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Calculation algorithm for the retention times of polychlorinated biphenyls and the control of its efficiency on a non-polar capillary column

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Abstract

A system for calculating the retention times of all 209 polychlorinated biphenyl (PCB) congeners is described. The injection of only twenty selected PCB congeners allows the calculation of the retention times of the other PCBs. The calculation was based on the comparison of the retention times of all 209 PCB congeners on the non-polar CP-Select for PCBs capillary column. Most of the calculated retention times were within 2% of the measured values. The efficiency of the calculation algorithm was investigated with literature data obtained on SE-54 and CP-Select for PCBs columns. An influence of the temperature programme on the calculations was observed. Therefore, a temperature programme which is suitable for the calculation algorithm for the retention times of PCBs is proposed.

1. Introduction

Since their detection in the environment by Jensen [1] in 1966, polychlorinated biphenyls (PCBs) have been recognized as ubiquitous organochlorine contaminants [2,3]. Owing to the complexity of technical PCB mixtures and PCB residues in the environment, their determination after high-resolution gas chromatographic (HRGC) separation is a matter of necessity. In 1984, Mullin et al. [4] established the SE-54 phase as a standard phase for PCB separations. However, several co-elutions were reported on this GC phase [4–7]. Therefore, alternative column coatings were proposed for the separation of PCBs. Even more, it was found that several GC columns such as C8 phases [8,9], CP-Select for PCBs [10] and phases coated with *p,p*-cyanobiphenyl [11] showed higher selectivity for the separation of PCBs than columns based on SE-54.

Calculations of retention times for polyhalogenated hydrocarbons have been described to some extent in the literature [12–17] following mainly the method of quantitative structure–retention relationships (QSRRs) [18].

Referring to the selectivity of the stationary phase for PCB separations, it has been reported that PCB separations are usually dependent on the number of chlorine atoms in *ortho* positions [4,8,10,19,20]. Only a few deviations from this rule were observed, with an increasing number

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of deviations when a more polar phase was applied [10]. Furthermore, holding one ring fixed, elution orders dependent on the substitution pattern of the other ring were reported [4,8,19].

However, the latter rule particularly might undergo several changes with increasing polarity of the stationary phase. The calculation algorithm presented in this paper allows the prediction of the elution order of all PCB congeners on a GC phase. The prediction of retention values for unsymmetrically substituted compounds (X1–R–X_2) has been proposed by Evans and Smith [21] for alkanes and by Sissons and Welti [12] for PCBs.

The advantages of such calculations are their suitability for predicting both retention times and co-elutions of PCB congeners. The efficiency of this new method is discussed in comparison with the results obtained on SE-54 and CP-Select for PCBs columns using different temperature programmes.

2. Experimental

2.1. Gas chromatography–mass spectrometry

All chromatograms were obtained after injection on to a Model 5890 gas chromatograph (Hewlett-Packard) connected with an HP 5971 MSD (Hewlett-Packard) mass spectrometer using electron impact ionization (GC–EI-MS) in the single-ion monitoring (SIM) mode. An HP 7673 autosampler (Hewlett-Packard) was used for splitless injections (1 min, injector temperature 270°C). Helium was used as the carrier gas.

The PCB standard solutions were separated on a CP-Select for PCBs capillary column (52 m × 0.25 mm I.D., film thickness 0.12 μm) (Chrompack, Middelburg, Netherlands). The temperature programme was 75°C for 2 min, increased at 15°C/min to 150°C and then at 1.5°C/min to 275°C. The total run time was 90.3 min.

The transfer line to the mass spectrometer was maintained at 280°C. Six time windows with four ions each were determined using m/z 188.0, 221.9, 255.9, 291.9, 325.8, 359.8, 395.8, 429.7, 463.7 and 497.7. The dwell time was set at 32 ms and the multiplier voltage at 2250 V.

2.2. Development of the calculation algorithm

At one phenyl ring twenty substitution patterns are possible (see Table 1, middle column). All PCB congeners with identical substitutions at ring a and ring b are selected to predict the elution order. These PCB congeners are listed in Table 1 with increasing retention time (t_R).

The elution order (increasing t_R) of biphenyl and the nineteen PCB congeners reflects the selectivity of the stationary phase for PCB separation. To predict the t_R values of all further PCB congeners, the measured t_R values of the twenty standard compounds must be divided by two. Rounded to half minutes, the resulting t_R represents the time increment of the phenyl ring under the GC conditions given above (see Table 1, last column). After the determination of the substitution pattern of a PCB congener at both

Table 1
Retention increments of biphenyl and nineteen PCBs with identical substitution on phenyl ring a and ring b (IUPAC nomenclature according to [22])

IUPAC No.	Substitution pattern	Time increment (min)
Biphenyl	2 × –	2[a]
PCB 4	2 × 2	8
PCB 11	2 × 3	12
PCB 54	2 × 2,6	12
PCB 15	2 × 4	12.5
PCB 52	2 × 2,5	16
PCB 47	2 × 2,4	16.5
PCB 40	2 × 2,3	17.5
PCB 155	2 × 2,4,6	20.5
PCB 80	2 × 3,5	21
PCB 136	2 × 2,3,6	21.5
PCB 77	2 × 3,4	23.5
PCB 133	2 × 2,3,5	26
PCB 153	2 × 2,4,5	27
PCB 128	2 × 2,3,4	29
PCB 202	2 × 2,3,5,6	30
PCB 197	2 × 2,3,4,6	31.5
PCB 169	2 × 3,4,5	34[a]
PCB 194	2 × 2,3,4,5	38
PCB 209	2 × 2,3,4,5,6	42[a]

[a] Time increment was slightly corrected compared to the measured t_R.

phenyl rings, the expected t_R can be calculated by adding the time increment of both rings corresponding to the substitution pattern of the PCB congener. For example, the expected t_R for PCB 138 (2,3,4,2',4',5'-hexachlorobiphenyl) under the GC conditions would be 56 min (29 min time increment for 2,3,4-substitution and 27 min time increment for 2,4,5-substitution). After application of this simple calculation algorithm, the accurate prediction of the t_R values of all further PCBs is possible.

The following three substitution patterns were corrected or assigned empirically (marked with superscript a in Table 1). First, the unsubstituted phenyl ring was assigned to a time increment of 2 min; second, the 3,4,5 pattern was corrected from 35 to 34 min; and third, the perchlorinated 2,3,4,5,6 pattern was corrected from 41 to 42 min (for further information, see Results and discussion).

3. Results and discussion

The efficiency of the system was tested with measurements on a non-polar CP-Select for PCBs capillary column. All 209 PCB congeners were separated on this GC phase. Table 1 gives the retention order on the CP-Select for PCBs column with regard to substitution of the rings. Ideally, on holding one ring fixed and changing the substitution at the second ring, the elution order should be as shown in Table 1. In fact, the PCBs follow this rule. The only deviations from this selectivity order were 2,6- and 3,5-dichloro-substituted rings. Such substitutions at one ring are highly affected by the substitution at the second ring. Thus, the 2,6-substituted PCB congeners might elute before, between or after the 3- and 4-substituted PCBs, and the 3,5-substituted PCBs might elute before, between or after PCBs with 2,4,6- and 2,3,6-substituted rings (assuming that the second ring is identically substituted).

Finally, under the GC conditions reported above, PCB 208 (2,3,4,5,6 + 2,3,5,6) eluted before PCB 195 (2,3,4,5,6 + 2,3,4). Table 2 gives both the measured and calculated t_R values of all 209 PCB congeners obtained on a CP-Select for PCBs capillary column.

The deviations of the calculated retention times (CRTs) and the measured retention times (MRTs) were less than 2.5% in most cases (see Table 1). The highest deviations were obtained in cases of unsubstituted and 2-chloro-substituted rings. This is due to the inaccuracy of the time increment at low t_R values, particularly for these substitution patterns, because biphenyl and PCB 4 (2,2'-dichlorobiphenyl) have longer t_R values than the time increment assigned to them. Therefore, in most cases the time increment of the unsubstituted phenyl ring empirically defined as 2 min is too high. However, this was not considered in the calculations (see Table 2).

PCB congeners with deviations of the MRT higher than 2.5% from the CRT were probably not eluted under optimum GC conditions. Therefore, we assume that the t_R values of these PCB congeners will be highly influenced by changing the temperature programme.

On the other hand, in most instances the agreement of CRTs and MRTs was exceptionally good. After exclusion of the unsubstituted and 2-chloro substitution on the second ring, all CRT/MRT ratios (in %) for the 2,4,5-substituted PCB congeners were between 98.3 and 102.9%. Both the mean value and the median for 2,4,5-substituted PCB congeners were 100.2%. The standard deviation was calculated using the theoretical value defined as 100% instead of the mean value. Therefore, the accuracy of the results for the 2,4,5-substituted rings is $100 \pm 1.0\%$.

Further, the accuracy of the CRTs of all regulation relevant PCBs (PCB 28, 52, 101, 138, 153 and 180 [23,24]) were closer than 1.1% to the MRTs, and the range for the toxic non-*ortho*-PCBs (PCB 77, 81, 126 and 169) was closer than 2.5%.

Recently, it was shown that the elution order on a CP-Select for PCBs column depends stringently on the number of chlorine atoms in *ortho* positions [10] (see Table 2, numbers in parenthesis). However, no correlation of the deviations (CRTs versus MRTs) with the number of *ortho*-chlorine atoms was observed. This also

Table 2
Measured and calculated retention times of all 209 PCBs on a CP-Select for PCBs phase (see Experimental)

IUPAC No. (x/y)[a]		Substituents		Time increment (min)	MRT[b]	CRT[b]	MoA[c] (%)
		On ring a	On ring b				
PCB 1	(1/1)	2		8 + 2	13.30	10	75.2
PCB 2	(1/0)	3		12 + 2	15.92	14	87.9
PCB 3	(1/0)	4		12.5 + 2	16.21	14.5	89.5
PCB 4[d]	(2/2)	2	2	8 + 8	16.32	16	98.0
PCB 10	(2/2)	2,6		12 + 2	16.51	14	84.8
PCB 9	(2/1)	2,5		16 + 2	18.98	18	94.8
PCB 7	(2/1)	2,4		16.5 + 2	19.17	18.5	96.5
PCB 6	(2/1)	2	3	8 + 12	19.54	20	102.4
PCB 5	(2/1)	2,3		17.5 + 2	19.82	19.5	98.4
PCB 8	(2/1)	2	4	8 + 12.5	20.20	20.5	101.5
PCB 19	(3/3)	2,6	2	12 + 8	20.26	20	98.7
PCB 14	(2/0)	3,5		21 + 2	22.54	23	102.0
PCB 30	(3/2)	2,4,6		20.5 + 2	22.75	22.5	98.9
PCB 18	(3/2)	2,5	2	16 + 8	23.02	24	104.3
PCB 17	(3/2)	2,4	2	16.5 + 8	23.49	24.5	104.3
PCB 11[d]	(2/0)	3	3	12 + 12	23.82	24	100.8
PCB 27	(3/2)	2,6	3	12 + 12	23.88	24	100.5
PCB 24	(3/2)	2,3,6		21.5 + 2	23.97	23.5	98.0
PCB 16	(3/2)	2,3	2	17.5 + 8	24.11	25.5	105.8
PCB 12	(2/0)	3,4		23.5 + 2	24.12	25.5	105.8
PCB 13	(2/0)	3	4	12 + 12.5	24.27	24.5	100.9
PCB 54[d]	(4/4)	2,6	2,6	12 + 12	24.31	24	98.7
PCB 15[d]	(2/0)	4	4	12.5 + 12.5	24.84	25	100.7
PCB 32	(3/2)	2,6	4	12 + 12.5	24.93	24.5	98.2
PCB 34	(3/1)	2	3,5	8 + 21	26.85	29	108.0
PCB 23	(3/1)	2,3,5		26 + 2	26.98	28	103.7
PCB 29	(3/1)	2,4,5		27 + 2	27.43	29	105.7
PCB 50	(4/3)	2,4,6	2	20.5 + 8	27.54	28.5	103.5
PCB 26	(3/1)	2,5	3	16 + 12	27.73	28	101.0
PCB 53	(4/3)	2,5	2,6	16 + 12	27.89	28	100.4
PCB 25	(3/1)	2,4	3	16.5 + 12	28.05	28.5	101.6
PCB 31	(3/1)	2,5	4	16 + 12.5	28.53	28.5	99.9
PCB 45	(4/3)	2,3,6	2	21.5 + 8	28.80	29.5	102.4
PCB 51	(4/3)	2,4	2,6	16.5 + 12	28.12	28.5	98.9
PCB 21	(3/1)	2,3,4		29 + 2	28.95	31	107.1
PCB 20	(3/1)	2,3	3	17.5 + 12	29.01	29.5	101.7
PCB 28	(3/1)	2,4	4	16.5 + 12.5	29.03	29	99.9
PCB 33	(3/1)	2	3,4	8 + 23.5	29.22	31.5	107.8
PCB 46	(4/3)	2,3	2,6	17.5 + 12	29.33	29.5	100.6
PCB 22	(3/1)	2,3	4	17.5 + 12.5	29.97	30	100.1
PCB 52[d]	(4/2)	2,5	2,5	16 + 16	31.79	32	100.7
PCB 43	(4/2)	2,3,5	2	26 + 8	31.82	34	106.9
PCB 73	(4/2)	2,6	3,5	12 + 21	31.90	33	103.4
PCB 69	(4/2)	2,4,6	3	20.5 + 12	32.19	32.5	101.0
PCB 104	(5/4)	2,4,6	2,6	20.5 + 12	32.23	32.5	100.8
PCB 96	(5/4)	2,3,6	2,6	21.5 + 12	33.35	33.5	100.4
PCB 49	(4/2)	2,4	2,5	16.5 + 16	32.39	32.5	100.3
PCB 48	(4/2)	2,4,5	2	27 + 8	32.45	35	107.9
PCB 36	(3/0)	3,5	3	21 + 12	32.67	33	101.0
PCB 65	(4/2)	2,3,5,6		30 + 2	32.81	32	97.5

Table 2 *(Continued)*

IUPAC No. (x/y)[a]	Substituents		Time increment (min)	MRT[b]	CRT[b]	MoA[c] (%)
	On ring a	On ring b				
PCB 47[d] (4/2)	2,4	2,4	16.5 + 16.5	33.09	33	99.7
PCB 62 (4/2)	2,3,4,6		31.5 + 2	33.11	33.5	101.2
PCB 44 (4/2)	2,3	2,5	17.5 + 16	33.15	33.5	101.1
PCB 39 (3/0)	3,5	4	21 + 12.5	33.39	33.5	100.3
PCB 75 (4/2)	2,4,6	4	20.5 + 12.5	33.59	33	98.2
PCB 59 (4/2)	2,3,6	3	21.5 + 12	33.65	33.5	99.6
PCB 38 (3/0)	3,4,5		34 + 2	33.78	36	106.6
PCB 42 (4/2)	2,3	2,4	17.5 + 16.5	33.88	34	100.4
PCB 41 (4/2)	2,3,4	2	29 + 8	34.36	37	107.7
PCB 71 (4/2)	2,6	3,4	12 + 23.5	34.58	35.5	102.7
PCB 40[d] (4/2)	2,3	2,3	17.5 + 17.5	34.74	35	100.7
PCB 35 (3/0)	3,4	3	23.5 + 12	34.81	35.5	102.0
PCB 64 (4/2)	2,3,6	4	21.5 + 12.5	35.15	34	96.7
PCB 37 (3/0)	3,4	4	23.5 + 12.5	35.61	36	101.1
PCB 103 (5/3)	2,4,6	2,5	20.5 + 16	36.48	36.5	100.1
PCB 72 (4/1)	2,5	3,5	16 + 21	36.79	37	100.6
PCB 94 (5/3)	2,3,5	2,6	26 + 12	36.89	38	103.0
PCB 68 (4/1)	2,4	3,5	16.5 + 21	37.20	37.5	100.8
PCB 95 (5/3)	2,3,6	2,5	21.5 + 16	37.65	37.5	99.6
PCB 100 (5/3)	2,4,6	2,4	20.5 + 16.5	37.70	37	98.1
PCB 93 (5/3)	2,3,5,6	2	30 + 8	37.74	38	100.7
PCB 57 (4/1)	2,3,5	3	26 + 12	37.80	38	100.5
PCB 102 (5/3)	2,4,5	2,6	27 + 12	37.91	39	102.9
PCB 98 (5/3)	2,4,6	2,3	20.5 + 17.5	38.08	38	99.8
PCB 67 (4/1)	2,4,5	3	27 + 12	38.29	39	101.9
PCB 58 (4/1)	2,3	3,5	17.5 + 21	38.34	38.5	100.4
PCB 88 (5/3)	2,3,4,6	2	31.5 + 8	38.37	39.5	102.9
PCB 61 (4/1)	2,3,4,5		38 + 2	38.68	40	102.9
PCB 91 (5/3)	2,3,6	2,4	21.5 + 16.5	38.87	38	97.8
PCB 63 (4/1)	2,3,5	4	26 + 12.5	38.91	38.5	98.9
PCB 76 (4/1)	2	3,4,5	34 + 8	39.11	42	107.4
PCB 84 (5/3)	2,3,6	2,3	21.5 + 17.5	39.36	39	99.1
PCB 70 (4/1)	2,5	3,4	16 + 23.5	39.45	39.5	100.1
PCB 74 (4/1)	2,4,5	4	27 + 12.5	39.47	39.5	100.1
PCB 66 (4/1)	2,4	3,4	16.5 + 23.5	39.85	40	100.4
PCB 89 (5/3)	2,3,4	2,6	29 + 12	39.98	41	102.6
PCB 55 (4/1)	2,3,4	3	29 + 12	40.08	41	102.3
PCB 56 (4/1)	2,3	3,4	17.5 + 23.5	40.89	41	100.3
PCB 121 (5/2)	2,4,6	3,5	20.5 + 21	40.90	41.5	101.5
PCB 155[d] (6/4)	2,4,6	2,4,6	20.5 + 20.5	41.09	41	99.8
PCB 60 (4/1)	2,3,4	4	29 + 12.5	41.28	41.5	100.5
PCB 92 (5/2)	2,3,5	2,5	26 + 16	41.66	42	100.8
PCB 152 (6/4)	2,3,5,6	2,6	30 + 12	41.92	42	100.2
PCB 150 (6/4)	2,3,6	2,4,6	21.5 + 20.5	42.04	42	99.9
PCB 90 (5/2)	2,3,5	2,4	26 + 16.5	42.55	42.5	99.9
PCB 80[d] (4/0)	3,5	3,5	21 + 21	42.57	42	98.7
PCB 101 (5/2)	2,4,5	2,5	27 + 16	42.61	43	100.9
PCB 113 (5/2)	2,3,6	3,5	21.5 + 21	42.70	42.5	99.5
PCB 136[d] (6/4)	2,3,6	2,3,6	21.5 + 21.5	42.95	43	100.1

(Continued on p. 178)

Table 2 *(Continued)*

IUPAC No. (x/y)[a]	Substituents		Time increment (min)	MRT[b]	CRT[b]	MoA[c] (%)
	On ring a	On ring b				
PCB 145 (6/4)	2,3,4,6	2,6	31.5 + 12	42.97	43.5	101.2
PCB 99 (5/2)	2,4,5	2,4	27 + 16.5	43.44	43.5	100.4
PCB 83 (5/2)	2,3,5	2,3	26 + 17.5	43.37	43.5	100.3
PCB 86 (5/2)	2,3,4,5	2	38 + 8	43.93	46	104.7
PCB 112 (5/2)	2,3,5,6	3	30 + 12	43.94	42	95.6
PCB 109 (5/2)	2,3,4,6	3	31.5 + 12	44.11	43.5	98.6
PCB 97 (5/2)	2,4,5	2,3	27 + 17.5	44.13	44.5	100.8
PCB 125 (5/2)	2,6	3,4,5	12 + 34	44.26	46	103.9
PCB 119 (5/2)	2,4,6	3,4	20.5 + 23.5	44.28	44	99.4
PCB 87 (5/2)	2,3,4	2,5	29 + 16	44.43	45	101.3
PCB 116 (5/2)	2,3,4,5,6		42 + 2	44.91	44	98.0
PCB 79 (4/0)	3,4	3,5	23.5 + 21	45.16	44.5	98.5
PCB 117 (5/2)	2,3,5,6	4	30 + 12.5	45.24	42.5	93.9
PCB 85 (5/2)	2,3,4	2,4	29 + 16.5	45.35	45.5	100.3
PCB 115 (5/2)	2,3,4,6	4	31.5 + 12.5	45.63	44	96.4
PCB 110 (5/2)	2,3,6	3,4	21.5 + 23.5	45.75	45	98.4
PCB 78 (4/0)	3	3,4,5	12 + 34	45.77	46	100.5
PCB 148 (6/3)	2,3,5	2,4,6	26 + 20.5	45.97	46.5	101.2
PCB 82 (5/2)	2,3,4	2,3	29 + 17.5	46.24	46.5	100.6
PCB 81 (4/0)	3,4,5	4	34 + 12.5	46.64	46.5	99.7
PCB 154 (6/3)	2,4,5	2,4,6	27 + 20.5	47.22	47.5	100.6
PCB 151 (6/3)	2,3,5,6	2,5	30 + 16	47.27	46	97.3
PCB 111 (5/1)	2,3,5	3,5	26 + 21	47.32	47	99.3
PCB 135 (6/3)	2,3,5	2,3,6	26 + 21.5	47.42	47.5	100.2
PCB 77 (4/0)	3,4	3,4	23.5 + 23.5	47.60	47	98.7
PCB 120 (5/1)	2,4,5	3,5	27 + 21	48.02	48	100.0
PCB 144 (6/3)	2,3,4,6	2,5	31.5 + 16	48.04	47.5	98.9
PCB 147 (6/3)	2,3,5,6	2,4	30 + 16.5	48.57	46.5	95.7
PCB 149 (6/3)	2,3,6	2,4,5	21.5 + 27	48.58	48.5	99.8
PCB 143 (6/3)	2,3,4,5	2,6	38 + 12	48.88	50	102.3
PCB 134 (6/3)	2,3,5,6	2,3	30 + 17.5	48.97	47.5	97.0
PCB 139 (6/3)	2,3,4,6	2,4	31.5 + 16.5	49.34	48	97.3
PCB 140 (6/3)	2,3,4	2,4,6	29 + 20.5	49.38	49.5	100.2
PCB 131 (6/3)	2,3,4,6	2,3	31.5 + 17.5	49.71	49	98.6
PCB 142 (6/3)	2,3,4,5,6	2	42 + 8	49.73	50	100.5
PCB 124 (5/1)	2,5	3,4,5	16 + 34	49.96	50	100.1
PCB 108 (5/1)	2,3,4	3,5	29 + 21	50.02	50	100.0
PCB 107 (5/1)	2,3,5	3,4	26 + 23.5	50.32	49.5	98.4
PCB 106 (5/1)	2,3,4,5	3	38 + 12	50.45	50	99.1
PCB 123 (5/1)	2,4	3,4,5	16.5 + 34	50.62	50.5	99.8
PCB 132 (6/3)	2,3,4	2,3,6	29 + 21.5	50.71	50.5	99.6
PCB 188 (7/4)	2,3,5,6	2,4,6	30 + 20.5	50.77	50.5	99.5
PCB 118 (5/1)	2,4,5	3,4	27 + 23.5	51.07	50.5	98.9
PCB 122 (5/1)	2,3	3,4,5	17.5 + 34	51.31	51.5	100.4
PCB 114 (5/1)	2,3,4,5	4	38 + 12.5	51.75	50.5	97.6
PCB 179 (7/4)	2,3,5,6	2,3,6	30 + 21.5	51.85	51.5	99.3
PCB 133[d] (6/2)	2,3,5	2,3,5	26 + 26	51.90	52	100.2
PCB 184 (7/4)	2,3,4,6	2,4,6	31.5 + 20.5	52.01	52	100.0
PCB 165 (6/2)	2,3,5,6	3,5	30 + 21	52.60	51	97.0
PCB 146 (6/2)	2,3,5	2,4,5	26 + 27	52.84	53	100.3
PCB 105 (5/1)	2,3,4	3,4	29 + 23.5	52.89	52.5	99.3

Table 2 *(Continued)*

IUPAC No. (x/y)[a]	Substituents		Time increment (min)	MRT[b]	CRT[b]	MoA[c] (%)
	On ring a	On ring b				
PCB 176 (7/4)	2,3,4,6	2,3,6	31.5 + 21.5	53.06	53	99.9
PCB 161 (6/2)	2,3,4,6	3,5	31.5 + 21	53.12	52.5	98.8
PCB 186 (7/4)	2,3,4,5,6	2,6	42 + 12	53.54	54	100.9
PCB 153[d] (6/2)	2,4,5	2,4,5	27 + 27	53.70	54	100.6
PCB 168 (6/2)	2,4,6	3,4,5	20.5 + 34	53.86	54.5	101.2
PCB 141 (6/2)	2,3,4,5	2,5	38 + 16	54.28	54	99.5
PCB 130 (6/2)	2,3,4	2,3,5	29 + 26	55.01	55	100.0
PCB 137 (6/2)	2,3,4,5	2,4	38 + 16.5	55.09	54.5	98.9
PCB 164 (6/2)	2,3,6	3,4,5	21.5 + 34	55.73	55.5	99.6
PCB 138 (6/2)	2,3,4	2,4,5	29 + 27	55.85	56	100.3
PCB 129 (6/2)	2,3,4,5	2,3	38 + 17.5	55.93	55.5	99.2
PCB 163 (6/2)	2,3,5,6	3,4	30 + 23.5	56.07	53.5	95.4
PCB 160 (6/2)	2,3,4,5,6	3	42 + 12	56.18	54	96.1
PCB 127 (5/0)	3,4,5	3,5	34 + 21	56.20	55	97.9
PCB 158 (6/2)	2,3,4,6	3,4	31.5 + 23.5	56.64	55	97.1
PCB 178 (7/3)	2,3,5,6	2,3,5	30 + 26	56.76	56	98.7
PCB 175 (7/3)	2,3,4,6	2,3,5	31.5 + 26	57.55	57.5	99.9
PCB 166 (6/2)	2,3,4,5,6	4	42 + 12.5	57.84	54.5	94.2
PCB 128[d] (6/2)	2,3,4	2,3,4	29 + 29	57.95	58	100.1
PCB 187 (7/3)	2,3,5,6	2,4,5	30 + 27	58.00	57	98.3
PCB 182 (7/3)	2,3,4,5	2,4,6	38 + 20.5	58.12	58.5	100.7
PCB 183 (7/3)	2,3,4,6	2,4,5	31.5 + 27	58.73	58.5	99.6
PCB 126 (5/0)	3,4,5	3,4	34 + 23.5	58.78	57.5	97.8
PCB 185 (7/3)	2,3,4,5,6	2,5	42 + 16	59.18	58	98.0
PCB 174 (7/3)	2,3,4,5	2,3,6	38 + 21.5	59.38	61.5	103.6
PCB 159 (6/1)	2,3,4,5	3,5	38 + 21	60.07	59	98.2
PCB 177 (7/3)	2,3,5,6	2,3,4	30 + 29	60.22	59	98.0
PCB 202[d] (8/4)	2,3,5,6	2,3,5,6	30 + 30	60.26	60	99.6
PCB 162 (6/1)	2,3,5	3,4,5	26 + 34	60.58	60	99.0
PCB 181 (7/3)	2,3,4,5,6	2,4	42 + 16.5	60.94	58.5	96.0
PCB 171 (7/3)	2,3,4,6	2,3,4	31.5 + 29	61.03	60.5	99.1
PCB 173 (7/3)	2,3,4,5,6	2,3	42 + 17.5	61.08	59.5	97.4
PCB 167 (6/1)	2,4,5	3,4,5	27 + 34	61.32	61	99.5
PCB 204 (8/4)	2,3,4,5,6	2,4,6	42 + 20.5	62.42	62.5	100.1
PCB 197[d] (8/4)	2,3,4,6	2,3,4,6	31.5 + 31.5	62.79	63	100.3
PCB 201 (8/4)	2,3,4,6	2,3,5,6	31.5 + 30	61.59	61.5	99.9
PCB 156 (6/1)	2,3,4,5	3,4	38 + 23.5	63.32	61.5	97.1
PCB 200 (8/4)	2,3,4,5,6	2,3,6	42 + 21.5	63.37	63.5	100.2
PCB 157 (6/1)	2,3,4	3,4,5	29 + 34	63.47	63	99.3
PCB 172 (7/2)	2,3,4,5	2,3,5	38 + 26	64.42	64	99.3
PCB 192 (7/2)	2,3,4,5,6	3,5	42 + 21	64.88	63	97.1
PCB 180 (7/2)	2,3,4,5	2,4,5	38 + 27	65.36	65	99.4
PCB 193 (7/2)	2,3,5,6	3,4,5	30 + 34	65.41	64	97.8
PCB 191 (7/2)	2,3,4,6	3,4,5	31.5 + 34	65.89	65.5	99.5
PCB 170 (7/2)	2,3,4,5	2,3,4	38 + 29	67.39	67	99.4
PCB 190 (7/2)	2,3,4,5,6	3,4	42 + 23.5	68.42	65.5	95.7
PCB 198 (8/3)	2,3,4,5,6	2,3,5	42 + 26	68.44	68	99.4
PCB 199 (8/3)	2,3,4,5	2,3,5,6	38 + 30	68.56	68	99.2
PCB 196 (8/3)	2,3,4,5	2,3,4,6	38 + 31.5	69.46	69.5	100.1
PCB 169[d] (6/0)	3,4,5	3,4,5	34 + 34	69.69	68	97.6
PCB 203 (8/3)	2,3,4,5,6	2,4,5	42 + 27	69.71	69	99.0
PCB 208 (9/4)	2,3,4,5,6	2,3,5,6	42 + 30	71.26	72	101.0

(Continued on p. 180)

Table 2 *(Continued)*

IUPAC No. (x/y)[a]	Substituents		Time increment (min)	MRT[b]	CRT[b]	MoA[c] (%)
	On ring a	On ring b				
PCB 195 (8/3)	2,3,4,5,6	2,3,4	42 + 29	71.89	71	98.8
PCB 207 (9/4)	2,3,4,5,6	2,3,4,6	42 + 31.5	72.59	73.5	100.6
PCB 189 (7/1)	2,3,4,5	3,4,5	38 + 34	73.08	72	98.5
PCB 194[d] (8/2)	2,3,4,5	2,3,4,5	38 + 38	76.30	76	99.6
PCB 205 (8/2)	2,3,4,5,6	3,4,5	42 + 34	77.16	76	98.5
PCB 206 (9/3)	2,3,4,5,6	2,3,4,5	42 + 38	79.78	80	100.3
PCB 209[d] (10/4)	2,3,4,5,6	2,3,4,5,6	42 + 42	82.03	84	102.4

[a] IUPAC No. (x/y) = IUPAC nomenclature following the numbering according to Ref. [22] with numbers in parentheses giving the degree of chlorination (x) and the number of chlorine atoms in *ortho* positions (y) according to Ref. [10].
[b] MRT = measured retention time and CRT = calculated retention time.
[c] MoA (measure of agreement) is the CRT/MRT ratio in %.
[d] PCBs with identical substitution on phenyl rings a and b.

points to the fact that on the CP-Select for PCBs phase PCB congeners with non-ideal elution (i.e., deviation of calculated and measured t_R values >2.5%) might particularly be affected when the temperature programme is changed.

On the other hand, our method for calculating the t_R values for PCBs allows the prediction of co-elutions on a given GC phase also, as the calculated elution order is very close to the measured order. For example, PCB 186 and 153 show very similar MRTs and elute before PCB 138 on CP-Select for PCBs. This is opposite to the SE-54 phase on which PCB 186 has a t_R similar to PCB 138 [4]. The earlier elution of PCB 186 on CP-Select for PCBs compared with SE-54 was predicted by the theoretical calculations (see Table 2). This demonstrates the efficiency of the proposed calculation algorithm.

However, one important exception should be noted. Recently, it was shown that PCB 138 could be separated from both PCB 163 and 164 on CP-Select for PCBs [10], in accordance with calculations. However, the CRT of PCB 163 is shorter than that of PCB 138, and this is opposite to the MRTs for PCB 138 and 163 (see Table 2). Interestingly, the deviation of the CRT from MRT of PCB 163 is the highest observed for both phenyl ring substitutions (2,3,5,6 + 3,4), except for PCB 117 (2,3,5,6 + 4). Consequently, PCB 163 shows a very individual chromatographic behaviour.

In 1984, Mullin et al. [4] published the relative retention times (RRTs) of all 209 PCB congeners on an SE-54 phase. The elution order of the symmetrically substituted PCB congeners is very close to that on a CP-select for PCBs column with the exception of PCB 15 and 54 and of PCB 80 and 155, which eluted in the reverse order (see Table 2 here and Table 6 in Ref. [4]).

On the basis of the data of Mullin et al. [4], the RRTs of eleven selected PCB congeners were calculated by application of the proposed calculation algorithm (see Table 3).

Table 3 shows that the calculated RRTs of most of the PCBs were close to the RRTs measured by Mullin et al. [4]. Differences are observable for PCB 180, 186 and 163. All of these three PCB congeners carry one highly substituted ring with at least four chlorine atoms. Therefore, we assume that this discrepancy in measured and calculated RRTs is due to the time increment assigned to PCBs with highly chlorinated rings, which is not a typical one.

Obviously, the temperature programme applied by Mullin et al. for the SE-54 column (1°C/min increase from 100 to 240°C [4]) was not optimum for the elution of symmetrically substituted PCBs with highly chlorinated rings and it is therefore not compatible with the proposed calculation algorithm of t_R values. Apparently, the temperature programme has an important influence on the elution of PCBs. To

Table 3
Ring substitution and corresponding time increments, RRTs measured by Mullin et al. [4] and calculated RRTs and the measure of agreement (MoA) of calculated and measured values

IUPAC No.	Ring a	Time increment (min)	Ring b	Time increment (min)	RRT		MoA (%)
					Calculated	Measured [4]	
PCB 28	2,4	0.232	4	0.169	0.401	0.4031	99.5
PCB 52	2,5	0.228	2,5	0.228	0.456	0.4557	100.0
PCB 101	2,4,5	0.352	2,5	0.228	0.580	0.5816	99.7
PCB 118	2,4,5	0.352	3,4	0.315	0.667	0.6693	99.7
PCB 153	2,4,5	0.352	2,4,5	0.352	0.704	0.7036	100.1
PCB 138	2,3,4	0.388	2,4,5	0.352	0.740	0.7403	100.0
PCB 180	2,3,5,6	0.404	2,4,5	0.352	0.756	0.8362	90.4
PCB 105	2,3,4	0.388	3,4	0.315	0.703	0.7049	99.7
PCB 186	2,3,4,5,6	0.525	2,6	0.190	0.715	0.7416	96.4
PCB 163	2,3,5,6	0.404	3,4	0.315	0.719	0.7396	97.2
PCB 126	3,4,5	0.431	3,4	0.315	0.746	0.7512	99.3

investigate this hypothesis, calculations were made on the basis of earlier reported data obtained on a CP-Select for PCBs column. The RRTs of 81 PCBs on CP-Select for PCBs were analysed with a faster temperature programme [10], and the RRTs were used for calculations with the proposed algorithm. Table 4 gives the calculated and measured RRTs of eleven selected PCB congeners (regulation-relevant and toxic PCBs and also interfering PCBs).

As in the case with data obtained by Mullin et al. [4] on an SE-54 column on the CP-Select for PCBs column, deviations of the measured and calculated RRTs were obtained for PCB 180, 186

Table 4
Ring substitution and corresponding time increments, measured RRTs according to Vetter et al. [10], the calculated RRTs and the measure of agreement (MoA) of calculated and measured values

IUPAC No.	Ring a	Time increment (min)	Ring b	Time increment (min)	RRT		MoA (%)
					Calculated	Measured [10]	
PCB 28	2,4	0.169	4	0.128[a]	0.297	0.303	98.0
PCB 52	2,5	0.162	2,5	0.162	0.324	0.325	99.7
PCB 101	2,4,5	0.273	2,5	0.162	0.435	0.424	102.6
PCB 118	2,4,5	0.273	3,4	0.239	0.512	0.518	98.8
PCB 153	2,4,5	0.273	2,4,5	0.273	0.546	0.546	100.0
PCB 138	2,3,4	0.296	2,4,5	0.273	0.569	0.570	99.8
PCB 180	2,3,5,6	0.307	2,4,5	0.273	0.580	0.675	85.9
PCB 105	2,3,4	0.296	3,4	0.239	0.535	0.538	99.4
PCB 186[b]	2,3,4,5,6	0.425	2,6	0.129[c]	0.554	0.543	102.0
PCB 163	2,3,5,6	0.307	3,4	0.239	0.546	0.574	95.1
PCB 126	3,4,5	0.370	3,4	0.239	0.609	0.602	101.2
New TP:							
PCB 186[d]	2,3,4,5,6	0.425	2,6	0.129[c]	0.554	0.543	102.0

[a] The time increment for 4-chloro-substituted rings was calculated from PCB 74 (RRT of PCB 15 was not available).
[b] RRT of PCB 186 as given in Ref. [10].
[c] Time increment for 2,6-dichloro-substituted rings was calculated from PCB 53 (RRT of PCB 54 was not available).
[d] RRT of PCB 186, new temperature programme (final temperature now 300°C).

and 163. However, the calculated and measured RRTs of all further PCB congeners showed a very good correlation (see Table 4).

All the data in Table 4 were obtained using the same GC phase (CP-Select for PCBs) as for the data in Table 2. Therefore, the modified temperature programme must be responsible for the higher deviations observed in the latter instance. As an additional proof of this hypothesis, the RRT of PCB 186 was measured with a new temperature programme ending at 300°C instead of 270°C [10]. The new temperature programme did not affect the MRT of PCB 186 but PCB 209 now eluted ca. 10 min earlier. As the time increment of the perchlorinated ring is determined by application of the MRT of PCB 209, the CRT of PCB 186 was recalculated this time using the new time increment for the perchlorinated ring. After chromatography with a final temperature of 300°C instead of 270°C, the CRT of PCB 186 was clearly smaller and in good agreement with the MRT of PCB 186 owing to the diminished time increment (see Table 4).

The calculation algorithm for the CRTs of PCBs is strongly influenced by the temperature programme. Therefore, the temperature programme should be similar to that in this work. A suitable temperature programme should start with a fast heating rate (10–20°C/min) to a ramp at 140–160°C (Temperature 1) followed by a slow rate (1–2°C/min) which allows the elution all PCB congeners before the final temperature (temperature 2) is reached. If a higher temperature 1 is chosen, the subsequent heating rate to the final temperature 2 should be smaller.

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