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Short communication

Retention index system for identification of polychlorinated biphenyl congeners in gas chromatographic analysis

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Abstract

A retention index system is proposed based on a series of individual PCB congeners: PCB8, PCB31, PCB44, PCB101, PCB138, PCB180, PCB194. The retention indices of 59 PCB congeners were determined using this system under different GC conditions. This index system is suitable for electron-capture detection in the examination of environmental samples by temperature-programmed capillary gas chromatography and will have universal applicability.

Keywords: Retention index system; Polychlorinated biphenyls

1. Introduction

Polychlorinated biphenyls (PCBs) are used extensively as dielectric fluids in transformers, plasticizers, heat-exchange fluids, heat resistance materials, etc. The environmental persistence of PCBs is well known, and it has been proposed that their presence in organisms adversely affects a number of biological systems [1]. Although analyses for PCBs have made great advances in the last decade, it is not easy to identify individual PCB congeners in normal measurements. Not only do the 209 theoretically possible PCB congeners make the separation of individual congeners from their mixtures difficult, but also GC–MS can only determine the number of chlorine atoms in a PCB molecule, providing almost no information on the chlorine substitution pattern [2].

To solve this problem, retention data are very useful for the identification of individual PCB congeners. Fischer and Ballschmiter [3] determined the relative retention times with respect to the PCB congeners Nos. 52 and 180 for 179 of the 209 possible congeners. Mullin et al. [4] determined the relative retention times with respect to octachloronaphthalene of 209 PCB congeners. However, the retention index has much greater usage than all other retention systems. The relative values for PCBs characterized by NMR, together with many individual synthesized PCBs, have been analysed using the Kováts retention index (RI) system [5]. *n*-Alkyl trichloroacetates have also been described as retention index standards to identify polychlorobenzenes and PCBs [6,7]. Unfortunately, these retention index systems have not been widely

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applied. In this paper, an alternative retention index system, which may overcome some of the shortcomings of earlier work and permit valid application to environmental samples, is proposed.

2. Experimental

The gas chromatograph used was a Varian Model 3740 with a ^{63}Ni electron-capture detector and equipped with a Varian split–splitless capillary inlet system. The carrier gas was nitrogen. An 18 m × 0.2 mm I.D. fused-silica capillary column coated with SE-54 (J & W Scientific) was used to separate the PCB congeners. The injector and detector temperatures were 300 and 350°C, respectively. Data acquisition was accomplished with a Shimadzu C-R3A Chromatopac.

Commercial PCB products, Aroclor 1254, 1242 and 1260 (Supelco), diluted with hexane to about 2 ppm, were used as standards. The determination of the retention indices of PCBs was based on the use of these secondary standard samples, in which the composition of individual congeners have been determined [8].

The new PCB retention indices were generated as follows: the congeners of PCB8, PCB31, PCB44, PCB101, PCB138, PCB180 and PCB194 were used as internal standards instead of normal alkanes. The relationship between N, the number of chlorine atoms in each of these PCB molecules, and t_R, the retention time of the corresponding PCB congener, is described by

$$100N = A + Bt_R \quad (1)$$

We assume A and B to be constants and they can be calculated by the linear least-squares method. The retention index of PCB congeners is defined as

$$I_{PCB} = A + Bt_R \quad (2)$$

Although it does not assume a linear relationship between the retention indices and the number of chlorine atoms in the molecule for each individual PCB congener, it is even more convenient for calculating their retention indices. For example, under a particular set of chromatographic conditions, the retention times of PCB8, PCB31, PCB44, PCB101, PCB138, PCB180 and PCB194 are 26.70, 31.24, 33.99, 37.13, 42.33, 45.36 and 49.46 min, respectively, and the numbers of chlorine atoms in these PCB molecules are known to be 2, 3, 4, 5, 6, 7 and 8, respectively. A and B in Eq. 1 can be calculated to be −508.6 and 26.52, respectively, and Eq. 2 can then be written as

$$I_{PCB} = -508.6 + 26.52t_R \quad (3)$$

The retention index of any PCB congener under the same chromatographic conditions, can then be calculated from Eq. 3.

It should be emphasized that for different gas chromatographic parameters the retention indices of the internal standard compounds may have different values, which is different from earlier retention index systems. However, with a computer or calculator this would not result in much trouble.

3. Results and discussion

After the introduction of the *n*-alkanes as reference standards, other alternative index schemes were suggested and widely used in different situations [9]. The considerations in selecting alternative reference standard series for our index system were based on a number of factors: (1) the reference standards should be suitable for electron-capture detection; (2) the more similar the reference standards are to the analytes the greater will be the reliability of the index system; (3) the increments of the retention time between adjacent standard reference compounds should be approximately the same; and (4) the reference standards should be readily available.

In fact, there is no single standard reference series that can meet all these requirements. However, we considered that factors (1) and (2) are the most important for analyses for complex PCB congeners, so the standard reference series PCB8, PCB31, PCB44, PCB101, PCB138, PCB180 and PCB194, with 2, 3, 4, 5, 6, 7 and 8 chlorine atoms in each PCB molecule, respec-

tively, are suggested. These congeners also occur in most environmental samples and commercial products. For meeting consideration (3), it is suggested that the index increment between adjacent standard reference compounds may not be an integer. In an ordinary homologous index system the indices of standard compounds usually have values of a multiple of 100 ($100N$), where N is number of the carbon atoms or of rings [10,11]. However, we deem that this is not necessary or obligatory for all reference series. In fact, when the index unit is based on the number of carbon atoms or rings in a homologous index system, the plot of elution value as a function of retention indices for the standards versus the number of carbon atoms or rings of the standard compounds may not approach linearity. Also, in a homologous index system this may introduce serious errors in the determination of some compounds, especially those eluted before the first standard or after the last standard when an extension of the first or last standard interval has to be introduced [11].

Table 1 gives the different temperature programme conditions used and the retention indices of some congeners thus obtained are listed in Table 2. For each set of conditions three parallel determinations were made.

In most cases the results are fairly good and consistent even under different temperature programming conditions, and the maximum variation for most congeners is within 3 index units. The PCB retention index system maintained excellent reproducibility over 6 months of heavy column usage, the maximum variation being 2.1 index unit.

Plots of the number of chlorine atoms on each PCB congeners chosen as a retention standard versus their respective elution times are shown in Fig. 1 for different initial temperatures and in Fig. 2 for different heating rates. In Fig. 1, the different initial temperatures result in changes in the value of A in Eq. 2. In Fig. 2, the different heating rates result in changes in the values of both A and B in Eq. 2. As a splitless injector was used in these experiments, too high an initial temperature is unsuitable.

It can be seen from the results that the proposed retention index system is satisfactory for distinguishing PCB congeners, and especially useful in the environmental studies. We have identified many PCB congeners in biota samples and photodegradation products of PCB congeners, which were confirmed satisfactorily by GC–MS.

4. Conclusion

A retention index system for PCB congeners has been proposed that shows good reproducibility under various chromatographic conditions. The introduction of a series of readily available reference standards, for which both their indices and the index increments between adjacent reference standards are not integers, gives the system additional significance. Based on this example, other alternative reference series might be intro-

Table 1
Temperature programme conditions used for establishing the PCB retention index system

No.	Initial temperature (°C)	Initial time (min)	Heating rate (°C/min)	Final temperature (°C)
1	40	2	4	280
2	50	2	4	280
3	60	2	4	280
4	50	0	4	280
5	50	2	3	280
6	50	2	5	280
7	50	2	7	280

Table 2
Retention indices for some PCB congeners under the conditions indicated in Table 1

IUPAC No.	Temperature programme conditions						
	1	2	3	4	5	6	7
4	139.4	138.6	139.3	139.7	139.3	138.7	138.6
7	177.8	177.0	179.1	177.7	178.6	176.9	175.5
6	192.4	191.1	193.0	192.3	192.7	190.7	190.9
8[a]	200.1	199.0	200.3	199.7	200.1	198.6	198.9
19	225.7	226.3	224.8	225.7	225.6	226.2	226.7
18	257.9	258.2	256.8	258.1	259.3	257.9	258.2
16 + 32	283.1	283.1	282.7	282.4	282.9	283.3	283.7
26	309.3	309.1	308.9	309.0	309.7	308.4	308.2
25	312.2	311.4	312.1	312.0	311.8	311.7	311.2
31 + 28[a]	319.8	319.4	319.3	319.9	320.1	321.0	319.9
33	333.1	333.0	332.9	332.6	333.2	334.4	333.6
22	343.3	343.1	343.1	343.6	343.2	343.1	343.6
45	348.1	348.7	347.4	347.4	347.9	349.4	350.4
46	359.2	359.0	359.0	358.4	358.7	359.8	361.3
52	365.5	365.9	365.8	365.8	365.9	367.2	365.3
49	371.5	371.8	370.3	371.2	371.4	372.1	371.0
47 + 48	374.5	375.4	374.8	374.4	374.4	374.6	376.0
44[a]	391.1	392.7	391.4	391.3	391.7	393.2	391.9
37 + 42	394.7	395.8	395.0	394.4	395.2	395.6	397.2
41 + 64	406.6	407.3	406.5	406.7	406.7	407.9	408.1
40	417.5	418.2	416.9	417.2	417.0	419.0	418.4
74	438.4	437.5	438.3	438.2	438.6	437.8	437.3
70	442.6	442.7	443.8	443.4	443.9	443.3	442.4
66	447.0	447.4	446.9	447.6	447.7	447.8	447.4
60	470.0	469.4	470.0	470.5	472.0	469.3	468.8
56	470.0	469.4	470.0	470.5	472.0	469.3	468.8
101[a]	475.9	476.1	476.0	476.5	476.7	476.6	476.1
99	481.6	483.5	483.1	482.4	482.4	483.5	482.7
83	495.7	497.3	496.6	496.2	496.6	497.8	496.3
97	502.8	503.3	503.8	502.5	503.3	503.6	503.5
87	509.2	509.2	510.3	510.3	510.1	510.1	509.9
85	513.2	514.5	514.4	514.4	514.4	514.7	515.6
136	516.6	517.7	516.5	518.0	516.7	517.0	517.7
110	522.0	522.3	521.3	522.3	521.8	522.3	521.9
82	534.9	536.3	536.4	536.1	535.5	536.7	536.1
151	540.7	542.6	540.8	542.3	541.1	540.8	541.6
144	550.2	551.3	550.1	551.1	550.3	550.7	550.6
118 + 108	553.0	553.3	554.1	554.3	554.7	554.5	553.2
146	580.0	581.1	580.4	580.2	580.2	581.2	580.4
153	587.2	586.1	587.8	587.6	587.6	587.4	586.4
141	595.6	596.7	596.1	596.4	596.5	596.7	595.6
137	605.6	605.9	607.5	604.5	607.4	606.4	605.6
138[a]	613.1	614.4	613.9	614.0	614.0	614.6	614.3
178	623.4	623.9	624.1	623.8	623.4	624.6	623.9
175	632.5	634.6	633.6	633.3	632.8	634.5	633.5
187	639.0	640.4	639.5	640.3	638.9	639.4	639.9
159	639.0	640.4	639.5	640.3	638.9	639.4	639.9
128	647.4	648.1	648.2	648.0	647.5	648.4	647.3

Table 2 (*Continued*)

IUPAC No.	Temperature programme conditions						
	1	2	3	4	5	6	7
185	660.8	662.3	661.9	661.8	660.5	661.6	662.4
174	667.6	669.3	667.5	668.6	666.9	668.3	668.6
177	676.6	675.3	673.7	673.5	673.1	674.9	675.4
172	687.3	687.6	687.3	687.8	687.0	686.7	686.7
180[a]	695.2	695.0	695.6	695.7	695.4	695.9	694.6
170	730.9	730.8	731.6	731.0	731.2	731.1	730.4
196	738.4	739.4	739.2	739.1	738.3	738.6	739.1
201	745.1	745.9	745.0	745.3	744.0	745.4	744.7
195	780.1	780.7	780.8	780.3	779.7	780.0	781.0
194[a]	804.9	803.9	804.6	804.2	803.7	803.1	803.9

[a] Standard reference compound.

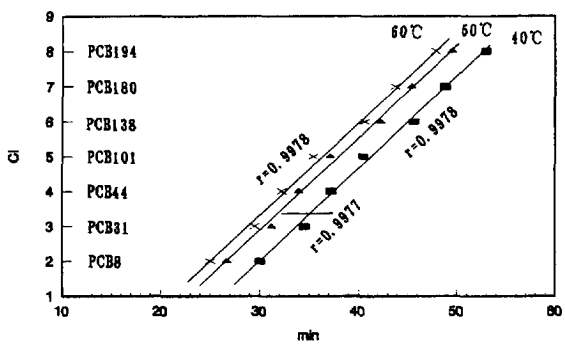

Fig. 1. Plots of the number of chlorine atoms in each PCB congener chosen as a retention standard versus the elution time with different initial temperatures.

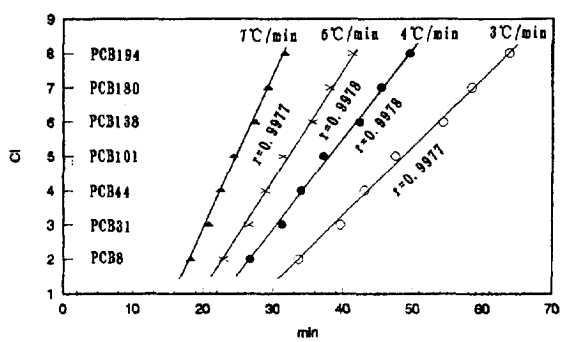

Fig. 2. Plots of the number of chlorine atoms in each PCB congener chosen as a retention standard versus the elution time with different heating rates.

duced similarly. Further work needs to be carried out with the proposed index system, e.g., the determination of the indices of PCB congeners using other columns and under different conditions are suggested, as an SE-54 capillary column still has some problems in separating all 209 PCB condeners. Also, the relationship between the retention indices and the molecular structures of PCBs is an important problem for chromatographic theory and toxicology.

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