

A New Retention Index System for PCBs

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1. Introduction

Purpose

A trend exists for the congener-specific analysis of polychlorinated biphenyls (PCBs) by Gas Chromatography-Mass Spectrometry (GC-MS). Considering that there are 209 possible PCBs, it is a challenging task for an analyst to specifically identify an individual congener—the hexachlorobiphenyl homologue group alone consists of 42 different isomers. Even though standards are available for all PCBs, their cost may be prohibitively expensive, especially if the only goal is to identify a subset of congeners in a sample for monitoring purposes. Full qualitative analysis of all PCBs in a sample should be possible through the use of retention indices. A new retention index (RI) system for PCBs is proposed here.

Background

Kovats RI system, with n-alkanes as retention markers, has been used for years for qualitative identification (mainly with flame ionization detectors). Relative retention times of unknowns based on the reference series by definition are RI numbers, and can be searched against tables containing compounds with known retention indices. Even with MS, where qualitative information is strong, isomers may not be differentiated on the basis of mass spectra alone. Retention time, or retention index, can help provide an unequivocal identification, when combined with the power of MS.

N-alkanes may not be appropriate retention markers for PCB MS analysis, since their spectra are relatively simple, and might be confused with other contaminating peaks in environmental samples. Chlorinated compounds, including PCBs, which have more distinct mass spectra, have been proposed as retention markers. To qualify as a reference series, the chosen PCBs must exhibit linear retention behavior on a wide variety of gas chromatography stationary phases. It is also desirable that the reference series exist in the PCB technical mixes used industrially (e.g. Aroclors), since they are the source of most environmental contamination. A resident reference series eliminates the spiking of each sample.

2. Experimental Conditions

Proposed Reference PCBs

The reference PCBs are, according to IUPAC (CI#): 1 (1), 8 (2), 31 (3), 44 (4), 101 (5), 138 (6), 180 (7), 203 (8), and 206 (9). PCB 1 elutes first, and PCB 206 elutes last on almost every stationary phase tested in a recent study that mapped retention times for all PCBs. The PCBs also exhibit linear retention behavior on these same phases, and they are resident in Aroclors and many environmental samples.

Retention Indices for Aroclor PCBs on DB-XLB

Retention Index Method is part of the LECO ChromaTOF® software, the control and processing platform for the

LECO Pegasus® III Gas Chromatograph—Time-of-Flight Mass Spectrometer (GC-TOFMS). PCBs found in Aroclors were given retention indices (starting with 100 for PCB 1, 200 for PCB 8, etc.) based on the reference series, when chromatographed on a DB-XLB (J&W Scientific) column (Table 1). The reference series is emboldened in blue. Instrumental conditions are listed below.

Standards

One ng/ μ L PCB mixes (AccuStandard), and Aroclor 1221:1242:1254:1262 mix.

Instrumentation

LECO Pegasus III GC-TOFMS

Column:

40 m x 0.10 mm x 0.10 μ m DB-XLB with 4 m retention gap

Carrier:

Hydrogen at 0.7 mL/minute, constant flow

Injection:

One μ L splitless at 260°C

Oven Program:

75°C (1 minute) to 125° at 50°/minute, to 260° at 5°/minute

Mass Spectrometry

Ionization: Electron ionization at 70eV

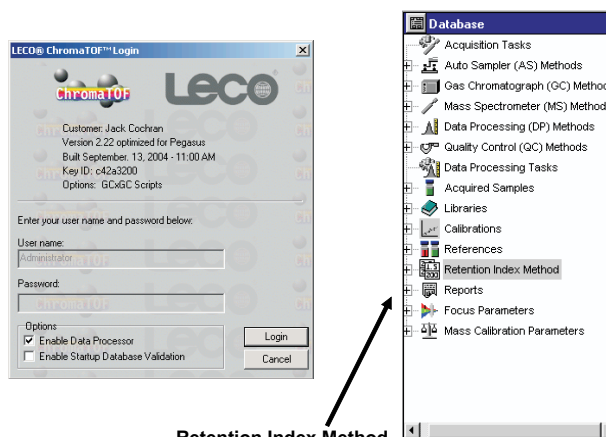
Source Temperature: 225°C

Stored Mass Range: 120 to 520 u

Acquisition Rate: 5 spectra/second

Data Processing

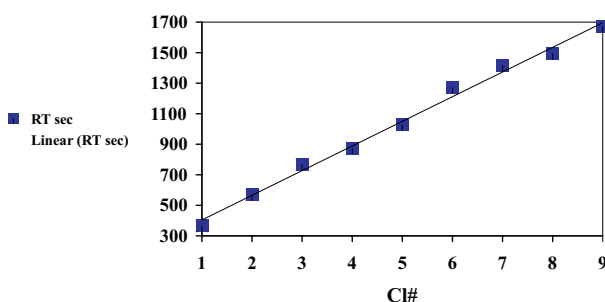
LECO ChromaTOF software with Automated Peak Find and Deconvolution; RI Method: Van den Dool and Kratz (built into ChromaTOF software)



Retention Index Table - "Rin 10"			
#	Name	Absolute RT (seconds)	Retention Index
1*	1	564.096	100.00
2	8	588.096	200.00
3	31	787.41	300.00
4	44	874.296	400.00
5	101	1026.88	500.00
6	138	1270.29	600.00
7	180	1414.49	700.00
8	203	1494.29	800.00
9	206	1969.89	900.00

The Retention Index Method is selected for use from a Data Processing Method.

The regression for the reference series of PCBs (retention time versus CI #) is shown below, and demonstrates that the behavior is linear for the DB-XLB phase. Similar results were obtained for other phases ranging from non-polar (100% methyl polysiloxane) to polar (6% cyanopropyl phenyl methyl polysiloxane).



3. Retention Index Test

An Aroclor mix was analyzed under the same GC-MS conditions. The resident reference series was located based on retention time, and the data was processed using a Retention Index Method. Each PCB congener was then identified based on its retention index. Mass spectrometry was used to confirm the assignment. Table 2 shows the results for this test, including the difference between a standard RI and the RI determined for the Aroclor work. The reference series is again emboldened in blue. Additional PCBs important for environmental monitoring purposes are highlighted in red.

4. Conclusions

Mass spectrometry is a powerful tool for qualitative analysis, but it cannot always distinguish the difference between isomers, especially PCBs of the same homologue group. Retention time, or a Retention Index Method, can supplement mass spectrometry for qualitative purposes. Having Retention Index Method built into the LECO Pegasus III ChromaTOF software makes it easy to take advantage of this approach.

5. References

- J.W. Cochran and G.M. Frame, **Recent developments in the high-resolution gas chromatography of polychlorinated biphenyls**, *J. Chromatogr. A* 843 (1999) 323-368.
- S. Chu, X. Miao, and X. Xu, Retention index system for identification of polychlorinated biphenyl congeners in gas chromatographic analysis, *J. Chromatogr. A* 724 (1996) 392-397.
- G. Castello and G. Testini, Gas chromatographic retention index system for polychlorinated biphenyls: possibilities and limitations, *J. Chromatogr. A* 787 (1997) 215-225.

Table 1. Retention Indices for PCBs

PCB #	CI #	CI Structure	RT (sec.)	RI
1	1	2	364.49	100.00
3	1	4	452.89	143.42
4	2	2-2	472.69	153.14
10	2	26	473.61	153.60
9	2	25	531.69	182.12
7	2	24	533.61	183.07
6	2	2-3	549.69	190.96
5	2	23	562.21	197.11
8	2	2-4	568.09	200.00
19	3	26-2	596.09	214.05
18	3	25-2	649.29	240.74
17	3	24-2	654.81	243.51
12	2	34	659.10	245.66
13	2	3-4	668.73	250.49
27	3	26-3	668.88	250.57
24	3	236	674.21	253.24
16	3	23-2	685.89	259.10
15	2	4-4	690.28	261.30
32	3	26-4	694.21	263.28
34	3	35-2	713.88	273.14
29	3	245	724.88	278.66
26	3	25-3	743.81	288.16
25	3	24-3	749.29	290.91
31	3	25-4	767.41	300.00
53	4	25-26	768.53	301.05
28	3	24-4	772.69	304.94
33	3	34-2	777.10	309.07
20	3	23-3	778.08	309.98
51	4	24-26	780.93	312.65
45	4	236-2	796.61	327.32
22	3	23-4	801.69	332.07
46	4	23-26	809.41	339.30
43	4	235-2	829.97	358.54
52	4	25-25	835.69	363.88
48	4	245-2	840.21	368.12
49	4	24-25	844.90	372.50
47	4	24	852.68	379.78
75	4	246	856.73	383.57
44	4	23	874.29	400.00
59	4	236	881.70	404.86
42	4	23	882.68	405.50
35	3	34	889.53	410.00
71	4	26	893.69	412.73
41	4	234	896.41	414.52
64	4	236	911.30	424.29
40	4	23	913.48	425.72
37	3	34	914.61	426.46
67	4	245	945.69	446.85
102	5	245	951.56	450.71
63	4	235	963.10	458.28
95	5	236	969.01	462.16
74	4	245	972.09	464.18
70	4	25	978.61	468.46
91	5	236	984.70	472.45
66	4	24	986.29	473.50
84	5	236	1011.81	490.25
89	5	234	1011.92	490.32
92	5	235	1013.48	491.34
56	4	23	1014.09	491.74
60	4	234	1024.41	498.51
101	5	245-25	1026.68	500.00
99	5	245-24	1037.29	504.36
119	5	246-34	1053.28	510.92
83	5	235-23	1053.61	511.06
97	5	245-23	1065.10	515.77
87	5	234-25	1084.49	523.73
136	6	236-236	1086.28	524.47
117	5	2356-4	1089.73	525.88

PCB #	CI #	CI Structure	RT (sec)	RI
115	5	2346-4	1091.81	526.74
85	5	234-24	1094.30	527.76
110	5	236-34	1105.89	532.52
82	5	234-23	1123.69	539.82
151	6	2356-25	1125.28	540.47
135	6	235-236	1130.01	542.42
77	4	34-34	1133.90	544.01
144	6	2346-25	1136.08	544.91
147	6	2356-24	1144.29	548.28
149	6	236-245	1147.21	549.48
139	6	2346-24	1152.16	551.51
124	5	345-25	1156.53	553.30
123	5	345-24	1166.30	557.31
109	5	235-34	1167.21	557.69
134	6	2356-23	1169.47	558.62
131	6	2346-23	1178.01	562.12
118	5	245-34	1178.28	562.23
133	6	235-235	1184.16	564.64
122	5	345-23	1191.53	567.67
114	5	2345-4	1197.70	570.20
146	6	235-245	1198.89	570.69
132	6	234-236	1209.41	575.01
153	6	245-245	1213.29	576.60
179	7	2356-236	1223.89	580.95
105	5	234-34	1231.68	584.15
141	6	2345-25	1236.21	586.01
176	7	2346-236	1239.50	587.36
137	6	2345-24	1248.50	591.06
130	6	234-235	1257.73	594.85
164	6	236-345	1261.81	596.52
138	6	234-245	1270.29	600.00
163	6	2356-34	1273.93	602.53
129	6	2345-23	1275.30	603.48
178	7	2356-235	1277.41	604.94
158	6	2346-34	1279.68	606.51
175	7	2346-235	1289.53	613.35
187	7	2356-245	1295.89	617.75
166	6	23456-4	1304.92	624.02
183	7	2346-245	1307.81	626.02
128	6	234-234	1327.68	639.80
185	7	23456-25	1331.10	642.17
174	7	2345-236	1339.49	647.99
167	6	245-345	1348.70	654.38
202	8	2356-2356	1351.33	656.20
177	7	2356-234	1359.49	661.86
201	8	2346-2356	1368.53	668.13
171	7	2346-234	1368.61	668.19
173	7	23456-23	1373.69	671.71
197	8	2346-2346	1385.21	679.70
156	6	2345-34	1394.50	686.14
172	7	2345-235	1398.81	689.13
157	6	234-345	1401.48	690.98
180	7	2345-245	1414.49	700.00
200	8	23456-236	1416.73	702.81
193	7	2356-345	1418.81	705.42
191	7	2346-345	1428.28	717.28
170	7	2345-234	1472.01	772.09
198	8	23456-235	1474.97	775.80
199	8	2345-2356	1478.49	780.20
190	7	23456-34	1482.28	784.95
196	8	2345-2346	1491.61	796.65
203	8	23456-245	1494.29	800.00
208	9	23456-2356	1536.68	824.14
189	7	2345-345	1554.30	834.18
195	8	23456-234	1556.09	835.19
194	8	2345-2345	1606.89	864.12
205	8	23456-345	1621.21	872.28
206	9	23456-2345	1669.89	900.00

Table 2. PCB Congener Assignments for an Aroclor Mix Using Retention Index

PCB #	RI	Difference
1	100.00	0.00
4	152.95	-0.19
6	190.77	-0.19
8	200.00	0.00
18	240.56	-0.18
15	261.24	-0.06
31	300.00	0.00
28	304.69	-0.25
52	363.79	-0.09
49	372.42	-0.08
47	380.11	0.33
44	400.00	0.00
95	969.11	0.01
74	971.91	-0.17
66	473.30	-0.20
101	500.00	0.00
99	504.19	-0.17
97	515.63	-0.14
17	243.37	-0.14
16	258.94	-0.16
32	263.15	-0.13
26	288.05	-0.11
33	308.82	-0.25
45	327.20	-0.12
22	331.89	-0.18
48	368.11	-0.01
42	405.50	0.00
64	424.21	-0.08
37	426.31	-0.15
70	468.46	0.00
84	490.31	0.06
56	491.36	-0.38
60	498.30	-0.21
119	510.77	-0.15
136	524.42	-0.05
82	539.64	-0.18

PCB #	RI	Difference
87	523.60	-0.13
85	527.55	-0.21
110	532.48	-0.04
151	540.54	0.07
149	549.42	-0.06
118	562.25	0.02
153	576.64	0.04
105	584.21	0.06
141	585.94	-0.07
138	600.00	0.00
187	617.73	-0.02
128	639.89	0.09
180	700.00	0.00
170	772.29	0.20
199	780.35	0.15
203	800.00	0.00
194	864.09	-0.03
206	900.00	0.00
135	542.35	-0.07
77	543.75	-0.26
114	570.23	0.03
146	570.64	-0.05
132	575.00	-0.01
179	580.84	-0.11
163	602.63	0.10
178	604.99	0.05
158	606.51	0.00
183	626.04	0.02
174	647.78	-0.21
167	654.29	-0.09
177	661.77	-0.09
171	668.32	0.13
156	685.87	-0.27
172	689.20	0.07
157	691.04	0.06
195	835.11	-0.08

