Gas-Chromatographic Properties of the 209 PCB Congeners on Non-Polar, Chiral, and Liquid-Crystal columns

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Introduction

Of the 209 possible PCB congeners 36 are considered environmentally harmful "the McFarland PCBs" due to their potential toxicity, occurrence in biota and in commercial PCB products (1). The PCB congeners are numbered according to the IUPAC rules. Further, 7 indicator congeners are frequently in use for analysis of biological samples and for the monitoring of PCBs in the environment, due to the high abundance in environmental samples and technical formulations. No existing gas chromatography (GC) column has been able to resolve all 209 PCBs, nor the 36 McFarland PCBs, nor even the 7 indicator congeners, but the elution orders and profiles have been published for a variety of columns (2-5). This study was performed to search for useful separation properties of two additional columns, one chiral (Chirasil-Dex) and one liquid-crystalline (LC-50). A non-polar DB-5 column was also included as a reference.

Materials and methods

All 209 PCB congeners were obtained from AccuStandard Inc. (New Haven, CT, USA) as nine mixtures in iso-octane. Five of the mixtures contain PCB congeners that are abundant in Aroclor formulations, and four contain PCBs that are absent or less abundant in Aroclors. An aliquot corresponding to 120 ng was transferred to a GC vial, 310 ng of octachloronaphtalene (OCN; Promochem, Wesel, Germany) was added as a syringe spike, and the volume was adjusted to 110 µL. Thus, the final concentration of the PCBs and of OCN was 1.1 ng/µL and 2.8 ng/µL.

Analyses of the nine PCB mixtures were carried out on three different columns: a 60m x 0.32mm 5% diphenyl polydimethylsiloxane column (0.25µm film; DB-5, J&W Scientific, Folsom, CA, USA); a 20m x 0.25mm 50% liquid-crystalline polydimethylsiloxane column (0.15µm film; LC-50, J & K Environmental Ltd., Sydney, Nova Scotia, Canada); and a 25m x 0.25mm 10% permethylated cyclodextrin polydimethylsiloxane column (0.12µm film; Chirasil-Dex CB, Chrompack, Middelburg, The Netherlands).

Gas chromatography –mass spectrometry (GC-MS) analyses were performed using a MD800 system (Fisons, Manchester, UK), operating in single ion recording mode under electron ionisation condition (70eV). The two most intense ions of the molecular ion isotope distribution clusters were monitored for detection of mono- to decachlorobiphenyls and of octachloronaphtalene. The GC oven was temperature programmed as follows: 80°C (3min),

Table 1. Elution order of all 209 PCBs, relative retention time (RRT), numbering according to IUPAC rules, and uncertain congener identifications is underlined.

DB-5						Chirasil-Dex						LC-50					
PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT	PCB	RRT
1	0.2668	63	0.4534	142	0.5197	1	0.2667	64	0.4528	161	0.5187	1	0.1729	38	0.4439	85	0.5492
2	0.2932	94	0.4552	165	0.5200	2	0.3010	58	0.4529	148	0.5190	10	0.2252	41	0.4441	107	0.5497
3	0.2960	74	0.4558	188	0.5209	4	0.3077	102	0.4531	134	0.5193	4	0.2269	92	0.4443	109	0.5504
4	0.3113	61	0.4563	146	0.5212	10	0.3094	155	0.4534	168	0.5201	2	0.2313	150	0.4456	106	0.5536
10	0.3114	70	0.4581	161	0.5223	3	0.3131	37	0.4535	153	0.5220	9	0.2487	58	0.4477	178	0.5545
9	0.3289	76	0.4588	153	0.5245	9	0.3298	61	0.4558	122	0.5232	6	0.2710	84	0.4494	175	0.5584
7	0.3291	98	0.4591	184	0.5247	7	0.3316	80	0.4568	165	0.5234	7	0.2730	101	0.4513	182	0.5584
6	0.3362	102	0.4594	132	0.5262	6	0.3359	88	0.4577	114	0.5276	19	0.2828	40	0.4540	82	0.5590
8	0.3403	80	0.4598	168	0.5263	5	0.3442	76	0.4583	127	0.5303	3	0.2840	80	0.4542	141	0.5638
5	0.3409	66	0.4603	105	0.5267	19	0.3483	93	0.4601	179	0.5320	30	0.2878	91	0.4557	187	0.5639
14	0.3499	93	0.4606	127	0.5269	30	0.3491	95	0.4610	132	0.5334	5	0.2919	152	0.4582	118	0.5656
19	0.3538	95	0.4607	141	0.5318	8	0.3501	74	0.4613	141	0.5334	14	0.2970	145	0.4614	183	0.5675
30	0.3598	121	0.4624	179	0.5330	14	0.3525	63	0.4635	176	0.5346	18	0.3011	61	0.4631	123	0.5679
11	0.3628	88	0.4624	137	0.5358	18	0.3663	70	0.4649	137	0.5368	8	0.3015	148	0.4646	202	0.5709
12	0.3666	91	0.4645	176	0.5369	11	0.3674	66	0.4656	105	0.5371	17	0.3178	70	0.4649	60	0.5714
13	0.3669	55	0.4654	130	0.5372	17	0.3700	91	0.4675	186	0.5390	27	0.3203	76	0.4659	204	0.5742
18	0.3690	155	0.4691	164	0.5400	27	0.3733	92	0.4703	160	0.5425	24	0.3259	113	0.4695	122	0.5767
15	0.3704	56	0.4702	163	0.5401	12	0.3774	55	0.4718	130	0.5426	54	0.3268	90	0.4698	201	0.5772
17	0.3704	60	0.4706	138	0.5404	24	0.3806	101	0.4732	158	0.5428	11	0.3328	35	0.4709	184	0.5809
27	0.3760	92	0.4712	158	0.5410	16	0.3808	90	0.4749	138	0.5431	34	0.3349	15	0.4711	137	0.5816
24	0.3761	84	0.4734	160	0.5416	13	0.3824	150	0.4752	182	0.5432	50	0.3360	154	0.4716	185	0.5818
32	0.3761	89	0.4746	186	0.5422	54	0.3831	89	0.4756	175	0.5446	23	0.3391	63	0.4723	130	0.5827
16	0.3812	101	0.4748	129	0.5449	34	0.3840	119	0.4763	178	0.5450	16	0.3403	89	0.4755	197	0.5829
34	0.3875	90	0.4747	178	0.5454	29	0.3860	84	0.4768	164	0.5451	32	0.3418	84	0.4760	127	0.5885
23	0.3880	113	0.4767	126	0.5455	32	0.3872	56	0.4773	129	0.5470	26	0.3464	99	0.4786	180	0.5919
29	0.3901	99	0.4778	175	0.5484	23	0.3878	89	0.4775	187	0.5484	29	0.3476	136	0.4820	174	0.5932
54	0.3901	79	0.4785	166	0.5487	50	0.3880	113	0.4790	163	0.5484	53	0.3503	125	0.4830	138	0.5939
26	0.3933	119	0.4816	159	0.5500	15	0.3906	112	0.4808	183	0.5487	51	0.3628	74	0.4880	129	0.5942
25	0.3947	150	0.4820	182	0.5500	26	0.3938	152	0.4816	159	0.5517	104	0.3681	83	0.4873	159	0.5949
31	0.3985	112	0.4829	187	0.5500	25	0.3966	148	0.4827	186	0.5560	52	0.3703	112	0.4893	81	0.5975
50	0.3988	83	0.4842	183	0.5529	28	0.4078	60	0.4838	162	0.5566	25	0.3729	86	0.4919	163	0.5998
28	0.3993	108	0.4843	162	0.5531	31	0.4098	145	0.4846	126	0.5579	31	0.3748	116	0.4927	114	0.6037
21	0.4050	78	0.4845	128	0.5559	53	0.4006	83	0.4850	167	0.5584	45	0.3748	120	0.4927	162	0.6048
33	0.4054	152	0.4864	167	0.5564	51	0.4078	97	0.4856	185	0.5594	12	0.3767	108	0.4927	158	0.6065
20	0.4055	97	0.4872	185	0.5589	20	0.4081	86	0.4858	181	0.5640	73	0.3785	151	0.4933	200	0.6070
53	0.4060	86	0.4881	174	0.5631	33	0.4097	79	0.4866	128	0.5642	69	0.3797	188	0.4944	172	0.6136
51	0.4090	125	0.4888	181	0.5640	69	0.4103	154	0.4868	204	0.5651	43	0.3830	97	0.4954	181	0.6173
22	0.4102	116	0.4892	177	0.5662	21	0.4111	125	0.4869	202	0.5652	13	0.3834	144	0.4959	77	0.6192
45	0.4134	117	0.4899	202	0.5682	45	0.4138	108	0.4872	174	0.5657	49	0.3873	119	0.4959	167	0.6194
36	0.4138	87	0.4903	171	0.5688	36	0.4139	116	0.4884	201	0.5677	48	0.3882	184	0.4986	180	0.6241
46	0.4183	145	0.4903	156	0.5693	46	0.4165	78	0.4888	171	0.5698	46	0.3882	135	0.5009	177	0.6241
39	0.4193	81	0.4905	173	0.5722	73	0.4168	120	0.4898	197	0.5701	20	0.3901	55	0.5041	192	0.6281
69	0.4202	111	0.4908	157	0.5725	43	0.4201	111	0.4905	177	0.5727	38	0.3956	87	0.5045	173	0.6297
52	0.4213	115	0.4909	201	0.5726	52	0.4207	115	0.4928	173	0.5739	103	0.3970	149	0.5088	171	0.6312
73	0.4216	148	0.4925	204	0.5736	48	0.4210	136	0.4955	192	0.5767	33	0.3975	66	0.5126	198	0.6394
43	0.4234	120	0.4926	172	0.5751	104	0.4212	85	0.4962	172	0.5768	65	0.4035	111	0.5133	105	0.6416
49	0.4240	85	0.4928	192	0.5755	22	0.4215	87	0.4965	156	0.5769	72	0.4062	133	0.5143	193	0.6418
38	0.4253	136	0.4945	197	0.5768	75	0.4217	117	0.5013	180	0.5793	96	0.4062	140	0.5156	166	0.6437
47	0.4258	110	0.4961	180	0.5787	62	0.4242	151	0.5035	157	0.5820	62	0.4070	56	0.5195	199	0.6438
75	0.4261	77	0.4961	193	0.5802	47	0.4251	144	0.5035	191	0.5829	155	0.4079	147	0.5209	208	0.6455
48	0.4264	154	0.4967	191	0.5825	49	0.4256	110	0.5043	200	0.5859	44	0.4089	148	0.5223	191	0.6474
65	0.4282	82	0.5027	200	0.5854	38	0.4298	135	0.5059	193	0.5861	21	0.4120	79	0.5247	196	0.6492
62	0.4291	151	0.5038	169	0.5904	39	0.4328	81	0.5059	198	0.5980	75	0.4164	139	0.5257	203	0.6500
104	0.4313	135	0.5059	170	0.5951	65	0.4329	139	0.5068	169	0.6011	59	0.4183	179	0.5285	207	0.6532
35	0.4315	144	0.5063	190	0.5958	44	0.4353	140	0.5077	190	0.6014	100	0.4199	110	0.5290	128	0.6700
44	0.4339	124	0.5065	198	0.5980	42	0.4374	82	0.5084	199	0.6016	94	0.4200	124	0.5303	126	0.6702
59	0.4354	147	0.5082	199	0.5997	72	0.4376	124	0.5089	203	0.6016	47	0.4215	177	5303	156	0.6723
37	0.4361	107	0.5085	203	0.6026	103	0.4386	149	0.5094	196	0.6018	102	0.4259	143	0.5311	157	0.6859
42	0.4361	109	0.5087	196	0.6029	59	0.4392	147	0.5099	170	0.6018	28	0.4285	153	0.5313	170	0.6913
72	0.4393	123	0.5100	189	0.6106	35	0.4411	77	0.5103	208	0.6165	57	0.4307	165	0.5328	190	0.7030
71	0.4408	149	0.5104	208	0.6184	100	0.4413	188	0.5111	189	0.6176	71	0.4308	176	0.5337	194	0.7126
64	0.4415	139	0.5105	195	0.6191	96	0.4418	143	0.5124	207	0.6187	121	0.4311	181	0.5363	195	0.7172
41	0.4417	118	0.5114	207	0.6227	71	0.4430	107	0.5129	195	0.6242	68	0.4315	142	0.5369	189	0.7176
68	0.4423	106	0.5116	194	0.6297	68	0.4430	184	0.5136	194	0.6346	22	0.4355	78	0.5370	209	0.7183
96	0.4444	140	0.5123	205	0.6328	41	0.4454	123	0.5137	205	0.6380	95	0.4358	134	0.5374	189	0.7250
40	0.4465	143	0.5158	206	0.6497	67	0.4474	106	0.5146	206	0.6539	42	0.4360	115	0.5377	206	0.7271
103	0.4468	134	0.5165	209	0.6660	57	0.4477	118	0.5147	209	0.6699	98	0.4388	186	0.5403	205	0.7365
57	0.4474	133	0.5175			40	0.4488	109	0.5149			93	0.4407	131	0.5414		
67	0.4501	114	0.5178			94	0.4490	133	0.5165			67	0.4412	132	0.5464		
100	0.4501	122	0.5192			98	0.4514	131	0.5169			39	0.4419	168	0.5466		
58	0.4520	131	0.5192			121	0.4522	142	0.5180			88	0.4433	37	0.5469		

3°C/ min to a final temperature of 250°C (Chirasil-Dex, 10 min), 270°C (LC-50, 20min), or 300°C (DB-5, 10min). Two microliter injections were made in splitless mode (250°C), with helium as carrier gas at a head pressure of 10 psi (Chirasil-Dex and LC-50) or 14 psi (DB-5).

Results and discussion

The relative retention times (RRT) of all 209 congeners were calculated relative to the sum of the retention times of PCB 52 and 180. Frame's retention and coelution database (4), mass spectrometric fragmentation patterns, and structure-retention relationships were used for congener identification. The RRT of all 209 PCB congeners are compiled in Table 1.

On the DB-5 column 14 of the 36 McFarland PCBs and two of the 7 indicator congeners were separated at a resolution of 0.5. Only 10 McFarland and 4 indicator congeners were resolved on the Chirasil-Dex and LC-50 columns, respectively, probably due to broader peaks. Some major differences in elution order were observed between the columns. For example, PCB 101 coelutes with 89 and 90 on the DB-5 column while it is free of interferences on Chirasil-Dex and LC-50 columns. PCB 118 coelutes with PCB 106 on DB-5, and with PCB 106 and 109 on Chirasil-Dex, while it is free of interferences on the LC-50 column, Table 2.

By comparing RRT and PCB retention indexes (6-8) we can compare the selectivity of the columns. Volatility is the most significant factor that controls retention in GC, especially in non-polar columns that have no selective interactions. In the LC-50 and Chirasil-Dex columns it seems like some specific interactions also influence retention, see Figure 1. By correlating RRT data to a PCB retention index subset – specific retention indexes can be obtained according to Xu (7). As can be seen in Figure 1, the LC-50 column seems to better separate congeners with similar volatilities than do Chirasil-Dex.

Table 2. PCB indicator interfences for each column. NI (Non-interference).

PCB	DB-5	Chirasil-Dex	LC-50
28	NI	NI	NI
52	73	22/43/48/75/104	12/25/31/45/69/73/10
101	89/90	NI	143
118	106	106/109	NI
138	163/164	130/158/160/182	129/159/174
153	184	NI	143
180	NI	NI	NI

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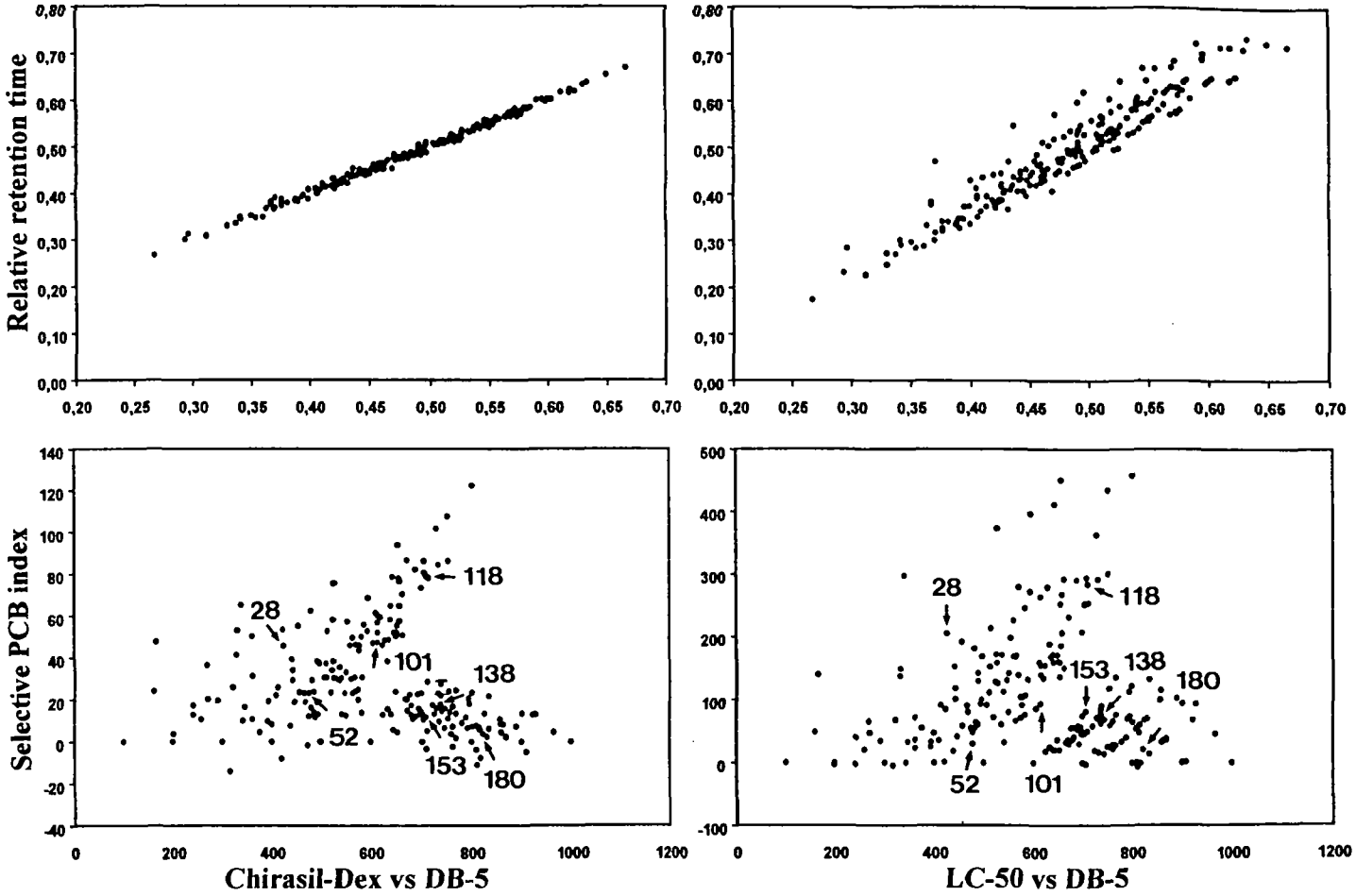

Figure 1. On top, Relative retention time (RRT) on Chirasil-Dex (left panel) and LC-50 (right panel) vs. RRT of DB-5. Below, selective PCB indexes vs. PCB index of DB-5.