Retention-time database of 126 polybrominated diphenyl ether congeners and two Bromkal technical mixtures on seven capillary gas chromatographic columns

Peter Korytár[a,b], Adrian Covaci[c,*], Jacob de Boer[a], Anke Gelbin[d],
Udo A.Th. Brinkman[b]

[a] *Netherlands Institute for Fisheries Research, Animal Sciences Group, Wageningen UR, P.O. Box 68, 1970 IJmuiden, The Netherlands*
[b] *Department of Analytical Chemistry and Applied Spectroscopy, Free University of Amsterdam, de Boelelaan 1083,*
1081 HV Amsterdam, The Netherlands
[c] *Toxicological Center, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium*
[d] *AccuStandard, 125 Market St., New Haven, CT 06513, USA*

Abstract

The elution order of 126 polybrominated diphenyl ethers (PBDE) was determined for seven different gas chromatographic (GC) stationary phases. The resulting database facilitates selection of the most suitable GC columns for developing a quantitative, congener-specific BDE analysis and the testing of retention prediction algorithms based on structure relationships of GC phases and congener substitution patterns. In addition, co-elutions of the principal BDE congeners with other BDEs and/or with other brominated flame retardants were investigated and, as an application, the composition of two Bromkal mixtures (70-5DE and 79-8DE) was studied.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Polybrominated diphenyl ethers; Gas chromatography; Stationary phase; Elution order

1. Introduction

Polybrominated diphenyl ethers are a group of brominated flame retardants (BFRs) widely used in polymers used in electronic circuit boards and cases, furniture, building materials, textiles, carpets, airplanes and vehicles [1]. There are 209 congeners and because of their structural relationship to PCBs, they have been numbered in an identical way [2,3]. In environmental samples, BDEs are present in relatively simple mixtures of 20–25 congeners [4]. However, additional congeners may be encountered in samples where processes such as photolytic debromination [5], microbial debromination in soil [6], and biological debromination [7,8] or metabolism in higher animals [9,10] have changed the initial distribution of

a technical mixture. Many research applications, particularly those investigating the alteration processes listed above, thus require comprehensive, quantitative and congener-specific analyses.

The method of choice for the analysis of BDE congeners is high-resolution gas chromatography (HRGC) on a capillary column with detection by an electron-capture detector (ECD) or, preferably, selected-ion-monitoring mass spectrometry (SIM-MS) both in the electron ionisation (EI) and electron-capture negative ionisation (ECNI) mode [11].

In recent years, there has been a rapidly increasing number of reported findings of BDEs in the environment. This has triggered interest in properly optimised analytical procedures. Unfortunately, progress in this area was hampered by the availability of less than 50 individual BDEs. In inter-laboratory studies, this problem as well as the suspected co-elution of, e.g., BDE 99 with other Br-containing compounds

* Corresponding author. Tel.: +32 3 820 2702; fax: +32 3 820 2722.
E-mail address: adrian.covaci@ua.ac.be (A. Covaci).

and the frequently occurring, thermal degradation during GC analysis of some highly substituted congeners such as, e.g., BDE 209 was discussed [12]. The lack of standards also adversely affected studies on the composition of technical BDE mixtures [13,14] and on the elution order of the BDEs from an often used column such as a DB-5 or equivalent column [15]. The situation briefly sketched above has now improved considerably by some eighty additional BDE congeners having become commercially available (for details and names, see Section 2 and Table 2). As a consequence, it is now justified to set up a comprehensive study of the elution order of all 126 BDEs available today on the various capillary columns mostly used in BDE analysis.

It is the purpose of this paper to present a retention-time database for seven stationary phases and discuss its usefulness in designing comprehensive and congener-specific BDE analyses. A similar approach was previously proposed for CB analysis [16] and the resulting extensive database has served as a departure point for many analysts who started developing methods for CB analysis and helped them in selecting the most appropriate column or column combination for their applications.

2. Experimental

2.1. Chemicals

One hundred and twenty-six individual BDE congeners (neat crystals, purity was usually >98.5%, with some exception for which it was >97%) were synthesised by AccuStandard (New Haven, CT, USA). Their synthesis, purity and spectroscopic and chromatographic properties were described in the documents delivered with the standards. Individual stock solutions in toluene were prepared at a concentration of 50–200 ng/μl. Individual standards of polybrominated biphenyls (PBBs) were also made available by AccuStandard, while technical BFR mixtures (Bromkal 70-5DE and Bromkal 79-8DE) were purchased from Great Lakes Chemical Corp. (Indianapolis, IN, USA). The technical BFR mixtures were diluted with toluene to a concentration suitable for GC analysis (no peak distortion and column overload).

2.2. GC systems

Elution data were acquired for the seven columns described in Table 1. The choice of capillary columns was influenced by the review of Covaci et al. [11] on the analytical determination of BDEs in environmental samples and by the results of the 1st InterLaboratory Study [12] for which participants have reported the columns used. All experiments were carried out with an 6890 Agilent Technologies (Palo Alto, CA, USA) gas chromatograph equipped with an ECD. One microlitre solutions were injected by an Agilent 6890 autosampler into a split/splitless inlet port equipped with a

Table 1
Survey of GC columns and experimental conditions used

Column[a]	Dimension (m × mm × μm)	Carrier gas		Injector temperature (°C)	Temperature programme							ECD temperature (°C)
		Inlet pressure (psi)	Average velocity[b] (cm/s)		Temperature (°C)	Hold (min)	Rate 1 (°/min)	Temperature (°C)	Rate 2 (°/min)	Temperature (°C)	Hold (min)	
DB-1	30 × 0.25 × 0.25	25	38.5	290	90	2	30	200	1.5	325	1	330
DB-5	30 × 0.25 × 0.25	25	38.5	290	90	2	30	200	1.5	325	7	330
HT-5	30 × 0.25 × 0.10	25	38.5	290	90	2	30	200	1.5	325	7	330
DB-17	30 × 0.25 × 0.25	25	38.5	290	90	2	30	200	1.5	325	30	330
DB-XLB	30 × 0.25 × 0.25	25	38.5	290	90	2	30	200	1.5	325	30	330
HT-8	25 × 0.22 × 0.25	25	35.8	290	90	2	30	200	1.5	325	50	330
CP-Sil 19	17 × 0.15 × 0.30	35	33.4	290	90	2	30	200	1.5	270	150	290

[a] DB-1 (100% methylpolysiloxane), DB-5 (5% phenyl-methylpolysiloxane), DB-17 (50% phenyl-methylpolysiloxane) and DB-XLB (Proprietary) from J&W Scientific, Folsom, CA, USA. HT-5 (5% phenyl-methylpolysiloxane (carborane)) and HT-8 (8% phenyl-methylpolysiloxane (carborane)) from SGE International, Ringwood, Australia. CP-Sil 19 (14% cyanopropyl-methylpolysiloxane) from Chrompack, Middelburg, The Netherlands.
[b] Average linear velocity was calculated from column dimensions and pneumatic parameters using the Hewlett-Packard flow calculator at 200 °C.

Table 2
Elution order of 126 BDE congeners on seven capillary columns and their RRTs vs. BDEs 47 + 183

DB-1		DB-5		HT-5		DB-17		DB-XLB		HT-8		CP-Sil 19	
BDE	RRT	BDE	RRT	BDE	RRT	BDE	RRT	BDE	RRT	BDE	RRT	BDE	RRT
1	0.100	1	0.095	1	0.091	2	0.086	1	0.086	1	0.084	1	0.083
2	0.102	2	0.097	2	0.091	1	0.087	2	0.088	2	0.085	2	0.083
3	0.103	3	0.099	3	0.093	3	0.088	3	0.090	3	0.087	3	0.086
10	0.125	10	0.123	10	0.112	14	0.114	10	0.117	10	0.116	10	0.116
9	0.131	9	0.129	9	0.116	10	0.117	9	0.123	9	0.122	14	0.118
14	0.133	14	0.130	14	0.117	9	0.117	14	0.124	14	0.124	9	0.120
4	0.134	7	0.133	7	0.121	7	0.122	4	0.127	7	0.129	7	0.125
7	0.134	4	0.133	6	0.121	11	0.124	6	0.128	6	0.130	6	0.127
6	0.135	6	0.134	4	0.122	6	0.125	7	0.128	4	0.131	11	0.130
11	0.139	11	0.137	11	0.124	12	0.129	11	0.133	11	0.134	4	0.130
8	0.139	8	0.139	8	0.126	13	0.129	8	0.135	8	0.137	8	0.134
12	0.142	12	0.142	12	0.128	8	0.129	12	0.138	12	0.139	12	0.135
13	0.142	13	0.142	13	0.128	4	0.129	13	0.140	13	0.140	13	0.136
15	0.146	15	0.147	15	0.133	15	0.133	15	0.147	15	0.147	15	0.142
30	0.172	30	0.174	30	0.152	30	0.166	30	0.174	30	0.175	30	0.167
27	0.180	27	0.184	27	0.162	36	0.177	27	0.184	27	0.188	27	0.185
19	0.181	19	0.187	19	0.168	34	0.179	19	0.186	19	0.196	34	0.189
18	0.186	18	0.191	18	0.169	27	0.184	18	0.192	18	0.196	29	0.193
34	0.188	34	0.192	34	0.169	26	0.184	34	0.196	34	0.196	18	0.193
32	0.190	26	0.195	26	0.172	29	0.186	26	0.198	26	0.200	19	0.193
26	0.190	32	0.195	29	0.173	18	0.188	29	0.198	29	0.202	26	0.194
29	0.193	29	0.197	32	0.175	39	0.189	32	0.199	32	0.205	36	0.194
17	0.196	36	0.199	36	0.178	32	0.191	36	0.203	36	0.206	32	0.197
36	0.196	17	0.202	31	0.182	19	0.194	17	0.205	25	0.213	25	0.204
25	0.198	25	0.204	25	0.182	31	0.195	25	0.208	31	0.213	39	0.205
31	0.199	31	0.205	17	0.183	25	0.195	31	0.212	17	0.214	31	0.206
39	0.203	39	0.208	39	0.186	17	0.199	39	0.215	39	0.217	17	0.206
16	0.207	16	0.214	33	0.193	38	0.204	16	0.218	16	0.226	38	0.214
33	0.207	33	0.214	16	0.193	28	0.206	33	0.218	33	0.226	28	0.216
28	0.207	28	0.214	38	0.193	16	0.209	38	0.220	38	0.226	16	0.217
38	0.212	38	0.217	28	0.194	35	0.209	28	0.223	28	0.227	33	0.218
20	0.214	35	0.221	20	0.201	20	0.209	35	0.228	20	0.235	20	0.223
35	0.215	20	0.221	35	0.201	33	0.210	20	0.228	35	0.235	35	0.224
22	0.223	22	0.231	37	0.211	22	0.221	37	0.242	37	0.247	22	0.235
37	0.223	37	0.232	22	0.211	37	0.221	22	0.242	22	0.247	37	0.236
53	0.253	53	0.264	53	0.232	80	0.255	53	0.268	53	0.272	69	0.264
73	0.257	73	0.266	73	0.234	72	0.261	73	0.269	73	0.273	73	0.264
69	0.258	69	0.268	69	0.238	73	0.262	69	0.274	69	0.278	53	0.269
50	0.261	50	0.272	50	0.247	69	0.265	50	0.278	50	0.287	50	0.272
72	0.274	72	0.281	72	0.253	53	0.275	72	0.289	72	0.291	72	0.277

Table 2 (*Continued*)

62	0.277	62	0.287	62	0.256	50	0.278	62	0.296	62	0.297	80	0.281
75	0.278	80	0.289	80	0.267	68	0.280	51	0.296	80	0.304	62	0.283
51	0.278	51	0.289	49	0.269	49	0.290	75	0.296	68	0.308	68	0.290
49	0.283	75	0.290	68	0.270	62	0.291	80	0.299	49	0.309	75	0.296
80	0.284	49	0.294	51	0.271	67	0.294	48	0.304	51	0.311	51	0.296
68	0.285	68	0.294	75	0.271	75	0.296	68	0.305	75	0.311	49	0.296
71	0.287	48	0.298	48	0.272	51	0.296	49	0.305	48	0.313	48	0.298
46	0.287	71	0.299	46	0.275	48	0.298	71	0.306	71	0.315	67	0.301
48	0.287	46	0.299	71	0.275	79	0.302	46	0.306	46	0.315	71	0.303
67	0.294	67	0.303	67	0.279	58	0.302	67	0.312	67	0.318	46	0.304
47	0.301	47	0.313	47	0.297	71	0.306	47	0.326	47	0.335	47	0.315
74	0.309	74	0.319	74	0.299	46	0.306	76	0.329	74	0.338	74	0.318
76	0.311	79	0.321	76	0.300	47	0.308	74	0.334	76	0.339	58	0.319
79	0.312	58	0.321	58	0.304	74	0.310	79	0.335	79	0.341	79	0.320
58	0.312	76	0.322	79	0.304	76	0.322	58	0.335	58	0.341	76	0.322
66	0.316	66	0.328	66	0.313	78	0.322	66	0.343	42	0.350	66	0.332
42	0.317	42	0.329	42	0.313	66	0.326	42	0.343	66	0.350	42	0.332
78	0.325	78	0.334	78	0.318	42	0.327	78	0.346	78	0.354	78	0.333
55	0.328	55	0.341	55	0.326	81	0.344	55	0.356	55	0.363	55	0.347
81	0.339	81	0.350	81	0.335	55	0.349	81	0.365	81	0.370	81	0.349
77	0.343	40	0.355	103	0.336	77	0.350	40	0.372	103	0.373	121	0.356
40	0.344	77	0.355	121	0.339	40	0.351	77	0.372	121	0.375	104	0.359
104	0.357	104	0.369	104	0.344	121	0.362	104	0.373	77	0.380	77	0.359
103	0.358	103	0.369	77	0.347	103	0.372	103	0.374	40	0.380	103	0.360
121	0.363	121	0.371	40	0.347	104	0.383	121	0.377	104	0.382	40	0.360
102	0.385	102	0.396	102	0.370	120	0.394	102	0.396	102	0.404	102	0.389
100	0.395	100	0.405	101	0.389	101	0.403	100	0.413	101	0.418	100	0.394
101	0.401	101	0.410	109	0.395	100	0.403	101	0.418	100	0.424	120	0.400
98	0.405	120	0.414	100	0.396	102	0.408	120	0.423	120	0.424	101	0.400
119	0.405	98	0.414	120	0.398	98	0.414	119	0.423	109	0.425	98	0.403
109	0.406	119	0.414	98	0.400	119	0.416	98	0.423	119	0.428	119	0.403
120	0.408	109	0.417	119	0.400	109	0.427	125	0.426	98	0.428	109	0.407
88	0.411	88	0.423	125	0.403	99	0.430	109	0.427	125	0.431	125	0.415
125	0.414	125	0.424	88	0.409	127	0.430	88	0.431	88	0.438	88	0.416
99	0.425	99	0.433	99	0.424	124	0.435	99	0.443	99	0.447	99	0.422
115	0.434	115	0.442	116	0.424	125	0.436	124	0.453	116	0.452	115	0.430
116	0.434	124	0.443	124	0.432	88	0.444	116	0.454	124	0.454	116	0.430
124	0.436	116	0.444	115	0.435	115	0.445	115	0.457	115	0.458	124	0.432
127	0.449	127	0.454	127	0.453	97	0.452	127	0.465	127	0.469	127	0.439
118	0.450	97	0.457	118	0.455	118	0.452	86	0.466	97	0.472	97	0.446
87	0.450	118	0.457	86	0.455	108	0.460	118	0.469	118	0.472	118	0.447

single tapered deactivated liner and operated in the splitless mode with split opening after 2 min. Helium and nitrogen (Hoek Loos, Schiedam, The Netherlands) with a purity of 99.999% were used as carrier and make-up (25 ml/min) gases. To enable comparison between stationary phases, a similar oven temperature programme was used for all columns. Mono- to octa-BDE congeners eluted in the slow temperature ramp on all columns except CP-Sil 19. All other relevant GC information is included in Table 1.

2.3. Experimental design

Using predicted retention-time data for BDEs on a DB-5 capillary column [15] as a guide, the 126 BDE congeners

Table 2 (*Continued*)

97	0.450	**87**	0.460	**97**	0.455	**123**	0.462	**97**	0.469	**108**	0.474	**123**	0.449
108	0.451	**108**	0.461	**108**	0.456	**116**	0.463	**123**	0.471	**86**	0.475	**108**	0.450
86	0.452	**86**	0.462	**87**	0.457	**87**	0.471	**108**	0.473	**87**	0.476	**86**	0.453
123	0.453	**123**	0.462	**123**	0.459	**106**	0.472	**87**	0.473	**123**	0.476	**87**	0.456
106	0.461	**106**	0.469	**106**	0.464	**86**	0.478	**106**	0.477	**106**	0.481	**106**	0.457
85	0.476	**85**	0.486	**155**	0.483	**126**	0.489	**155**	0.494	**155**	0.497	**155**	0.462
114	0.483	**114**	0.491	**114**	0.494	**114**	0.495	**85**	0.499	**114**	0.505	**114**	0.478
126	0.490	**126**	0.495	**85**	0.498	**85**	0.500	**114**	0.503	**85**	0.508	**85**	0.479
155	0.491	**155**	0.496	**154**	0.504	**155**	0.500	**126**	0.508	**126**	0.513	**126**	0.485
105	0.496	**105**	0.506	**126**	0.507	**154**	0.518	**154**	0.513	**154**	0.513	**154**	0.487
154	0.515	**154**	0.517	**144**	0.516	**105**	0.519	**105**	0.519	**105**	0.524	**105**	0.500
144	0.528	**144**	0.531	**105**	0.519	**161**	0.534	**144**	0.533	**144**	0.524	**161**	0.505
161	0.533	**161**	0.535	**161**	0.521	**144**	0.543	**161**	0.536	**161**	0.526	**144**	0.507
168	0.547	**168**	0.548	**168**	0.543	**168**	0.551	**168**	0.545	**168**	0.543	**168**	0.515
153	0.563	**153**	0.560	**153**	0.564	**153**	0.552	**153**	0.560	**153**	0.558	**153**	0.531
139	0.576	**139**	0.577	**160**	0.592	**159**	0.578	**139**	0.579	**141**	0.582	**139**	0.551
140	0.586	**141**	0.585	**141**	0.594	**141**	0.588	**141**	0.586	**139**	0.584	**131**	0.562
131	0.586	**131**	0.586	**139**	0.595	**167**	0.588	**140**	0.588	**160**	0.584	**141**	0.563
158	0.586	**158**	0.587	**158**	0.598	**131**	0.595	**158**	0.590	**131**	0.586	**158**	0.563
141	0.587	**140**	0.588	**131**	0.598	**158**	0.597	**131**	0.590	**158**	0.586	**159**	0.564
160	0.589	**159**	0.590	**159**	0.603	**140**	0.603	**159**	0.591	**159**	0.587	**140**	0.565
159	0.593	**160**	0.590	**142**	0.610	**160**	0.609	**160**	0.592	**167**	0.594	**160**	0.567
142	0.595	**167**	0.596	**167**	0.613	**139**	0.610	**167**	0.596	**140**	0.597	**167**	0.572
167	0.600	**142**	0.598	**140**	0.614	**142**	0.624	**142**	0.597	**142**	0.599	**142**	0.578
138	0.618	**138**	0.617	**166**	0.643	**138**	0.626	**138**	0.619	**138**	0.620	**166**	0.603
166	0.623	**166**	0.621	**138**	0.644	**166**	0.631	**166**	0.627	**166**	0.622	**138**	0.605
156	0.644	**156**	0.640	**156**	0.672	**156**	0.643	**156**	0.642	**156**	0.640	**184**	0.636
184	0.673	**184**	0.666	**184**	0.683	**184**	0.679	**184**	0.654	**184**	0.652	**156**	0.637
128	0.679	**128**	0.677	**183**	0.703	**183**	0.692	**183**	0.674	**183**	0.665	**183**	0.685
183	0.699	**183**	0.687	**185**	0.716	**128**	0.702	**128**	0.680	**182**	0.675	**182**	0.696
182	0.707	**182**	0.697	**182**	0.717	**182**	0.708	**182**	0.680	**185**	0.676	**128**	0.704
185	0.713	**185**	0.702	**192**	0.720	**192**	0.710	**185**	0.693	**192**	0.678	**185**	0.722
192	0.721	**192**	0.707	**128**	0.730	**185**	0.714	**192**	0.698	**128**	0.682	**192**	0.722
191	0.734	**191**	0.721	**191**	0.744	**191**	0.729	**191**	0.708	**191**	0.695	**191**	0.746
181	0.770	**181**	0.754	**181**	0.807	**181**	0.761	**181**	0.744	**181**	0.742	**181**	0.823
173	0.779	**173**	0.763	**173**	0.807	**173**	0.776	**173**	0.755	**190**	0.742	**173**	0.850
190	0.780	**190**	0.763	**190**	0.807	**190**	0.778	**190**	0.755	**173**	0.743	**190**	0.852
204	0.858	**204**	0.834	**204**	0.885	**204**	0.849	**204**	0.810	**204**	0.801	**204**	0.981
198	0.882	**198**	0.853	**198**	0.899	**203**	0.859	**198**	0.828	**198**	0.809	**198**	1.094
203	0.885	**203**	0.855	**203**	0.903	**198**	0.860	**203**	0.830	**203**	0.812	**203**	1.100

Table 2 (*Continued*).

205	0.922	205	0.891	205	0.944	205	0.904	205	0.865	205	0.842	205	1.254
208	1.029	208	0.988	208	1.073	208	1.004	208	0.955	208	0.939	208	1.661
207	1.042	207	1.001	207	1.089	207	1.024	207	0.965	207	0.972	207	1.741
206	1.074	206	1.027	206	1.111	206	1.048	206	0.997	206	1.009	206	2.091
209	1.219	209	1.171	209	1.290	209	1.282	209	1.196	209	1.281	209	> 2.54

RT (min)	DB-1		DB-5		HT-5		DB-17		DB-XLB		HT-8		CP-Sil19
47	21.46		25.81		21.59		27.92		31.29		35.18		32.23
183	49.82		56.72		51.00		62.63		64.67		69.69		70.25
209	86.9		96.7		93.6		116.1		114.8		134.3		>260

To enable the calculation of absolute retention times and indicate total run time on each column, retention times of BDEs 47, 183 and 209 are also given for each system.

were divided over 45 mixtures with a maximum of three congeners selected for elution at widely different times. A mixture containing BDEs 47 and 183 was re-injected every tenth sample in the injection sequence of 45 samples. Similar to the protocol described by Frame [16], relative retention times (RRTs) for all peaks were calculated against the sum of the retention times (RTs) of BDEs 47 and 183. These two RRT standards eluted in the middle of the first and last halves of the range of congener elutions, and their separate injection avoided co-elution with other congeners on the columns tested. BDEs 47 and 183 were also used to evaluate the drift in retention time. Repetitive injections of BDEs 47 and 183 on each GC column showed a variation of retention time within a narrow interval of 4–5 s over the whole study period. This indicates that the BDE analyses were performed under stable and reproducible conditions. Additionally, the technical BFR mixtures and individual BB congeners were injected into each of the seven GC systems using the same temperature programmes as used for the BDEs.

3. Results and discussion

3.1. Elution order on each of the stationary phases

Table 2 shows the elution order of the 126 BDE congeners on the seven columns presented in Table 1. The information is presented as a congener number plus the RRT relative to the sum of the RTs for BDEs 47 and 183. Two congeners were considered to be separated if the valley between the peaks had a height of <25% of the average peak height of the two compounds. In practice, BDE congeners were considered to co-elute if the difference between their RRTs was ≤0.001 for peaks eluting before BDE 47, and ≤0.002 for peaks eluting after BDE 47. This criterion is less exact than one requiring baseline separation, which produces more accurate quantification. Congener co-elutions in each system based on this less strict criterion are indicated in Table 2 by enclosing them in a box. The elution time of BDE 209 included in Table 2 is an indication of the system's total analysis time. In addition, the elution orders of other brominated flame retardants, such as hexabromocyclododecane (HBCD), dimethyl tetrabromobisphenol-A (MeTBBP-A) and polybrominated biphenyls (PBBs), which are present in many environmental samples, are given in Table 3.

Changes of parameters such as column dimensions, stationary phase thickness, carrier gas (H_2 versus He) pressure and flow rate, and column temperature programme, can all affect both the calculated RRTs and the resolution of congeners. The present database should, therefore, be used primarily as a guide to column selection prior to precise calibration of the selected system with congener standards in the analyst's lab. Tables 2 and 3 facilitate rapid evaluations for priority congeners to select the best column(s) for detailed study and

Table 3
Elution order of other brominated flame retardants and RRTs vs. BDEs 47 + 183

Compound	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
MeTBBP-A	0.514	0.515	0.487	0.510	0.502	0.494	0.497
HBCD	0.586	0.596	0.563	0.595	0.619	0.628	Degraded
BB 15	0.146	0.148	0.137	0.138	0.152	0.151	0.150
BB 52	0.229	0.237	0.212	0.228	0.245	0.248	0.235
BB 49	0.236	0.244	0.219	0.237	0.254	0.257	0.242
BB 101	0.353	0.364	0.347	0.358	0.369	0.382	0.354
BB 153	0.512	0.515	0.526	0.511	0.521	0.529	0.486
BB 169	0.697	0.689	0.754	0.676	0.697	0.700	0.732

method optimisation. The complete congener listings are especially valuable for designing BDE analyses that must deal with congeners derived from debromination processes.

As mentioned above, the column selection tested (non-polar and slightly polar capillary columns) was based on their use in analytical laboratories as reported during worldwide interlaboratory studies [12,17]. The use of more polar columns will result in unacceptably long analysis times, which will also increase the risk of degradation of higher brominated congeners.

The elution order of the present set of BDEs on the DB-5 column generally agrees with earlier studies done on DB-5 type columns for a limited number of congeners [15,18]. With a few exceptions, a grouping of BDE homologues in distinct retention-time clusters was observed for each tested GC column. Compared with CBs, much less co-elutions of BDE congeners with different bromine numbers were observed (examples include BDEs 40/77 with BDEs 103/104, BDE 85 or BDE 126 with BDE 155 or BDE 154, BDE 128 with BDE 182, and BDE 156 with BDE 184; see Table 2). This means that the use of MS detection in the EI mode which enables a separate quantification of co-eluting homologues with a different number of Br substituents is not of primary importance and that detection in the NCI mode will yield reliable results in many cases. However, the use of EI-MS becomes interesting when other brominated compounds, such as hydroxylated and methoxylated BDEs [19] and naturally occurring brominated compounds [20], are present in the same extract. Correct identification of BDE congeners then is very difficult when using ECNI-MS which acquires only the bromine ions (m/z 79 and 81).

While the number of co-elutions of BDEs from different homologue groups is rather small, co-elution within homologue groups is very frequent. On the basis of the data of Table 2, the number of co-elutions was calculated for each GC column in three different ways, viz. as number of BDEs involved in co-elutions, as number of co-eluting groups, and as co-elutions observed for major BDEs. The results, which

are presented in Table 3, show that the DB-XLB column ends up in first place irrespective of the criterion used, with the DB-1 column as runner-up.

3.2. Co-elutions of abundant BDE congeners

Detailed information on the co-elution of the BDEs most abundantly present in the environment with other BDE congeners or brominated flame retardants is given in Table 4. A discussion of part of the experimental findings is given below.

Rayne and Ikonomou [15] reported the co-elution of the lower brominated congeners, BDEs 28 and 33, on a 30 m DB-5 column. This co-elution is confirmed by our experiments and was observed also on DB-1, HT-5, HT-8 and CP-Sil 19, but not on DB-17 and DB-XLB columns (Table 2).

BDE 47 was reported to co-elute with CB 180 on a DB-5 column [21] and therefore, its quantification by means of an ECD may cause large errors. However, BDE 47 can be unambiguously determined by using ECNI-MS or EI-MS. BDE 47 was found to be completely separated from other BDE congeners on all of the seven GC columns studied.

BDEs 99 and 100 have a limited number of co-elutions with other BDE congeners on the present GC columns. BDE 99 co-eluted with BDE 127 only on DB-17 and with BDE 116 on HT-5. BDE 100 was found to co-elute with BDE 109 only on HT-5, with BDE 101 on DB-17 and with BDEs 109/120 on HT-8. BDE 99 and BDE 100 were reported to co-elute with naturally occurring chlorinated/brominated [22] and other brominated compounds, such as hydroxylated and methoxylated BDE metabolites [19].

The co-elution of BDE 154 with other brominated flame retardants that can be present in samples, such as BB 153 and dimethylated tetrabromobisphenol-A (MeTBBP-A) is of distinct importance. BB 153 has been found, in North American environment and human population [23,24], and in top-

Table 4

Co-elution of BDE congeners on seven GC columns according to three criteria

Major BDEs	DB-1	DB-5	HT-5	DB-17	DB-XLB	HT-8	CP-Sil 19
No. of co-eluting BDEs							
	62	63	66	67	56	62	72
No. of co-elutions							
	24	26	27	30	22	26	29
Co-elution with major BDEs							
28	16, 33	16, 33	16, 33, 38	–	–	16, 33, 38	16, 33
47	–	–	–	–	–	–	–
49	68,80	68	68	62	46, 48, 68, 71	68	51, 75
85	–	–	–	155	–	–	114
99	–	–	116	127	–	–	–
100	–	–	109	101	–	109, 120	–
138	–	–	166	–	HBCD	–	166
153	–	–	HBCD	168	–	–	–
154	MeTBBP-A, BB 153	MeTBBP-A, BB 153	–	105	–	126	BB 153
183	BB 169	BB 169	–	–	–	–	–

Table 5
Major and minor BDE congeners in Bromkal 70-5DE and Bromkal 79-8DE technical mixtures

Congeners	Bromkal 70-5DE		Bromkal 79-8DE	
	Sjödin et al. [13]	Present study	Björklund et al. [14]	Present study
Major	47, 99	47,99	183, 197, 207, 209	183, 197, 207, 209
Minor	100, 153, 154, 85	100, 153, 154, 85	203, 196, 208, 206	203, 196, 208, 206
Trace	138, 66, 28, 183, 17	138, 66, 28, 17, 183	Octa BDE:1	204
Other	Not identified	49, 74, 101, 97/118, 155, 139, 140	Not identified	181, 191, 173/190, 205

predators such as birds of prey [25] and some marine mammals [26]. BDE 154 co-elutes with BB 153 on DB-1, DB-5 and CP-Sil 19 but is baseline separated from BB 153 on all other columns. BDE 154 also co-elutes with MeTBBP-A on DB-1 and DB-5 columns. BDE 154 co-elutes with BDE 105 on DB-17 and with BDE 126 on HT-8.

BDE 153 was reported to co-elute on DB-5-type columns with TBBP-A [11], but this can be avoided by separating the base-soluble TBBP-A during the clean-up [27]. For the seven GC columns tested, BDE 153 was found to co-elute with BDE 168 on DB-17 and with HBCD on HT-5. Finally, BDE 183 was found to co-elute only with BB 169, a minor PBB congener, on the DB-1 and DB-5 columns.

According to the above, DB-XLB would be the best choice for single-column GC–ECNI-MS of abundant BDE congeners (Table 4). The most frequently used columns (DB-1 and DB-5 types) share the disadvantage of a larger number of co-elutions, specifically of BDE 154 and other brominated flame retardants present in environmental samples such as MeTBBP-A and BB 153.

3.3. Stability of hepta- and higher brominated BDE congeners

With all tested columns, nona-BDE congeners and BDE 209 showed a tendency to degrade (increase in baseline before the peak). Least degradation was observed on DB-1 and HT-5; on the other hand, with columns such as CP-Sil 19 and, to a lesser extent, HT-8 and DB-XLB, slight degradation of some hepta- and octa-BDE congeners also occurred. Possibly, the degradation is due to the very long retention times of the higher brominated BDEs in the column at high temperature. Therefore, short columns (10–15 m) with a high phase ratio (film thickness <0.15 μm) and, if desired, a small internal diameter [28], are recommended for the analysis of these congeners [29]. BDE 209 should receive special attention because of its relative rapid degradation at high temperatures. The maximum oven temperature should be 300 °C, which should, moreover, be used for only a short period of time at the end of the temperature programme.

Possibly, similar stationary phases from different manufacturers may lead to different stabilities of higher brominated BDEs and, specifically, BDE 209. For example, we observed considerably less degradation for BDE 209 on a 100% methyl polysiloxane phase from J&W Scientific (DB-

1) than on an equivalent stationary phase from Varian (VF-1) (data not shown). Similarly, Björklund et al. [28] showed that a better response for BDE 209 was obtained on a DB-1 (J&W Scientific) as compared with a HP-1 (Agilent Technologies) column. Here, one should add that batch-to-batch variations of selectivity possibly cannot be neglected either.

The stability of HBCD was also tested on all seven GC columns. Degradation was observed in all cases, and varied from slight degradation (DB-1, HT-5, DB-5 and DB-XLB), to high (DB-17 and HT-8) and even total degradation (CP-Sil 19).

3.4. Composition of penta- and octa-BDE technical mixtures

It can be expected that slight variations exist in the composition of technical BDEs mixtures produced by companies such as Great Lakes Chemical Corporation, Albemarle and the Dead Sea Bromine Group. Until now, information on the composition of penta- and octa-BDE technical mixtures has been limited (Table 5). With the synthesis of a much larger number of BDE analytical standards referred to above, minor congeners that may also be present in environmental samples, can now be identified.

The composition of the penta-BDE mixture Bromkal 70-5DE (Chemische Fabrik Kalk, Köln, Germany) was firstly reported by Sjödin et al. [13] using a DB-5 column. BDEs 47 and 99 were found to be the main congeners (ca. 35% weight each), while BDEs 85, 100, 153 and 154 each contributed between 1.5 and 7 wt.%. Other minor congeners were BDEs 17, 28, 66, 138 and 183. Several other BDE congeners (total, approx. 12 wt.%) were observed but not identified.

Using the extensive retention-time database generated in Table 2, we studied another Bromkal 70-5DE technical mixture (Great Lakes Chemical Corp.) analysed on a DB-5 column. While all major, minor and trace congeners reported in the quoted study were confirmed (Table 5), another six BDEs could be identified with a further peak being provisionally assigned to BDE 97 co-eluting with BDE 118. The pertinent GC trace is shown in Fig. 1a.

The composition of the octa-BDE mixture Bromkal 79-8DE was recently studied by Björklund et al. [14] using a DB-1 column. The major and minor BDE congeners identified by them are included in Table 5. Due to lack of standards, an OctaBDE:1 and several other minor peaks could not be

identified. Using the same approach as for the other Bromkal mixture, the OctaBDE:1 was now identified as BDE 204. In addition, BDEs 181, 191 and 179/190, which elute before OctaBDE:1, and BDE 205, which elutes after BDE 196 were identified as trace constituents (Fig. 1b and Table 5).

3.5. Predicted BDE elution order on DB-5

Until recently, analytical standards were available for only some 50 BDE congeners. Therefore, predictive tools for the identification of the remaining 160 BDE congeners were developed: a GC relative retention time (GC-RRT) model was set up using RRTs and physical parameters of 46 individual congeners [15]. Its purpose was to predict RRTs for the many BDE congeners for which no standards were available.

With the commercial availability of some eighty additional BDE congeners, it becomes possible to test the validity of the GC-RRT model for RRT prediction on a DB-5 column. Therefore, RRTs obtained on the DB-5 column in the present study were plotted against RRTs obtained experimentally by Rayne and Ikonomou [15] for 46 BDE congeners (Fig. 2a). Its logarithmic shape is probably due to the different col-

umn dimensions and temperature programmes used in the two studies. The following equation was obtained:

$$\mathrm{RRT_{exp\,2003}} = 0.4508 \ln \mathrm{RRT_{exp\,2004}} + 0.9798\,(r^2 = 0.98)$$

where $\mathrm{RRT_{exp2003}}$ and $\mathrm{RRT_{exp2004}}$ are the RRT experimentally obtained in [15] and this study, respectively. By using this equation, one can predict theoretical RRTs ($\mathrm{RRT_{th2004}}$) for the 80 BDE congeners for which experimental data were obtained in our study. In Fig. 2b, the theoretical values are plotted versus theoretical values obtained by Rayne and Ikonomou from their GC-RRT model ($\mathrm{RRT_{th2003}}$). The plot shows a good linear fit ($r^2 = 0.98$) with a few BDE congeners being relatively far from the regression line. Fig. 2c shows that for the di- to hexa-BDE congeners ($\mathrm{RRT_{exp2004}} < 1.8$) a homogeneous distribution of residuals is obtained, while for the hepta- and octa-BDEs ($\mathrm{RRT_{exp2004}} > 1.8$), a skewed distribution of residuals indicates that the model used in [15]
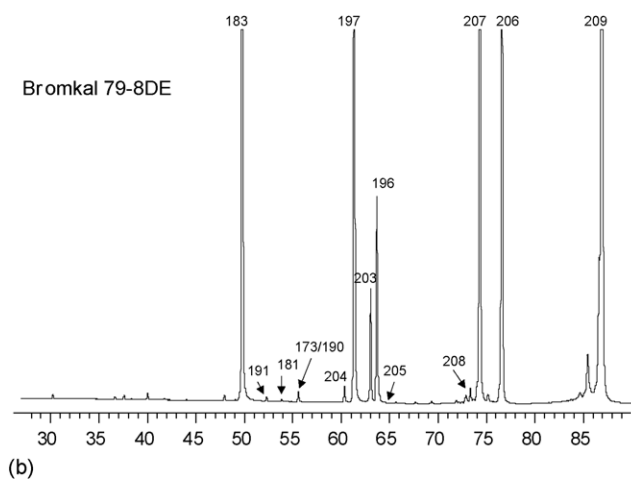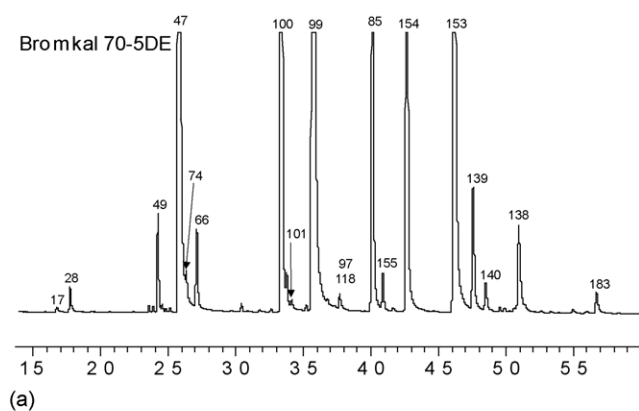

Fig. 1. GC-ECD chromatograms of penta-BDE Bromkal 70-5DE on a DB-5 column (a) and of octa-BDE Bromkal 79-8DE on a DB-1 column (b). For experimental details, see text.
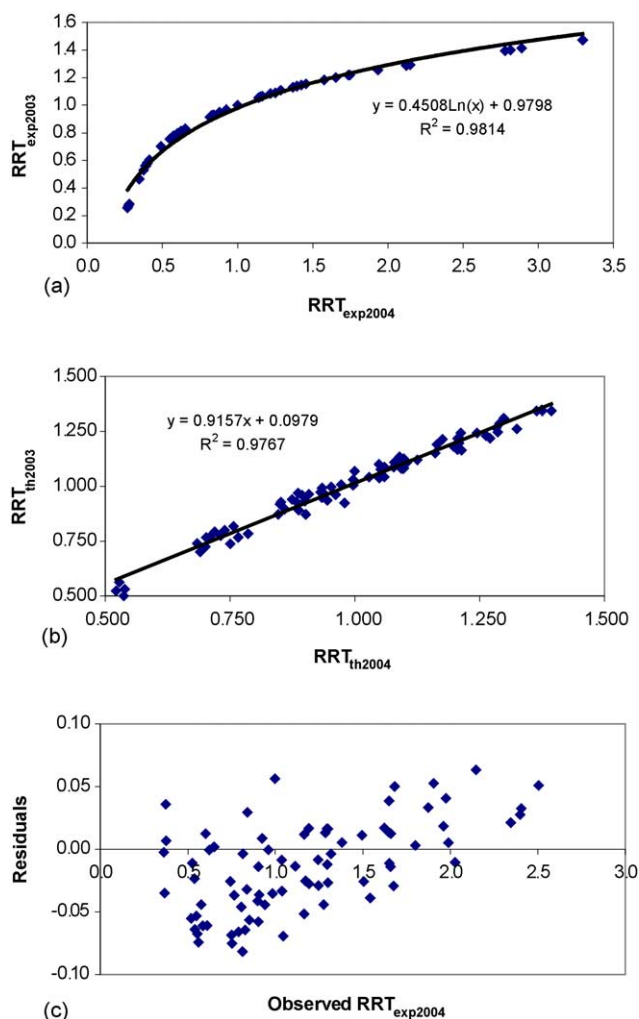

Fig. 2. Validation of GC-RRT model [15]. (a) Plot of RRTs obtained on DB-5 column (this study, $\mathrm{RRT_{exp2004}}$) vs. RRTs obtained experimentally by Rayne and Ikonomou ($\mathrm{RRT_{exp2003}}$) for 46 BDE congeners. (b) Plot of theoretical values ($\mathrm{RRT_{th2004}}$) vs. theoretical values ($\mathrm{RRT_{th2003}}$) for remaining 80 BDE congeners [15]. (c) Residuals plot of theoretical ($\mathrm{RRT_{th2004}}$) vs. experimental (Table 2) values.
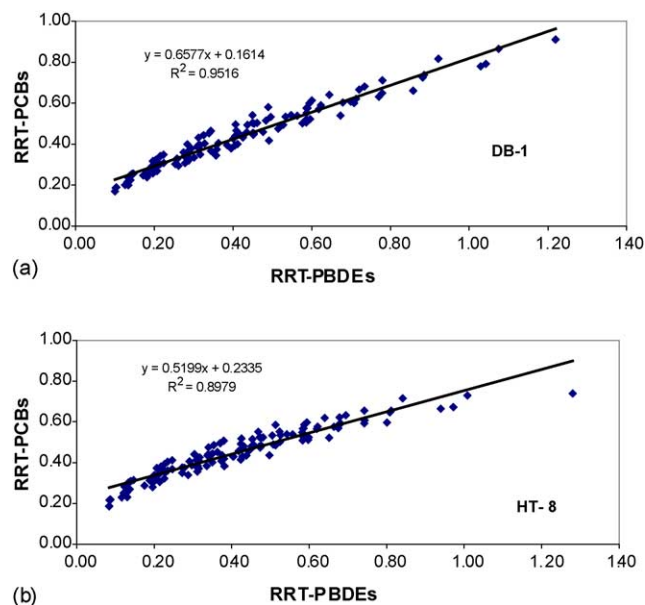
Fig. 3. Relationship between RRTs of BDEs and CBs on a DB-1 and a HT-8 column.

for predicting higher brominated BDE congeners is less accurate. This can also be observed in Table 2 of the original paper [15], where the same RRT (1.343) was obtained for seven (!) octa-BDE congeners (BDEs 199–205). This is probably due to the inclusion in the model of too small a number of hepta- and octa-BDE congeners (3 and 0, respectively).

3.6. Structure-related elution order for BDEs and CBs on similar stationary phases

By combining the retention database for CBs produced by Frame [16] with the present retention database for BDEs on similar stationary phases (DB-1, DB-5, DB-17, DB-XLB and HT-8), it is possible to correlate the elution orders of these two classes of pollutants. The best correlation between the two sets of data was found for DB-1 column ($r^2 = 0.95$), on which the elution order is primarily determined by volatility, while interactions with the stationary phase are relatively small (Fig. 3). When the polarity of the stationary phase increases, deviations from linearity between the two sets of RRTs increase and correlation coefficients become lower ($r^2 = 0.89$–0.91 for all other stationary phases). No doubt, this reflects the presence of an ether linkage in the BDEs, which causes interactions which are absent in the case of CBs. The overall result is a further indication of the usefulness of the present approach of retention-time prediction for various classes of polyhalogenated aromatic compounds.

4. Conclusions

A retention-time database of 126 BDE congeners is provided for seven capillary GC columns. Based on three criteria – number of BDEs involved in co-elutions, number of co-eluting groups and number of co-elutions observed for major BDEs – a DB-XLB column was found to be the most efficient for BDE congener-specific separation, with a DB-1 column as runner-up. The latter one is, however, preferred for routine analysis because it causes less degradation of hepta- and higher brominated congeners. By using the present retention-time database, new congeners were identified in two technical mixtures, viz. BDEs 49, 74, 101, 97/118, 155, 139 and 140 in Bromkal 70-5DE and BDEs 181, 191, 173/190, and 205 in Bromkal 79-8DE, and difficulties to construct accurate prediction model [15] were shown.

References

[1] BSEF, Bromine Science and Environmental Forum, http://www. bsef.com.
[2] K. Ballschmiter, R. Bacher, A. Mennel, R. Fischer, U. Riehle, M. Swerev, J. High Resolut. Chromatogr. 15 (1992) 260.
[3] A.M.C.M. Pijnenburg, J.W. Everts, J. de Boer, J.P. Boon, Rev. Environ. Contam. Toxicol. 141 (1995) 1.
[4] J. de Boer, K. de Boer, J.P. Boon, in: J. Paasivirta (Ed.), The Handbook of Environmental Chemistry, Part K, vol.3, Springer-Verlag, Berlin, Germany, 2000, p. 61.
[5] G. Söderström, U. Sellström, C.A. De Wit, M. Tysklind, Environ. Sci. Technol. 38 (2004) 127.
[6] N. Litz, J. Plant. Nutr. Soil Sci. 165 (2002) 692.
[7] H.M. Stapleton, M. Alaee, R.J. Letcher, J.E. Baker, Environ. Sci. Technol. 38 (2004) 112.
[8] H.M. Stapleton, R.J. Letcher, J.E. Baker, Environ. Sci. Technol. 38 (2004) 1054.
[9] R.J. Law, M. Alaee, C.R. Allchin, J.P. Boon, M. Lebeuf, P. Lepom, G.A. Stern, Environ. Int. 29 (2003) 757.
[10] P. Lindberg, U. Sellstrom, L. Haggberg, C.A. de Wit, Environ. Sci. Technol. 38 (2004) 93.
[11] A. Covaci, S. Voorspoels, J. de Boer, Environ. Int. 29 (2003) 735.
[12] J. de Boer, W.P. Cofino, Chemosphere 46 (2002) 625.
[13] A. Sjödin, E. Jakobsson, A. Kierkegaard, G. Marsh, U. Sellström, J. Chromatogr. A 822 (1998) 83.
[14] J. Björklund, T. Tollbäck, C. Östman, Organohalogen Compd. 61 (2003) 163.
[15] S. Rayne, M.G. Ikonomou, J. Chromatogr. A 1016 (2003) 234.
[16] G.M. Frame, Fresenius J. Anal. Chem. 357 (1997) 701.
[17] J. de Boer, D.E. Wells, K. Noren, Organohalogen Compd. 58 (2002) 197.

[18] E. Eljarrat, A. de la Cal, D. Barcelo, J. Chromatogr. A 1008 (2003) 181.

[19] G. Marsh, M. Athanasiadou, A. Bergman, L. Asplund, Environ. Sci. Technol. 38 (2004) 10.

[20] G.W. Gribble, Environ. Sci. Pollut. Res. 7 (2000) 37.

[21] M. Alaee, S. Backus, C. Cannon, J. Sep. Sci. 24 (2001) 465.

[22] W. Vetter, W. Jun, Chemosphere 52 (2003) 423.

[23] A. Sjödin, D.G. Patterson Jr., Å. Bergman, Environ. Sci. Technol. 35 (2001) 3830.

[24] A. Mazdai, N.G. Dodder, M.P. Abernathy, R.A. Hites, R.M. Bigsby, Environ. Health Perspect. 111 (2003) 1249.

[25] D. Herzke, G.W. Gabrielsen, A. Evenset, I.C. Burkow, Environ. Pollut. 121 (2003) 293.

[26] J. de Boer, P. Wester, J. Klamer, W.E. Lewis, J.P. Boom, Nature 394 (1998) 28.

[27] L. Hovander, M. Athanasiadou, L. Asplund, S. Jensen, E. Klasson-Wehler, J. Anal. Toxicol. 24 (2000) 696.

[28] J. Björklund, P. Tollbäck, C. Hiärne, E. Dyremark, C. Östman, J. Chromatogr. A 1041 (2004) 201.

[29] J. de Boer, C. Allchin, R. Law, B. Zegers, J.P. Booij, Trend. Anal. Chem. 20 (2001) 591.