Determination of retention indices of polychlorobiphenyls by using other compounds detectable by electron-capture detection or selected polychlorobiphenyls as the reference series

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Abstract

The highest sensitivity to polychlorobiphenyls (PCBs) is offered by electron-capture detection (ECD), but the easy identification of individual congeners remains unresolved. Published retention data are of limited usefulness, as the lack of a uniform style and the dependence on the analysis conditions do not permit their general use. Retention index values of PCBs cannot be easily referred to n-alkanes, due to the very low response of these compounds to ECD, whereas other well detected reference series can be used: n-alkyl iodides were found useful for the determination of retention indices of the first congeners of the PCB series. Retention indices obtained by using selected DCMA (Dry Colour Manufacturers' Association) PCB reference mixtures can be directly used or converted to standard Kováts indices. A mixture of PCBs that shows a linear dependence of retention on the number of chlorine atoms on both isothermal and programmed-temperature analysis is suggested for reference purposes. Other methods and standard mixtures used for identification and quantitation purposes are reviewed and discussed.

1. Introduction

The research of polychlorobiphenyls (PCBs) in the environment is of great importance, as they were widely used before their toxicity was fully understood. Therefore, these compounds are ubiquitous in terrestrial and marine organisms, where metabolic concentration and decomposition processes take place [1–7].

The identification of the 209 congeners of PCBs separated by high-resolution capillary gas chromatography (HRGC) and detected at very low con-

centrations by electron-capture detection (ECD) is necessary, as the toxicity of the various compounds differs widely [1,8–13]. If the risk due to their presence in the environment is evaluated on the basis of the total amount of PCBs found in a sample, without taking into account the different toxicity values, incorrect conclusions may be drawn. Transport mechanisms, accumulation and degradation are congener-dependent, and information on these phenomena cannot be obtained when commercial mixtures are used as reference material [3,14]. The concentration of indicator congeners, including some of the most toxic PCBs, has been limited in some countries [12,13].

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The direct identification of all congeners by using authentic samples is very complex, due to the lack or to the high cost of pure standards. Multidimensional HPLC–HRGC–ECD procedures have been reported which allow the accurate congener-specific determination of PCBs [6]. Structure–retention correlations, based on the fact that the structure of the various PCBs congeners shows a regular behaviour depending on the number of Cl atoms in the two aromatic rings and on their position [13,15–20], were also used to predict the retention times of individual congeners and to assist in their identification. In routine analysis, identification is often carried out by comparison with tabulated retention values and, when possible, confirmed by mass spectrometry (MS). However, small amounts of PCBs, easily detected with ECD, cannot be identified by MS, due to low sensitivity in total ion monitoring mode and to the small difference between the mass spectra of congeners with the same degree of chlorination. Single ion monitoring MS (SIM-MS) increases sensitivity but requires a knowledge of the characteristic fragment ions of the compounds, sometimes coincident between several congeners.

Preliminary identification through GC retention data is therefore an important step in PCB analysis. The choice of a restricted number of possible congeners, by comparison of their retention values obtained under standard GC conditions with tabulated values, is followed by further confirmation by the addition of authentic samples or NIS selected ions procedure. Retention values measured in isothermal or programmed-temperature HRGC runs were published [21–32].

The style of publication of retention data is not uniform, and therefore their usefulness in different laboratories is limited depending on the analysis conditions selected. Absolute and adjusted retention times under isothermal and programmed-temperature conditions, retentions relative to octachloronaphthalene [28] and to some PCBs taken as reference standards [31], and retention indices were used. Table 1 summarizes some of the data available and gives the analysis conditions. The uniform expression of the retention data through the Kováts retention index [33–36] or the conversion into them, when possible, of retention data previously published in other forms may permit the comparison of data between different laboratories.

The Kováts retention index system is based on the use of n-alkanes as calibration standards. As the columns used for the separation of PCBs are generally made with non-polar liquid phases, the polarity of the solvent and of both the reference and sample solutes are similar and no problem connected to non-linear partition isotherm or sorption effects is encountered [37,38]. In order to cover the entire range of retention times of the PCBs on non-polar or low-polarity liquid phases, n-alkanes with 14 to 29 carbon atoms are necessary; n-octacosane is eluted slightly before the last PCB congeners and extrapolation from the n-C_{27}–n-C_{28} interval yields acceptable I values. The n-alkanes series is therefore suitable as a reference when non-specific detection such as flame ionization detection (FID) is used. However, as the high-sensitivity analysis of PCBs requires the use of element-specific detection as ECD where the response of n-alkanes is negligible, the introduction of an alternative reference series of ECD-detectable compounds is necessary. Another solution may consist of connecting two detectors in parallel at the end of the column, with ECD being used to analyse the sample and FID to obtain the retention times of the n-alkanes. This arrangement was used by us to check the accuracy of the proposed calibration methods (see below) but is inadequate for general use.

In early reports [39–41], the use of n-alkyl iodides as reference standards with ECD was described. The conversion of the retention indices relative to n-alkyl iodides, I_{ni}, into the Kováts indices relative to n-alkanes, I, was found to be possible, as in isothermal analyses both homologous series show a linear behaviour of the logarithm of the adjusted retention time, t'_R, as a function of the number of carbon atoms in the chain. At a given temperature, the straight lines representing n-alkanes and n-alkyl iodides are parallel [42] and a linear relationship also exists between the ratio of adjusted retention times of n-alkyl iodides and n-alkanes and the reciprocal of the absolute temperature of the column [39], thus enabling the conversion between the two index values to be carried out at every temperature by simple mathematical correlations. The shift between the lines for n-alkanes and n-alkyl iodides, expressed as "equivalent methylenes number", M_e [42], i.e. the number of methylene groups that must be added to a paraffinic chain to have the same effect on retention as the addition of an iodine atom, ranges between

Table 1
List of some literature references where the retention values of many PCB congeners are shown with different methods and on various columns and with different analytical parameters

Reference	Column	Temperature	Congener number	Retention unit
[13]	CP Select PCB 52 m×0.25 mm	60° for 1.5 min to 200°C 40°C/min to 250°C 2°C/min to 270°C 6°C/min	81	Retention times
[16]	CP Select PCB 52 m×0.25 mm	75° for 2 min to 150°C 15°C/min to 275°C 1.5°C/min	All 209	Retention times
[21]	Apiezon L 50 ft.×0.02 in.	Isothermal 205°C		Indices referred to n-alkanes
[22]	Six phases packed 3–4 m×0.318 cm	Isothermal 190–200°C	44	Indices referred to n-alkanes
[23]	OV-101 60 m	Isothermal 180, 190, 200°C	40	Indices referred to n-alkanes
[24]	13 phases packed 2–3 m×0.2 cm	Isothermal 200°	24	Indices referred to n-alkanes
[25]	Dexil 410 50 m×0.25 mm	Isothermal 200°C	110	Indices referred to n-alkanes
[26]	Apiezon L 29 m×0.29 mm	70 to 130°C 10°C/min to 230°C 4°C/min	60	Retention times
[28]	SE-54 50 m×0.2 mm	100 to 240°C 1°C/min	All 209	RRT referred to OCN (octachloronaphthalene)
[29]	CPSil5 25 m×0.32 mm	150 to 200°C 3°C/min	79	Indices ref. to n-alkyl trichloroacetates
[30]	DB-5 30 m×0.25 mm	100 to 225°C 20°C/min	47	Retention times
[31]	CP-Sil5/C_{18} 100 m×0.25 mm	75 to 150°C 15°C/min to 300°C 0.75°C/min	All 209	RRT referred to (trPCB52 + trPCB180)
[32]	Dexil-410 and OV-101 (packed)	200°C	All 209	Retention indices vs. vapor pressure
[38]	Dimethyl silicone 10 m×0.21 mm	60 to 210°C 5°C/min	9	Indices referred to n-alkanes
[44]	C_{87} Quadrex 30 m×0.25 mm	120 to 255°C 2°C/min	16	Indices referred to n-alkanes

about five on non-polar columns and about seven on polar polyglycol columns. This means that n-alkyl iodides with 9 to 26 carbon atoms are necessary to cover the retention time span of PCBs. Unfortunately, the heaviest n-alkyl iodide commercially available is the compound with eighteen carbon atoms and therefore this method allows one to measure retention indices of PCBs containing up to four chlorine atoms.

n-Alkyl trichloroacetates were proposed for the identification of PCBs. n-Decyl, n-dodecyl, n-pentadecyl [43,44] and the n-octyl to n-eicosyl esthers [45] were used as external retention standards and a computer-assisted procedure for the determination of the 209 PCB congeners was described [44]. The series of n-alkyl-bis(trifluoromethyl)phosphine sulfides, detected by many GC detectors, was also suggested as a universal retention index reference [46].

When compounds having polarities different from that of PCB are used as retention probes, the dependence of the obtained retention index on temperature may be great, due to the different solute–solvent interactions of the sample and of the probes. The use of selected PCBs as reference compounds for the determination of retention indices

is therefore attractive, because the interaction mechanism is the same and the sensitivity to ECD of the sample and probe compounds with the same number of chlorine atoms are comparable. In order to obtain values that can be converted to Kováts indices, a number of PCBs showing linear behaviour as a function of the number of chlorine atoms should be selected. The relationship between the retention values of the *n*-alkanes and of this PCB series is therefore simple and the direct conversion of the values can be easily made. A mixture containing ten PCBs with one to ten chlorine atoms, used as the reference in the analysis of inks and paints containing PCBs, and known as DCMA, is readily available. The experiments described here were carried out to see if this mixture can be used as a reference series for the determination of retention indices and to find out if other PCB mixtures are better suited for this purpose.

2. Experimental

The analyses were carried out with non-polar or medium-polarity bonded-phase fused-silica capillary columns, all of which were 0.32 mm I.D. The non-polar (polydimethylsiloxane) bonded phase columns were SPB-1 30 m long, 0.25 μm film thickness (Supelco, Bellefonte, PA, USA); DB-1 30 m, 0.25 and 3 μm film, (J & W Scientific, Folsom, CA, USA). A series arrangement of two 30 m, 0.25 μm film, columns was also made by using glass press-fit connections, in order to increase the resolution of some PCB congeners with close retention times. By doubling the column length and changing the input pressure of the carrier gas from $1.42 \cdot 10^2$ to $1.93 \cdot 10^2$ kPa, an increase of 85% of the number of theoretical plates was obtained.

The columns were installed in Varian Model 3400 and 3600 gas chromatographs (Varian, Palo Alto, CA, USA), equipped with capillary split/splitless injectors, constant inlet pressure flow control and FID and ^{63}Ni pulsed type ECD. Pure nitrogen was used as the carrier gas. The injector and detector temperatures were 250°C. The analyses were carried out under isothermal conditions at 200°C or with different programming rates in the range of 100–260°C. Various samples were used with a concen-

tration of 10 mg/l in *n*-hexane and isooctane: commercial Aroclor, DCMA mixtures, pure isomers (obtained from Supelco) all injected with a 1–20 split ratio. The retention times were measured with an accuracy of ±0.005 min, using a Varian DS-650 data system. The analyses with coupled columns were also carried out with a Varian Saturn ion-trap mass spectrometer, under the same conditions as described above and using helium as the carrier gas. The use of selected ion monitoring allowed us to obtain separate mass chromatograms of the isomers having the same number of chlorine atoms and to distinguish between PCBs having similar retention times and different chlorination ratios.

3. Results and discussion

The components of the DCMA mixture and their retention indices are listed in Table 2. Fig. 1 shows a roughly linear dependence of the ln t'_R of these compounds as a function of the number of chlorine atoms, but a linear correlation does not exist with the *n*-alkane series. The DCMA mixture can be used in two ways, as described below.

The simplest method uses the DCMA PCBs as a direct reference series, by giving to the various members of the mixture a value that is 100 times the number of their chlorine atoms. Each PCB is therefore bracketed by two DCMA probes and its I_{DCMA} is calculated by using the formula of Kováts with the ln t'_R values [33] in isothermal analyses and that of van den Dool and Kratz [47] with direct retention values, in temperature programmed runs. Reproduc-

Table 2
IUPAC numbering and structure of PCB congeners belonging to the DCMA mixture

IUPAC number	Position of chlorine atoms
1	2
11	3,3'
29	2,4,5
47	2,2',4,4'
121	2,3',4,5',6
136	2,2',3,3',6,6'
185	2,2',3,4,5,5',6
194	2,2',3,3',4,4',5,5'
206	2,2',3,3',4,4',5,5',6
209	2,2',3,3',4,4',5,5',6,6'

Table 3

Retention indices I_{DCMA} calculated by assuming that for DCMA compounds $I = 100c$, where c is the number of chlorine atoms in the DCMA PCB. The precision of I_{DCMA} values for some PCB congeners is also shown

Congener number	Av. I_{DCMA}	S.D.	% dev.
28	325.4	0.31	0.10
52	389.5	0.37	0.09
77	602.7	0.34	0.06
81	586.2	0.73	0.12
101	539.7	0.40	0.07
105	649.6	0.17	0.03
114	635.9	0.09	0.01
118	627.7	0.22	0.04
126	679.1	0.36	0.05
133	638.8	0.15	0.02
137	665.1	0.43	0.06 .
180	729.0	0.10	0.01

ible results are obtained (Table 3) with a precision comparable to that of I values obtained by using n-alkanes (Table 4) and the calculated values correspond well with those calculated by using literature values (e.g. the data of Mullin et al. [28]) and can be used to identify PCBs in commercial mixtures (see Table 5). Direct conversion of the I_{DCMA} to I values is not possible, or yields values that are strongly dependent on the temperature, due to the poor linearity of the DCMA plot shown in Fig. 1.

The second method of using the DCMA mixture (indirect method) allows one to obtain the retention indices referred to n-alkanes, I, of each PCB by using the n-alkanes to measure the I of all the DCMA compounds. This can be obtained with FID of relatively large amounts of both standard series, or

Table 4

Retention indices referred to n-alkanes, I. Precision of t_R and I values for some PCB congeners

Congener number	Av. t_R	S.D.	% dev.	Av. I	S.D.	% dev.
1	18.546	0.051	0.27	1485.0	0.89	0.06
29	47.049	0.031	0.07	1812.1	0.76	0.04
136	71.141	0.123	0.17	2069.9	1.01	0.05
194	112.394	0.458	0.41	2658.4	1.83	0.07
206	125.386	0.057	0.05	2753.4	1.00	0.04

Table 5

Retention indices, I_{DCMA}, calculated by assuming that for DCMA compounds $I = 100c$, where c is the number of chlorine atoms in the DCMA PCB

Congener number	Run 1	Run 2	Run 3	Mullin et al. [28]	Aroclor 1232	Aroclor mixture
81	586.58	586.67		585.37	586.54	—
77	602.70	603.07		602.40	603.15	602.89
118	627.86	627.65		627.43	626.92	—
114	636.02	635.84		635.90	—	—
133	638.76	638.91		638.61	—	—
105	649.64	649.46		649.80	645.32	—
126	678.88	679.52		678.91	—	681.60
28	325.87	325.25	325.28	325.72	321.56	—
52	388.57	389.76	389.70	389.97	388.72	391.17
101	539.09	539.97	539.84	540.37	538.34	537.84
137	665.78	664.91	664.94	667.36	—	665.58
180	728.81	729.99	729.04	728.99	728.28	728.25

Comparison between experimental values and data reported by Mullin et al. [28]. Tentative identification of PCB congeners from Aroclor 1232 and an Aroclor 1232–1242–1254–1262 mixture. Column, DB-5 30×0.32 mm; 100 to 240°C at 1°C/min.
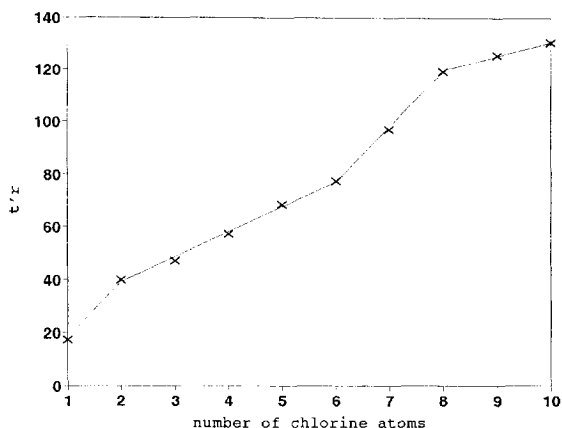
Fig. 1. Dependence of the t_R' of DCMA PCBs on the number of chlorine atoms in the molecule. Column DB-5: 30 m×0.32 mm I.D., 0.25 μm film thickness. Programmed temperature from 180 to 260°C at 8°C/min. The DCMA PCBs are listed in Table 2.

Table 6
Comparison between I values of some PCB congeners calculated with respect to the n-alkane series and those calculated with the indirect method, through the I values of DCMA PCBs. Column, DB-5, 30 m×0.32 mm

Programming rate	Congener	I alkanes	I indirect
100 to 240°C, 1°C/min	28	1840.1	1840.3
	52	1909.8	1910.0
	101	2082.2	2082.2
	137	2300.9	2303.8
	180	2473.1	2473.5
180°C×2 min	47	2002.7	2008.4
to 260°C, 3°C/min	121	2110.3	2111.1
	81	2212.5	2213.3
	77	2231.2	2233.4
	118	2278.9	2280.8
	114	2304.6	2304.5
	133	2301.2	2305.7
	153	2325.1	2330.2
	105	2334.6	2338.1
	126	2409.3	2410.4

by connecting FID and ECD, in parallel, to the end of the analytical column, if the concentration of PCBs is small. The formulae of Kováts and of van den Dool and Kratz [47] are then modified in order to obtain the I value of any PCB (X), because the initial value of the interval where X is eluted is taken as being equal to the I of the reference compound DCMA(c) eluting before the PCB (X), and the multiplying factor (equal to 100 in the standard formulae) is given by the difference between the I values of the two compounds DCMA(c) and DCMA($c+1$) bracketing X, where c is the number of chlorine atoms in the PCB–DCMA molecule. For programmed-temperature analysis, the equation is:

$$I_X = I_{DCMA(c)} + \frac{t_{R\ PCB(X)} - t_{R\ DCMA(c)}}{t_{R\ DCMA(c+1)} - t_{R\ DCMA(c)}} \times$$
$$(I_{DCMA(c+1)} - I_{DCMA(c)})$$

In isothermal conditions, the Kováts formula is used, with the logarithms of the adjusted retention times. Table 6 shows the I values calculated with respect of the n-alkanes series and those calculated with the indirect method through the I values of DCMA PCBs. The values obtained with simultaneous injection of PCBs and alkanes on DCMA mixtures agree very well (with a difference of one or two index units), whereas for those obtained in different runs, the agreement is poorer (up to six units).

Notwithstanding, the results obtained with the indirect method by using the indices of the DCMA compounds previously calculated with respect to n-alkanes, a direct method which yields the I values, without the need for prior calibration of the PCB probes with linear alkanes should give some advantages, as it can be applied to every column and
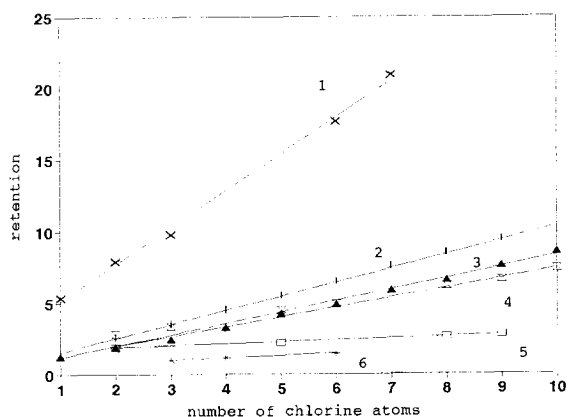

Fig. 2. Dependence of the retention values of the PCB reference series, shown in Table 7, on the number of chlorine atoms in the molecule. Values taken from references listed in Table 1 were used: 1, [26] (programmed temperature t_R); 2, [28] (RRT to octachloronaphthalene); 3, [31] (RRT to average times of PCBs 52 and 180); 4, [32] (retention indices); 5, [25] (retention indices); 6, [29] (indices referring to n-alkyl trichloroacetates).

Table 7
IUPAC numbering and structure of PCB congeners belonging to the proposed reference series that show linear behaviour

Congener number	Position of chlorine atoms
1	2
9	2,5
27	2,3',6
69	2,3',4,6
121	2,3',4,5',6
151	2,2',3,5,5',6
178	2,2',3,3',5,5',6
200	2,2',3,3',4,5,6,6'
207	2,2',3,3',4,4',5,6,6'
209	2,2',3,3',4,4',5,5',6,6'

programming rate, simply by adding the probe mixture to the sample, and it permits the use of ECD for both calibration and analysis.

The PCBs suitable for inclusion in the standard probe mixture should exhibit linear behaviour as a function of the number of chlorine atoms, should be commercially available as pure samples and have low toxicity. Some possibilities were investigated, and the best choice is shown in Table 7. Fig. 2 shows that these compounds have linear behaviour as a function of the number of chlorine atoms, independent of the retention values used: retention times, retention relative to the octachloronaphthalene or

Table 8
Series of PCBs proposed by various authors, organizations and countries for calibration, identification or control purposes

PCB	A	B	C	D	E	F	G	H	I	PCB	A	B	C	D	E	F	G	H	I
1	X			X	X	X	X			102		X							
2	X									104	X								
3	X			X						105			X						
4	X									115	X								
5	X				X					118		X	X					X	
7	X			X						120		X							
8	X		X							121						X	X		
9	X						X			126			X						
10	X									128			X						
11	X					X				136						X			
12	X									138		X	X					X	X
14	X									141	X								
15	X									143				X					
18			X							146		X							
26	X									149		X							
27						X				151	X						X		
28	X		X				X			153		X	X					X	X
29		X			X	X				154	X	X			X				
30				X						155	X								
33	X									167		X							
40	X									170			X						
44			X							171	X								
47						X				178							X		
48		X								180		X	X					X	X
50				X	X					183		X		X					
52	X		X					X	X	185	X					X			
54	X									187		X	X						
66			X						X	188				X					
67		X								194						X			X
69	X						X			195			X						
74		X								200							X		
77			X							201				X					
81	X									202			X						
87				X						204	X								
97		X	X							206			X			X			
99		X								207							X		
101	X	X				X	X			209	X		X	X	X	X	X		

(A) Cooper et al. [50]; (B) Vetter et al. [13]; (C) EPA for ECD calibration; (D) EPA for by-product analysis; (E) EPA Method 680; (F) DCMA mixture; (G) Retention index mixture (this paper); (H) PCB indicators [12]; (I) Heidmann [51].

retention index with respect to *n*-alkanes. The latter condition confirms that the conversion to Kováts indices of the indices obtained with the proposed PCB series is simple and can be carried out with linear correlations.

The retention values reported in different ways in some of the literature references listed in Table 1 were converted to Kováts *I* values, and a direct comparison was therefore possible. The use of the reference mixture proposed in Table 6 is therefore suitable for normalization of the retention indices obtained under different analysis conditions. Many other mixtures of PCB congeners were suggested for other reasons; prediction of retention times by structure–retention correlation and by addition of time increments [16,48], control of restricted concentration in some countries [12,13], application of standard methods for quantitation [49–51]. Table 8 shows that the PCBs included in these mixtures cover a wide range of congeners: 76 compounds are required to apply all the calibration procedures. Some of them are perhaps equivalent and a substantial reduction in their number would be necessary to permit the general use by all the laboratories involved in PCB analysis and to yield comparable data.

4. Conclusions

The methods suggested to convert the tabulated retention values into Kováts retention indices permit the comparison of data obtained in different laboratories. The introduction of new stationary phases and dedicated capillary columns may have the most effect in this analytical field, only if the results obtained under different conditions can be easily compared and made available on a common basis. The use of some selected PCBs that behave in a linear way as a function of the number of chlorine atoms as reference standards for retention index calculation will permit the preparation of mixtures suitable both for identification and quantitative calibration, showing the same solute–solvent interaction of the PCB samples and therefore a small temperature dependence.

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