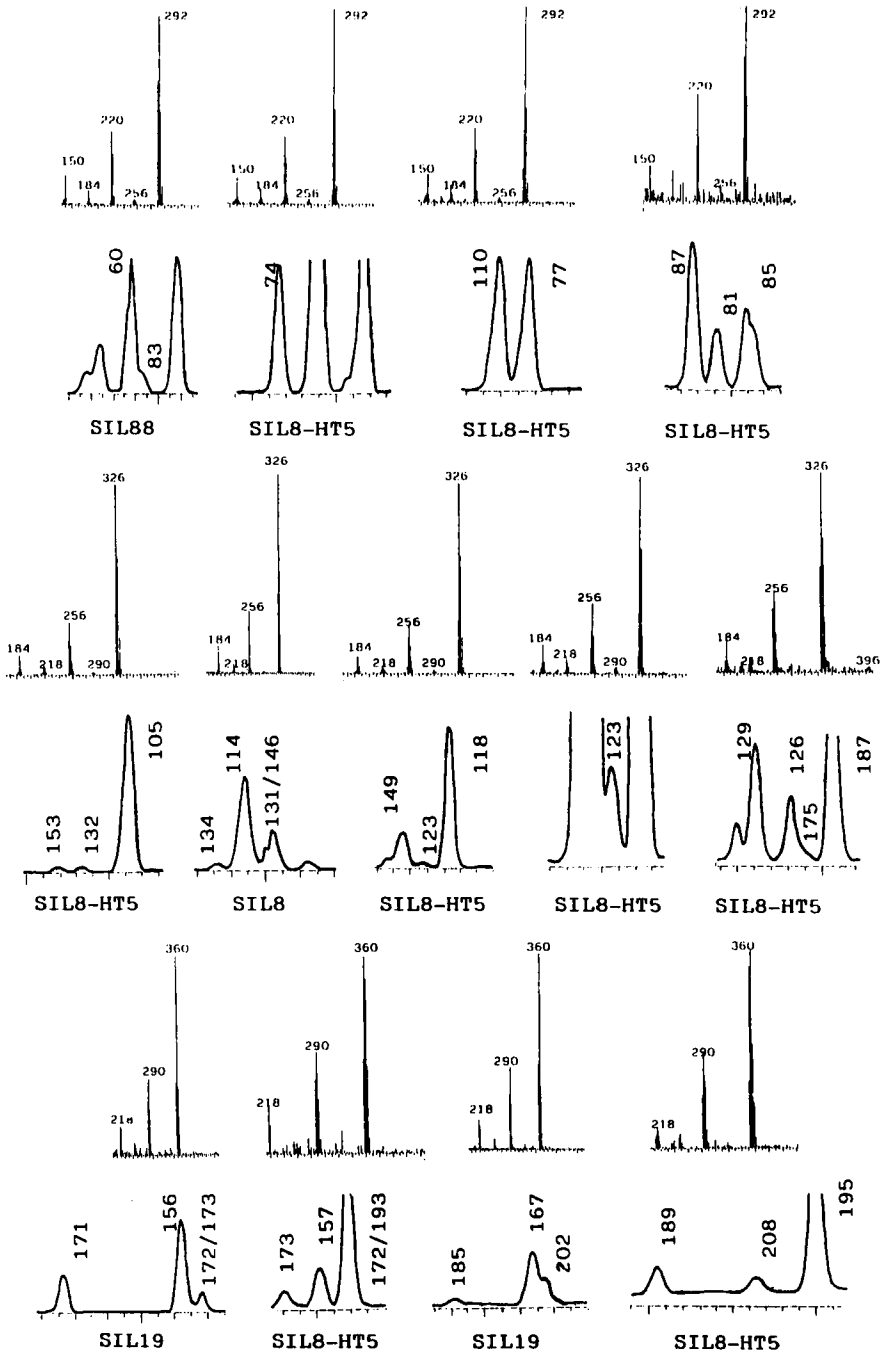


Figure 1 GC-MS key separations (selected ion monitoring) of toxic PCBs from technical mixtures.

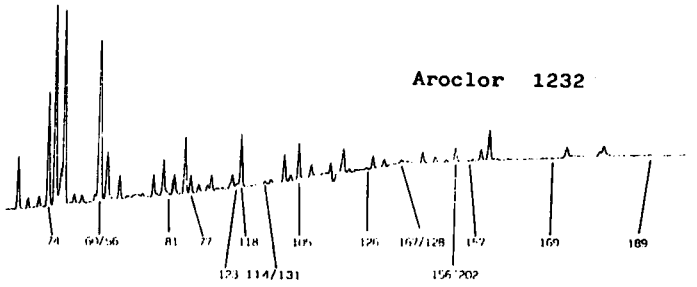


Figure 2 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 2 ng A1232.

the molecular ion it is evident that no interference from nearby eluting PCBs into the target congener was present for the following compounds: PCB-74/PCB-70, PCB-110/PCB-77, PCB-87/PCB-81/PCB-85, PCB-132/PCB-105, PCB-149/PCB-123/PCB-118, PCB-126/PCB-175 PCB-157/PCB-172/PCB-197, and PCB-189. A very small interference of PCB-149 with PCB-123 was indicated by the presence of an ion at 362 emu in the mass spectrum for PCB-123. A closer investigation of all HRGC-MS spectra revealed that in none of the technical mixtures did this interference exceed 5% (data not shown). The PCB-169 was not detected in the technical mixtures. However, full scan mass spectra proved the absence of any PCB at the retention time of this congener (data not shown). The absence of interfering PCBs at the retention time of PCB-169 was also clearly demonstrated by the HRGC-ECD chromatograms shown in Figures 2–8. Four toxic mono-*ortho*-substituted PCBs were affected by interference from co-eluting congeners viz. PCB-60/PCB-56, PCB-114/PCB-131, PCB-156/PCB-202 and PCB-167/PCB-128 (Figures 2–8). Of these con-

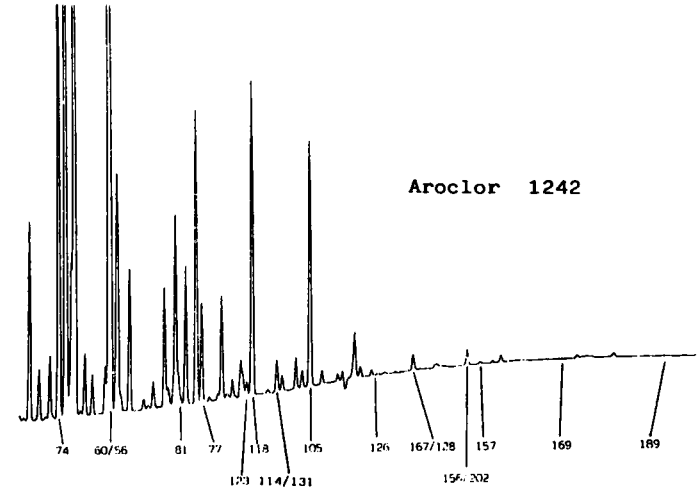


Figure 3 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 5 ng A1242.

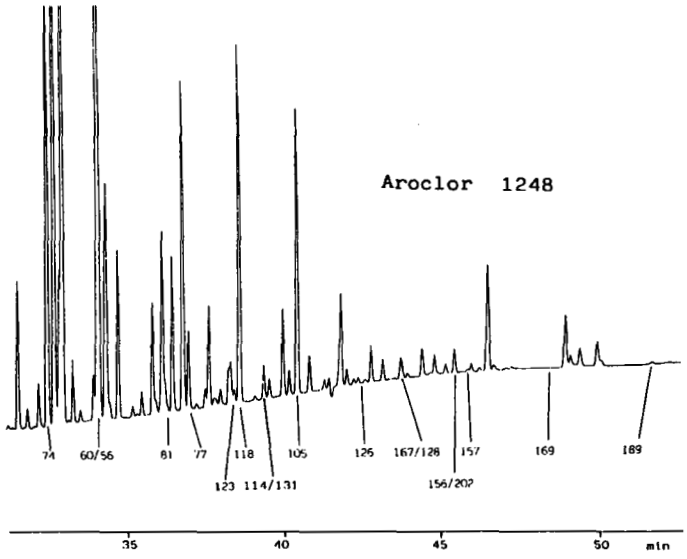


Figure 4 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 2.5 ng A1248.

geners PCB-156 and PCB-167 could be analyzed without interference on the CP-SIL-19 column (Figure 1). PCB-60 showed a weak interference from PCB-92 on this column and was analysed on the SIL-88 column. PCB-114 may be analyzed on the SIL-19 column where it appears as a shoulder on PCB-146 but was better analyzed on the SIL-8 column, where it was nearly baseline resolved from the potentially interfering PCB-134 and PCB-131 (Figure 1).

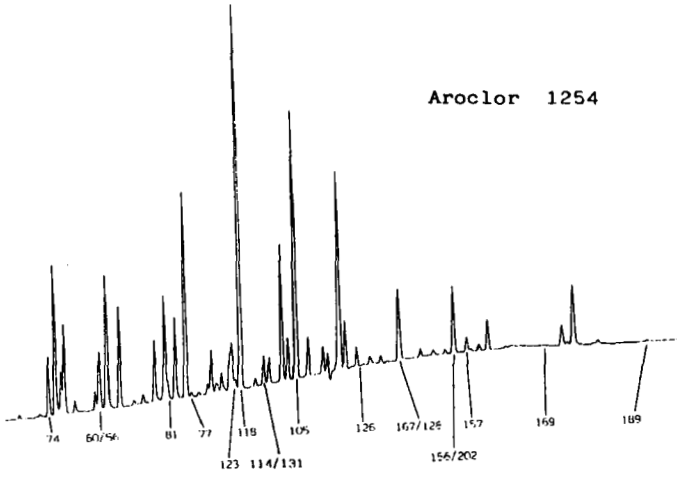


Figure 5 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 0.5 ng A1254.

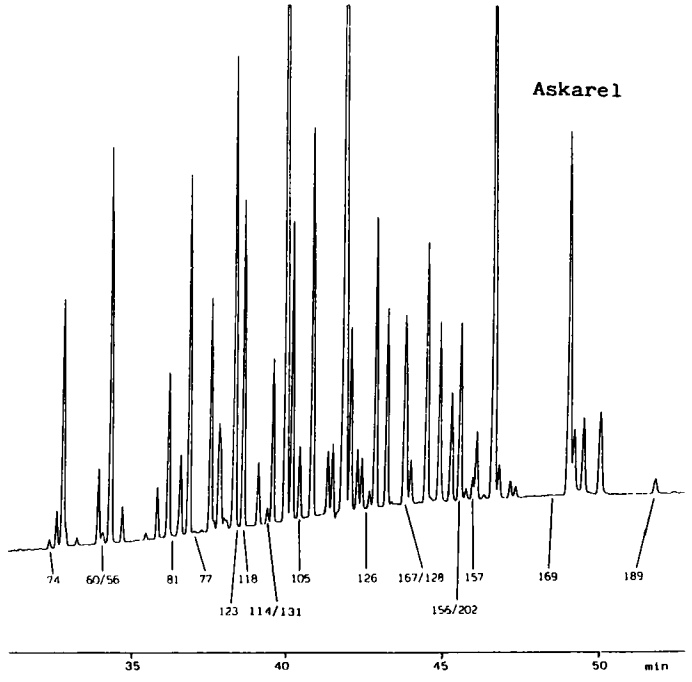


Figure 6 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 5 ng Askarel.

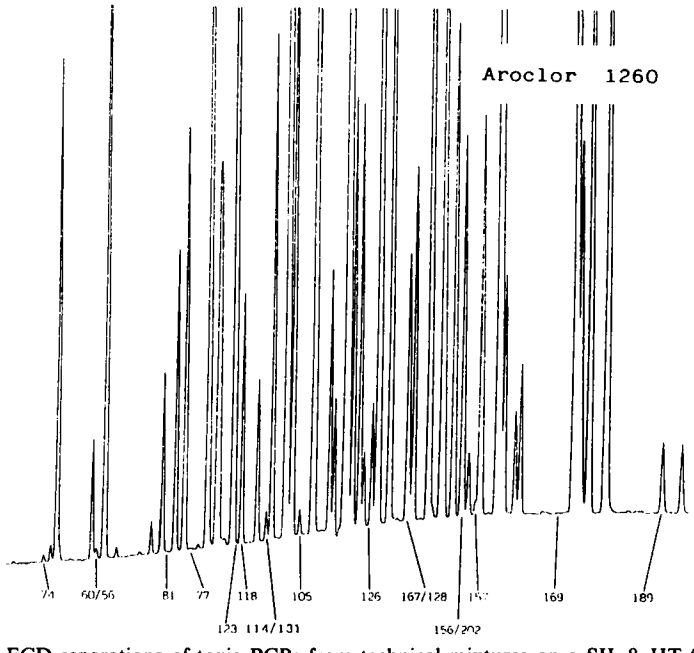


Figure 7 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 5 ng A1260.

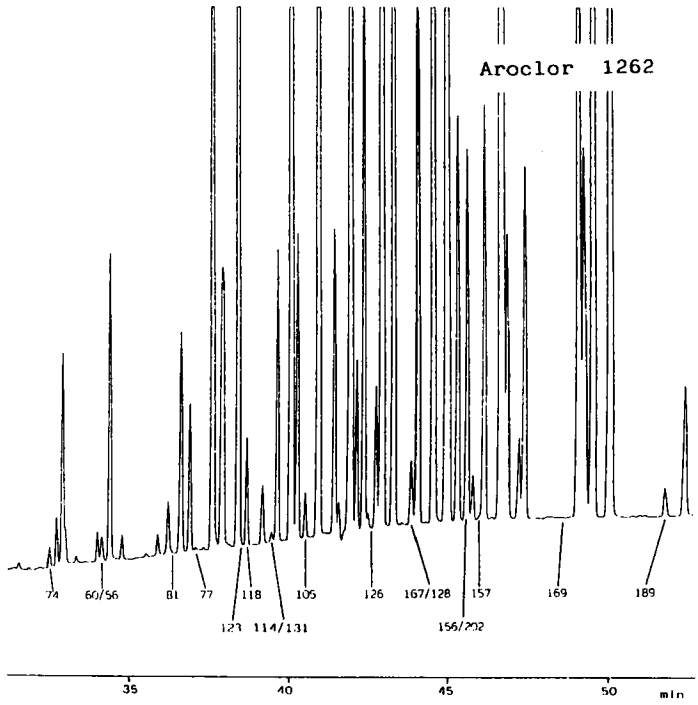


Figure 8 GC-ECD separations of toxic PCBs from technical mixtures on a SIL-8–HT-5 column. The injected amounts were 5 ng A1262.

The chromatographic behavior on the four different columns (SIL-8, SIL-8-HT-5, SIL-19 and SIL-88) of the toxic non-*ortho*- and mono-*ortho*-substituted PCBs is shown in Figures 9 and 10 after GC-ECD analyses of a complex PCB mixture (A1016, A1232, A1248 and A1260, 1:1:1:1) and the results are summarized in Table 4. For parallel analysis of toxic PCBs on two GC columns the best choice appears to be SIL-8-HT-5/SIL-19 or SIL-88/SIL-19. On these column pairs all toxic PCBs can be analyzed without interference. The latter combination includes the thermally unstable bis-cyanopropylphenyl phase and may only keep its efficiency over a period of a few months. Other combinations show co-elution for at least one congener: SIL-8/SIL-19 (PCB-123 and PCB-157), SIL-8/SIL-88 (PCB-77), SIL-8/SIL-8–HT-5 (PCB-60, PCB-156, PCB-157) and SIL-8–HT-5/SIL-88 (PCB-114).

Quantitative results

The measured concentrations (as weight percentage, %) of the toxic PCBs in technical mixtures are shown in Table 3. As a rule HRGC-ECD data were preferred due to their higher reproducibility. However, for some congeners (PCB-81, PCB-114, PCB-126, PCB-157 and PCB-169) concentrations were too low to remain in the linear detection range for the ECD and HRGC-MS data were used. In other cases (PCB-60,

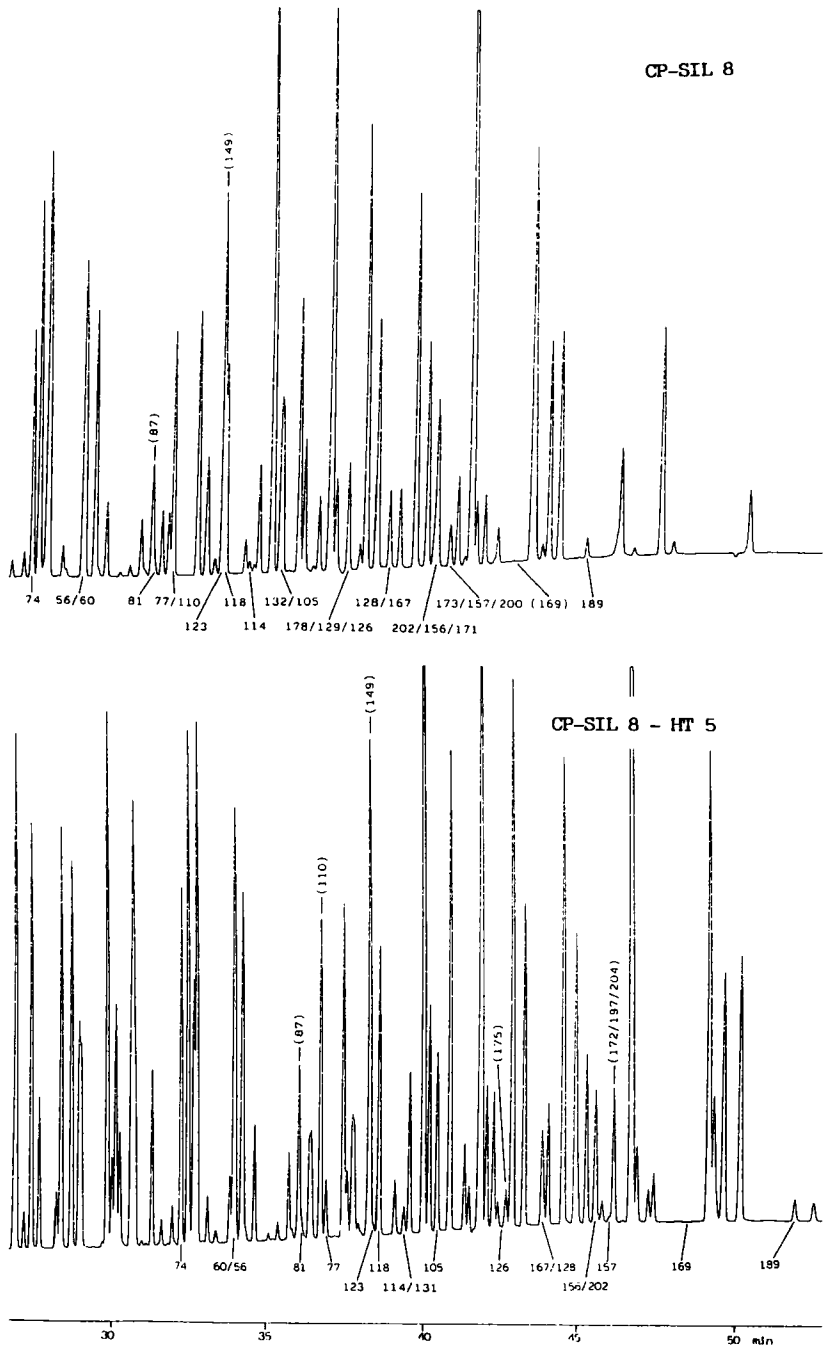


Figure 9 GC-ECD separations of toxic PCBs from a complex PCB mixture (A1016, A1232, A1248, A1260, 1:1:1:1) on a SIL-8 and a SIL-8–HT-5 column.

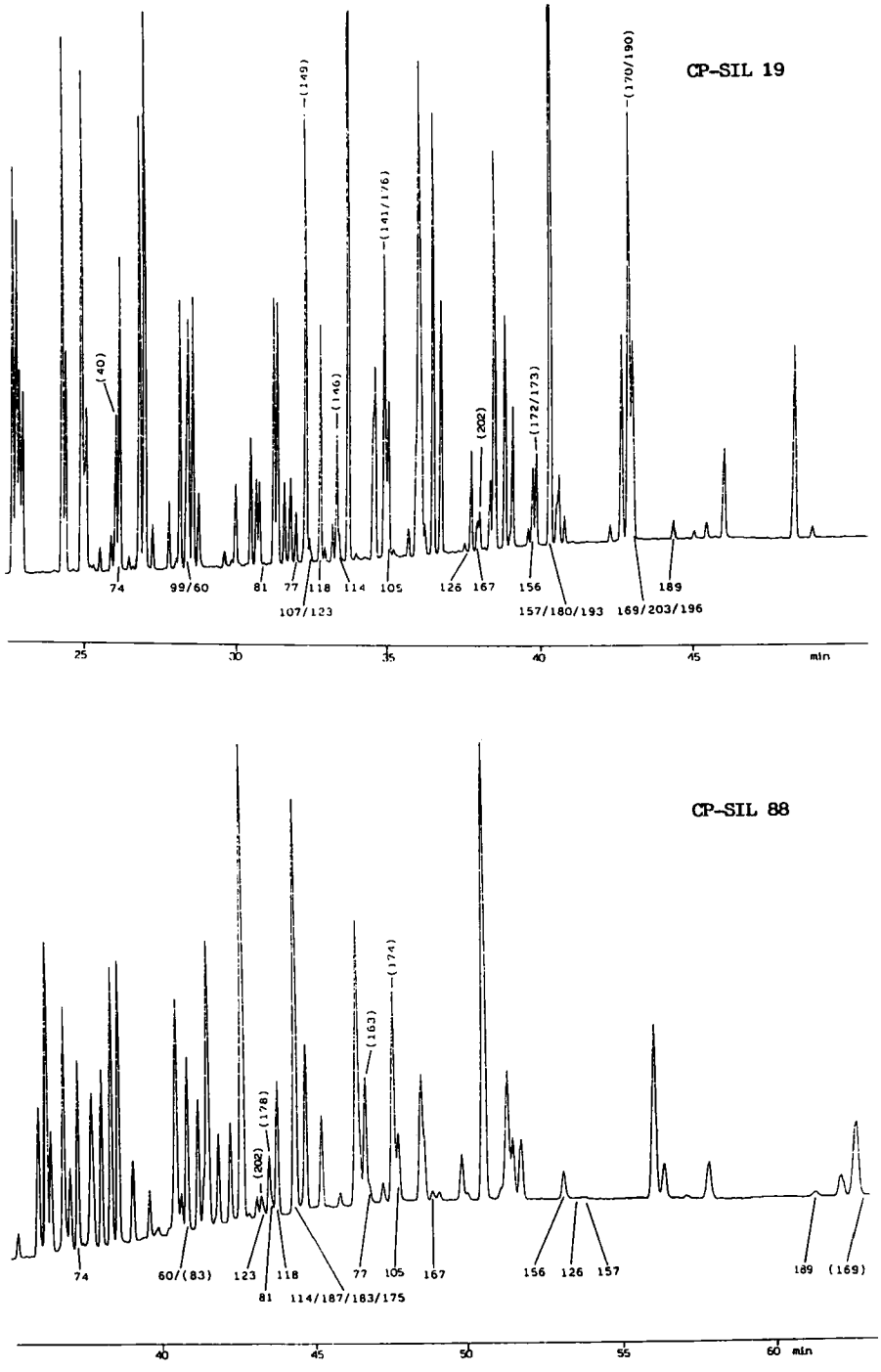


Figure 10 GC-ECD separations of toxic PCBs from a complex PCB mixture (A1016, A1232, A1248, A1260, 1:1:1:1) on a SIL-19 and a Sil-88 column.

Table 3 Concentration (weight percentage % w/w) of toxic congeners in technical PCB mixtures

PCB #	*Ref.*	*A1232*	*A1242*	*A1248*	*A1254*	*A1260*	*A1262*	*ASKAREL*
	a	0.46	0.66	1.32	0.56	0.011	0.027	0.039
PCB 60	(23)		1.33		0.54	ND(b)		
	a	0.86	1.37	2.65	1.77	0.023	0.061	0.070
PCB 74	(23)		2.17		0.78	ND(b)		
	a	0.12	0.25	0.40	0.12	0.0038	0.0081	0.014
	(23)		0.45		ND(b)	ND(b)		
PCB 77	(36)		0.50	0.30	ND(c)	ND(c)		
	(24)		0.51	0.62	0.062	0.026		
	(25)		0.22		0.25	0.017		
	(48)		0.24	0.34	0.02	ND(f)		
	a	0.0088	0.016	0.027	0.0062	ND(a)	ND(a)	
PCB 81	(23)		ND(b)		ND(b)	ND(b)		
	(36)		ND(c)	ND(c)	ND(c)	ND(c)		
	a	0.17	0.43	1.00	4.71	0.045	0.0079	0.32
PCB 105	(23)		0.86		3.83	0.07		
	(36)		0.33	0.55	2.03	0.08		
	(25)		0.29		6.90	0.052		
	a	0.0080	0.0098	0.019	0.043	0.0014	0.0003	0.0011
PCB 114	(23)		ND(b)		ND(b)	ND(b)		
	(36)		ND(c)	ND(c)	ND(c)	ND(c)		
	a	0.32	0.74	1.69	9.09	0.57	0.25	1.94
PCB 118	(23)		1.62		6.39	0.57		
	(36)		1.80	3.35	8.45	1.15		
	(a)	0.024	0.038	0.085	0.33	ND(a)	ND(a)	ND(a)
PCB 123	(23)		ND(b)		0.81	ND(b)		
	(36)		ND(c)	0.25	0.93	ND(c)		
	a	0.0013	0.0037	0.011	0.027	0.0004	ND(a)	ND(a)
	(23)		ND(b)		ND(b)	ND(b)		
PCB 126	(36)		ND(c)	ND(c)	ND(c)	ND(c)		
	(24)		0.0019	0.0052	0.0038	0.0003		
	(25)		0.0030		0.016	ND(e)		
	(48)		trace	trace	trace	ND(f)		
	a	0.059	0.026	0.083	1.07	0.48	0.59	0.56
PCB 156	(23)		0.090		1.62	0.88		
	(36)		0.13	0.35	2.40	1.05		
	a	0.0013	0.0026	0.011	0.026	0.024	0.0078	0.085
PCB 157	(23)		ND(b)		ND(b)	0.14		
	(36)		ND(c)	ND(c)	0.02	0.07		
	a	ND(a)	ND(a)	0.0014	0.045	0.030	0.017	0.059
PCB 167	(23)		ND(b)		0.21	0.26		
	(36)		ND(c)	ND(c)	0.05	0.15		
	a	ND(a)	ND(a)	ND(a)	ND(a)	ND(a)	ND(a)	ND(a)
	(23)		ND(b)		ND(b)	0.05		
PCB 169	(36)		ND(c)	ND(c)	0.08	0.05		
	(24)		ND(d)	ND(d)	0.00005	ND(d)		
	(25)		ND(e)		ND(e)	ND(e)		
	(48)		ND(f)	ND(f)	ND(f)	ND(f)		
	a	ND(a)	ND(a)	0.012	0.031	0.13	0.052	0.077
PCB 189	(23)		ND(b)		ND(b)	0.11		
	(36)		ND(c)	ND(c)	ND(c)	0.35		

Detection limits; ND(a) = 0.0001%, ND(b) = 0.05%, ND(c) = 0.01%, ND(d) = 0.00001%, ND(e) = 0.007%, ND(f) = 0.00004%.

a: present study.

Table 4 List of toxic PCBs which can be separated[a] from technical PCB mixtures on various GC columns

Column type	*PCB congeners (IUPAC numbers)*
SIL8	74, (81), (105), 114, 169 and 189
SIL-8–HT-5	74, 77, (81), 105, 118, (123), 126, 157, 169, 189
SIL-19	(60), 74, 77, 81, 105, (114), 118, 126, 156, 167 and 189
SIL-88	(60), 74, (81), 105, 118, 123, 126, 156, 157, 167, 169 and 189

[a] Sufficient separation was defined as less than 10% inteference on the GC-ECD peak maximum. Numbers in brackets indictaes that GC-MS selected ion monitoring was necessary to minimize interfence from closely eluting higher mass PCB.

PCB-123) interference was believed to be minimized in the reconstructed selected ion traces and also here HRGC-MS data were used. A comparison of the two different detection techniques is shown in Table 2 for PCB-77. It is clear, that due to the chromatographic isolation of this congener from possible interference on SIL-8–HT-5, the ECD and ITS-40 results are in good agreement.

Except for PCB-169, which was never found, all toxic PCBs were measurable at a detection limit of 0.001 mg g^{-1} (or 0.0001%) in at least four of the investigated technical mixtures. The concentrations varied from the low $\mu g\ g^{-1}$ range to several percentage with PCB-118 being relatively high in all mixtures. The most abundant toxic congener in each mixture was: PCB-74 in A1232, A1242 and A1248, PCB-118 in A1254, A1260 and Askarel and PCB-156 in A1262.

It is interesting to compare the present results with the previously published data on Aroclor mixtures. Most work has been done with the three non-*ortho*-substituted PCBs. For PCB-77 concentrations have been reported in the range of 0.22–0.51%, 0.30–0.62%, <0.01–0.25% and <0.01–0.026% in A1242, A1248, A1254 and A1260, respectively. For PCB-126 concentrations have been reported in the range of 0.0019–0.0037%, 0.0052–<0.01%, 0.0038–0.016% and 0.0003–<0.007% in A1242, A1248, A1254 and A1260, respectively. PCB-169 has been reported only in A-1254 and A-1260 in concentrations from 0.00005–0.08% and 0.05%, respectively.

The previously published results have been obtained with a variety of methods including carbon chromatography HRGC-ECD[48], carbon chromatography HRGC-MS[24], multi-dimensional GC-ECD[23,36] and multi-dimensional GC-MS[25]. The results of the present study are in the same range as the (scattered) previously published results with most of the congeners in the lower concentration end. A notable part of the scattering of results can be explained by batch to batch variations of the Aroclor mixtures. This is demonstrated by the data obtained on two different batches with the same analytical technique[23,36]. However, some part of the scattering may also be due to analytical errors. Especially, the relatively high concentrations of PCB-169 obtained by one technique[23,36] are outstanding and not confirmed by MS.

Toxicity implications

The total "dioxin like" toxicity of the technical PCB mixtures calculated by the two different TEF models is shown in Figure 10. The toxicity of the mixtures predicted

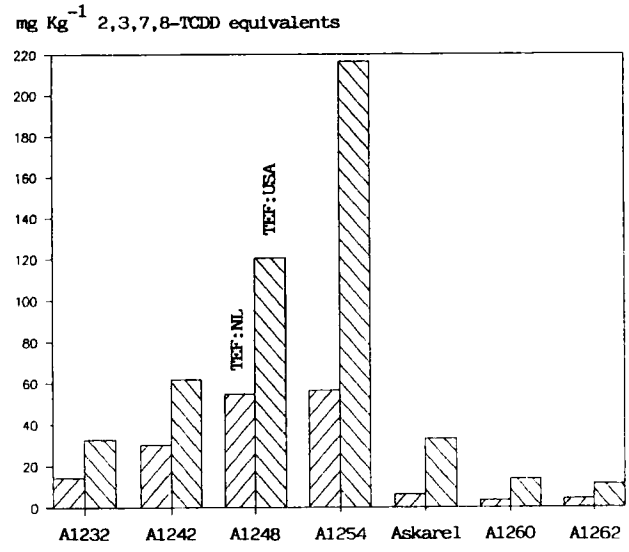


Figure 11 The total "dioxin like" toxicity of various PCB mixtures as predicted by two TEF models (NL[8] and USA[7]).

according to the two models are very different. The USA model is conservative and predict up to almost four times higher toxicity than the NL model. However, the qualitative comparison of the toxicity of the different mixtures gives the same picture for both models, namely increasing toxicity with the degree of chlorination from A1232 to A1254 and then decreasing with further chlorination.

The relative contribution from the six most important congeners is shown in Figure 11. According to the NL model PCB-77 predominates in the lower chlorinated mixtures, PCB-126 (PCB-118) in the medium chlorinated mixtures and PCB-156 in the higher chlorinated mixtures. According to the USA model PCB-74 and PCB-77 prevails in the lower chlorinated end, PCB-105 together with PCB-118 in the middle and PCB-118 together with PCB-156 in the higher end.

Interestingly, in all the technical mixtures the sum of the predicted toxicity of these six congeners account for between 80% and 99% of the total "dioxin like" toxicity no matter what TEF model is used. For biological samples this number may be a little lower (in human milk these six congeners account for 60–70%[34]). Nevertheless, it is still a high figure and it strongly suggests that future PCB legislations and environmental monitoring should be based on the toxic PCB congeners PCB-74, PCB-77, PCB-105, PCB-118, PCB-126, PCB-156.

CONCLUSION

The series coupling of two commercially available capillary columns (CP-SIL-8 and HT-5) facilitates the gas chromatographic separation of the three most toxic PCBs

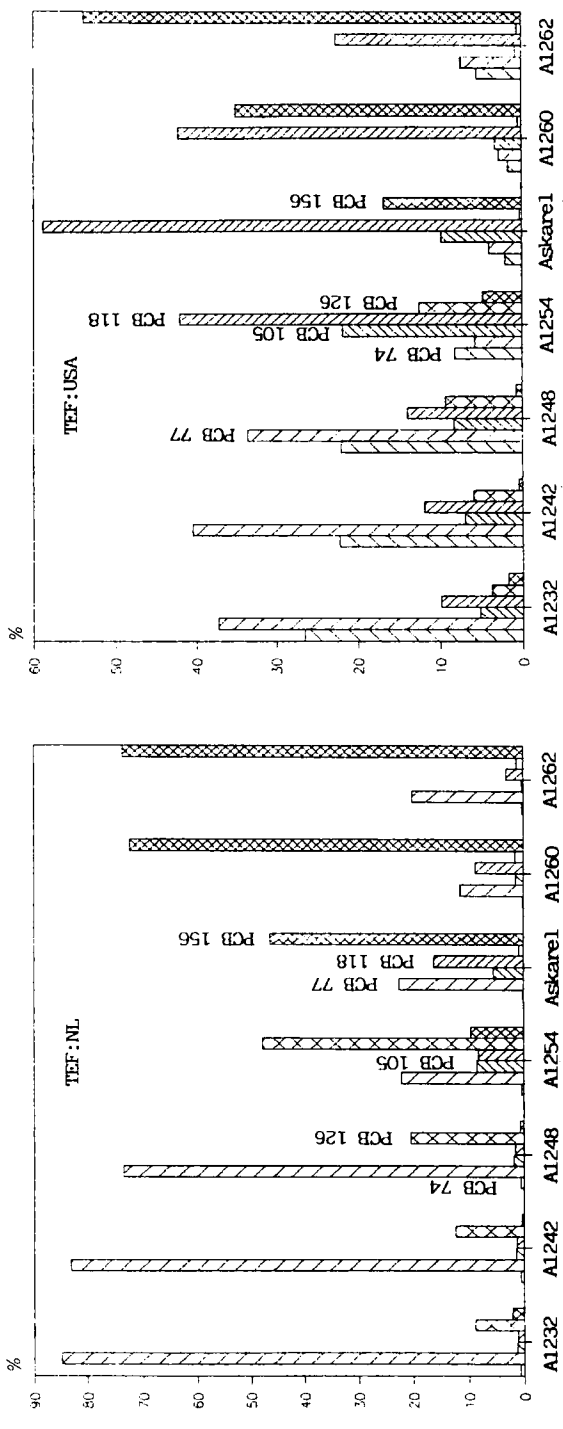


Figure 12 The relative contribution from the six most important congeners to the total "dioxin like" toxicity of technical PCB mixtures.

(PCB-77, PCB-126 and PCB-169) from any congener in technical PCB mixtures. Furthermore, the majority of other toxic congeners are well separated from potentially interfering PCBs (PCB-74, PCB-81, PCB-105, PCB-118, PCB-123, PCB-157 and PCB-189) with the exception of four congeners (PCB-60, PCB-114, PCB-167 and PCB-156). A parallel analysis on a CP-SIL-19 column gives a satisfactory analysis for all toxic PCBs.

The concentration of toxic PCB in the technical PCB mixtures, Askarel and Aroclors, varies from <0.0001% to 9% (w/w) with PCB-118 being the overall most prevalent.

The "dioxin like" toxicity predicted from toxicity equivalence models of the technical PCB varies from 4–11 mg kg^{-1} (A1262) to 55–216 mg kg^{-1} (A1254) depending on the TEF model used. Further toxicological studies of individual PCB congeners are needed in order to narrow the range of predicted toxicity by the TEF approach.

Six congeners account together for 80–99% of the total predicted "dioxin like" toxicity (PCB-74, PCB-77, PCB-105, PCB-118, PCB-126, PCB-156). Therefore, future PCB legislations should be based on these congeners.

References

1. S. Tanabe, *Environ. Pollut.* **50**, 5–28 (1988).
2. M. Mullin, C. Pochini, S. McCrindle, M. Romkes, S. Safe and L. Safe, *Environ. Sci. Technol.* **18**, 468–476 (1984).
3. S. Safe, L. Safe and M. Mullin, *J. Agric. Food Chem.* **33**, 24–29 (1985).
4. S. Safe, *CRC Crit. Rev. Toxicol.* **13**, 319–334 (1984).
5. J. Clarke, *Chemosphere* **15**, 275–287 (1986).
6. V. McFarland and J. Clarke, *Environ. Health Perspectives* **81**, 225–239 (1989).
7. S. Safe, C. Yao and D. Davis, Proc. Int. Conf. Organohalogen Compounds, (Bayreuth, 7–11 Sept. 1990) pp. 55–59.
8. LAC Stuurgroep "visverontreiniging" vergardering van 25 Oct. 1990, agendapunt 5.2.1 Netherlands Institute for Fishery Investigations.
9. A. Hanberg, F. Waern, L. Asplund, E. Haglund and S. Safe, *Chemosphere* **20**, 1161–1164 (1990).
10. P. Voogt, D. Wells, L. Reutergard and U. Brinkman, *Intern. J. Environ. Anal. Chem.* **40**, 1–46 (1990).
11. P. Haglund, L. Asplund, B. Jansson and H. Jarnberg, *Chemosphere* **20**, 887–894 (1990).
12. J. Van Rhign, W. Traag, A. Roos, P. Van de Spreng, J. Van Trijp, W. Kulik and L. Tuinstra, *J. High Res. Chromatogr. Chromatogr. Cmmun.* in print (1991).
13. P. Haglund, L. Asplund, H. Jarnberg and B. Jansson, *J. Chromatogr.* **507**, 389 (1990).
14. D. Patterson, C. Lapeza, E. BArnhart, D. Groce and V. Burse, *Chemosphere* **19**, 127–134 (1990).
15. A. Niimi, and B. Oliver, *Chemosphere* **18**, 1413 (1988).
16. J. Tarhanen, J. Koistinen, J. Paasivirta, P. Vuorinen, J. Koivusaari, I. Nuuja, N. Kannan and R. Tatsukawa, *Chemosphere* **18**, 1067–1070 (1989).
17. H. Beck, A. Dross and W. Mathar, *Chemosphere* **19**, 1805–1810 (1989).
18. J. Koistinen, J. Paasivirta and P. Vuorinen, *Chemosphere* **19**, 527–530 (1989).
19. K. Noren, A. Lunden, J. Sjovall and A. Bergman, *Chemosphere* **20**, 935–941 (1990).
20. L. Asplund, A. Grafstrom, P. Haglund, B. Jannson, U. Jarnberg, D. Mace, M. Strandell and C. DeWit, *Chemosphere* **20**, 1481–1488 (1990).
21. J. Koistinen, *Chemosphere* **20**, 1043–1048 (1990).
22. J. Mes and D. Weber, *Chemosphere* **19**, 1357–1365 (1990).
23. D. Schultz, G. Petrick and J. Duinker, *Environ. Sci. Technol.* **23**, 852–859 (1989).
24. N. Kannan, S. Tanabe, T. Wakimoto and R. Tatsukawa, *J. Assoc. Off. Anal. Chem.* **70**, 451–454 (1987).
25. K. Himberg and E. Sippola, Proc. Int. Conf. Organohalogen Compounds, (Bayreuth, 7–11 Sept. 1990) pp. 183–186.

26. S. Tanabe, N. Kannan, A. Subramanian, S. Watanabe and R. Tatsukawa, *Environ. Pollut.* **47**, 147–163 (1987).
27. S. Tanabe, N. Kannan, A. Subramanian, S. Watanabe, M. Ono and R. Tatsukawa, *Chemosphere* **16**, 1965–1970 (1987).
28. S. Tanabe, N. Kannan, T. Wakimoto and R. Tatsukawa, *Intern. J. Environ. Anal. Chem.* **29**, 199–213 (1987).
29. S. Tanabe, N. Kannan, T. Wakimoto and R. Tatsukawa, *Chemosphere* **16**, 1631–1634 (1987).
30. N. Kannan, S. Tanabe and R. Tatsukawa, *Bull. Environ. Contam. Toxicol.* **41**, 267–276 (1988).
31. N. Kannan, S. Tanabe, T. Okamoto, R. Tatsukawa and D. Phillips, *Environ. Pollut.* **62**, 223–235 (1989).
32. N. Kannan, S. Tanabe and R. Tatsukawa, *Environ. Pollut.* **56**, 65–76 (1989).
33. B. Larsen, S. Bøwadt and R. Tilio, *Intern. J. Environ. Anal. Chem.* (in press).
34. B. Larsen, T. Nilsson, S. Facchetti, L. Turrio-Baldassarri, N. Iacovella and A. Di Domenico, *Bull. Environm. Contam. and Toxicol.* (submitted).
35. J. DeBoer and Q. T. Dao, *Intern. J. Environ. Anal. Chem.* **43**, 245–251 (1991).
36. J. Duinker, D. Schultz and G. Petrick, *Anal. Chem.* **60**, 478–484 (1988).
37. E. Storr-Hansen, *Intern. J. Environ. Anal. Chem.* **43**, 253–266 (1991).
38. R. Fisher and K. Ballschmiter, *Anal. Chem.* **332**, 441–446 (1988).
39. D. Willams and G. LeBel, *Chemosphere* **21**, 487–494 (1990).
40. J. Duinker and M. Hillebrand, *Environ. Sci. Technol.* **17**, 449–456 (1983).
41. G. Sovocool, R. Mitchum and J. Donnelly, *Biomed. Mass Spectrom.* **14**, 579–584 (1987).
42. B. Larsen and J. Riego, *Intern. J. Environ. Anal. Chem.* **40**, 59–68 (1990).
43. N. Kannan, G. Petrick, D. Schulz, J. Duinker, J. Boon, Van Arnhem and S. Jansen, Proc. Int. Conf. Organohalogen Compounds (Bayreuth, 7–11 Sept. 1990) pp. 165–168.
44. J. De Boer and Q. T. Dao, *J. High Res. Chromatogr. Chromatogr. Commun.* in print (1991).
45. K. Ballschmiter, W. Schafer and H. Buchert, *Fresenius Z. Anal. Chem.* **326**, 253–257 (1987).
46. A. Bergman, A. Nilsson, J. Riego, and U. Orn, *Acta Chem. Scand.* **44**, 1071–1078 (1990).
47. J. Schneider, S. Bourne and A. Boparai, *J. Chromatogr. Sci.* **22**, 203–209 (1984).
48. J. Hucklins, D. Stalling and J. Petty, *J. Assoc. Off. Anal. Chem.* **63**, 750–755 (1980).
49. R. Williams and H. Mitchell, *J. Chromatogr.* **541**, 59–75 (1991).