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Comprehensive two-dimensional gas chromatography of polybrominated diphenyl ethers☆

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Abstract

Comprehensive two-dimensional gas chromatography with micro electron-capture detection (GC × GC–μECD) was evaluated for the separation of 125 polybrominated diphenyl ethers (PBDEs). From among the six column combinations that were evaluated, DB-1 × 007-65HT was found to be the most suitable because of: (i) the highest number of BDE congeners separated; (ii) the least decomposition of higher brominated congeners; and (iii) the most suitable maximum operating temperature. The separation of the 125 BDE congeners from five hydroxy- and two methoxy-BDEs and nine other brominated flame retardants (polybrominated biphenyls, tetrabromobisphenol-A, methyl-tetrabromobisphenol-A and hexabromocyclododecane) was also studied. Fluorinated BDEs were found to be valuable internal standards for the determination of BDEs because of their very similar physico-chemical properties and excellent separation from the parent BDEs, mainly in the second dimension. GC × GC–time-of-flight MS and GC × GC–μECD were shown to be useful tools to identify decomposition products of nona- and deca-substituted BDEs, which are formed during the GC run. Three nona-BDEs were shown to be the major decomposition products of BDE 209.

Keywords: Polybrominated diphenyl ethers; Comprehensive two-dimensional gas chromatography; GC × GC; Brominated flame retardants; Fluorinated brominated diphenyl ethers; Decomposition

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in polymers, textiles, electronic boards and various other materials [1]. The 209 congeners are numbered in the same way as the structurally related polychlorinated biphenyls [2,3]. PBDEs with more than three bromine atoms are very hydrophobic and rather non-volatile with molecular masses of over 482 and up to 950. They may be classified as persistent compounds and are ubiquitous contaminants [3]. The technical PBDE mixtures are relatively simple and consist of 20–25 congeners [4]. Additional congeners are encountered in environmental samples where processes such as photolytic debromination [5], microbial debromination in soil [6], biological debromination [7] or metabolism in higher animals [8] have changed the initial composition of a technical mixture. Especially for studies dealing with such processes, but also for other trace-level applications, high-resolution separation methods are urgently needed [9].

In recent years, progress in this area was hampered by the availability of less than 50 individual BDE congeners. Recently, the situation improved when some 80 additional BDE congeners became commercially available [10]. The next problem is that even state-of-the-art gas chromatography (GC), which is the method of choice for the analysis of PBDEs, cannot separate all or nearly all congeners. In a previous paper on the elution order of the 125 BDE[1] congeners on seven stationary phases,

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[1] In the course of an internal quality control audit, it was discovered just after publishing our previous paper [10] that the congener designated as BDE 75 was in fact congener BDE 51. Therefore, the correct number of congeners evaluated is 125 instead of 126 and the reported co-elution BDE 75/BDE 51/BDE 62 is just co-elution of BDE 51 and BDE 62.

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we reported that 55 congeners were involved in 22 co-elutions on even the most efficient phase [10]. Using mass-spectrometric instead of electron-capture detection will only slightly improve the situation because the majority of the co-eluting pairs has the same degree of bromine substitution and, thus, closely similar mass spectra.

In the present study, comprehensive two-dimensional gas chromatography (GC × GC), well known for its excellent separation potential [11,12], was used to improve the separation of the 125 BDEs. Possible interferences in environmental samples of common co-extractants, such as hydroxy- and methoxy-BDE metabolites, polybrominated biphenyls (PBBs), dimethyltetrabromobisphenol-A (Me-TBBP-A), tetrabromobisphenol-A (TBBP-A) and hexabromocyclododecane (HBCD) and the suitability of mono- and di-fluorinated BDEs as internal standards, were also addressed. In addition, attention was paid to the decomposition of nona- and decabrominated congeners.

Table 1
BDE congeners included in test set

No.	Structure	No.	Structure	No.	Structure
Mono-BDEs		50	2,2',4,6	124	2',3,4,5,5'
1	2	51	2,2',4,6'	125	2',3,4,5,6'
2	3	53	2,2',5,5'	126	3,3',4,4',5
3	4	55	2,3,3',4	127	3,3',4,5,5'
Di-BDEs		58	2,3,3',5'	Hexa-BDEs	
4	2,2'	62	2,3,4,6	128	2,2',3,3',4,4'
6	2,3'	66	2,3',4,4'	131	2,2',3,3',4,6
7	2,4	67	2,3',4,5	138	2,2',3,4,4',5'
8	2,4'	68	2,3',4,5'	139	2,2',3,4,4',6
9	2,5	69	2,3',4,6	140	2,2',3,4,4',6'
10	2,6	71	2,3',4',6	141	2,2',3,4,5,5'
11	3,3'	72	2,3',5,5'	142	2,2',3,4,5,6
12	3,4	73	2,3',5',6	144	2,2',3,4,5',6
13	3,4'	74	2,4,4',5	153	2,2',4,4',5,5'
14	3,5	76	2',3,4,5	154	2,2',4,4',5,6'
15	4,4'	77	3,3',4,4'	155	2,2',4,4',6,6'
Tri-BDEs		78	3,3',4,5	156	2,3,3',4,4',5
16	2,2',3	79	3,3',4,5'	158	2,3,3',4,4',6
17	2,2',4	80	3,3',5,5'	159	2,3,3',4,5,5'
18	2,2',5	81	3,4,4',5	160	2,3,3',4,5,6
19	2,2',6	Penta-BDEs		161	2,3,3',4,5',5
20	2,3,3'	85	2,2',3,4,4'	166	2,3,4,4',5,6
22	2,3,4'	86	2,2',3,4,5	167	2,3',4,4',5,5'
25	2,3',4	87	2,2',3,4,5'	168	2,3',4,4',5',6
26	2,3',5	88	2,2',3,4,6	Hepta-BDEs	
27	2,3',6	97	2,2',3',4,5	173	2,2',3,3',4,5,6
28	2,4,4'	98	2,2',3',4,6	181	2,2',3,4,4',5,6
29	2,4,5	99	2,2',4,4',5	182	2,2',3,4,4',5,6'
30	2,4,6	100	2,2',4,4',6	183	2,2',3,4,4',5',5
31	2,4',5	101	2,2',4,5,5'	184	2,2',3,4,4',6,6'
32	2,4',6	102	2,2',4,5,6'	185	2,2',3,4,5,5',6
33	2',3,4	103	2,2',4,5',6	190	2,3,3',4,4',5,6
34	2',3,5	104	2,2',4,6,6'	191	2,3,3',4,4',5',6
35	3,3',4	105	2,3,3',4,4'	192	2,3,3',4,5,5',6
36	3,3',5	106	2,3,3',4,5	Octa-BDEs	
37	3,4,4'	108	2,3,3',4,5'	198	2,2',3,3',4,5,5',6
38	3,4,5	109	2,3,3',4,6	203	2,2',3,4,4',5,5',6
39	3,4',5	114	2,3,4,4',5	204	2,2',3,4,4',5,6,6'
Tetra-BDEs		115	2,3,5,5',6	205	2,3,3',4,4',5,5',6
40	2,2',3,3'	116	2,3,4,5,6	Nona-BDEs	
42	2,2',3,4'	118	2,3',4,4',5	206	2,2',3,3',4,4',5,5',6
46	2,2',3,6'	119	2,3',4,4',6	207	2,2',3,3',4,4',5,6,6'
47	2,2',4,4'	120	2,3'4,5,5'	208	2,2',3,3',4,5,5',6,6'
48	2,2',4,5	121	2,3',4,5',6	Deca-BDEs	
49	2,2',4,5'	123	2',3,4,4',5	209	2,2',3,3',4,4',5,5',6,6'

2. Experimental

2.1. Samples and chemicals

A standard mixture containing the 125 BDEs (for list, see Table 1) was prepared by mixing standard solutions of each BDE congener, which were previously prepared by dissolving the neat crystals (purity >97%) in nanograde toluene (Promochem, Wesel, Germany). The final congener concentration in the mixture was approximately 100 ng/ml. The BDE crystals were kindly provided by Accustandard (New Haven, CT, USA). For the decomposition study of the nona-brominated congeners and deca-brominated BDE 209, a mixture with a 10-fold excess of the nona-BDEs and a 100-fold excess of the BDE 209 compared to lower brominated congeners was prepared.

For the co-elution studies, three more mixtures were prepared. One was a mixture of the 125 BDE congeners and nine other flame retardants (BB 15, BB 49, BB 52, BB 101, BB 153, BB 169, HBCD, TBBP-A, Me-TBBP-A), all purchased from Accustandard. The final concentration of the added compounds was ca. 500 ng/ml. The second one was a mixture of the 125 BDE congeners and the seven BDE biodegradation products, i.e. two methoxy-BDEs (6-MeO-BDE 47 and 4-MeO-BDE 49) and five hydroxy-BDEs (2-OH-BDE 28, 4-OH-BDE 42, 6-OH-BDE 47, 4-OH-BDE 49 and 6-OH-BDE 99), kindly provided by Prof. Å. Bergman (Department for Environmental Chemistry, Stockholm University, Stockholm, Sweden). The final concentration of all compounds was ca. 100 ng/ml. The third one was a mixture of the 125 BDE congeners and 12 fluorinated BDEs (4′-F-BDE 25, 4′-F-BDE 27, 3′-F-BDE 28, 6-F-BDE 47, 6-F-BDE 66, 4′-F-BDE 69, 3-F-BDE 100, 3-F-BDE 119, 4′-F-BDE 160, 4′,6-F-BDE 199, 2,4′-F-BDE 198 and 4′-F-BDE 208), kindly provided by Chiron (Trondheim, Norway). The final concentration of all compounds was ca. 100 ng/ml.

A dust sample of household origin was prepared according to a method validated for PCA and PBDE determination by GC–electron-capture negative ionization (ECNI) MS. A brief summary is given in reference [13].

2.2. GC × GC–μECD

The GC × GC system was built from an HP6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with a loop-type carbon dioxide jet modulator (KT2002 CO_2 system; Zoex, Lincoln, NE, USA). The hot air pulse duration was 200 ms, the hot-jet temperature 400 °C, and the modulation period 5 or 8 s, depending on the column combination used. At the start of each run, the CO_2 flow was adjusted by means of a needle valve to keep the cold-jet temperature at 0–10 °C, at an initial oven temperature of 90 °C. Helium gas (Hoek Loos, Schiedam, The Netherlands) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. An Agilent micro-ECD system was operated at 300 °C, with 99.999% pure nitrogen (Hoek Loos) as make-up gas at a flow-rate of 150 ml/min. The data acquisition rate was 50 Hz. One microlitre samples were injected

manually into a split/splitless inlet port operated in the splitless mode at 280 °C, with the split opening 2 min after injection. A 30 m × 0.25 mm, 0.25 μm DB-1 (100% methylpolysiloxane) and 30 m × 0.25 mm × 0.25 μm DB-XLB (proprietary) fused-silica columns purchased from J&W Scientific (Agilent) were used as first-dimension column. Three columns were used as second-dimension columns: 1 m × 0.10 mm, 0.1 μm 007-65HT (65% phenyl-methylpolysiloxane) from Quadrex (New Haven, CT, USA), 1.5 m × 0.10 mm × 0.1 μm VF-23ms (proprietary—high cyano-containing polymer; with absolute cyano content 70–90%) from Varian (Middelburg, The Netherlands) and 0.8 m × 0.1 mm, 0.1 μm LC-50 (50% liquid crystalline-methylpolysiloxane) from J&K Environmental (Sydney, Nova Scotia, Canada). The columns were coupled to each other via a 1.5 m × 0.1 mm i.d. uncoated fused-silica deactivated column (BGB Analytik, Aldiswil, Switzerland), which served as the modulator loop. Mini press-fits (Techrom, Purmerend, The Netherlands) were used for the connections. The various temperature programmes are specified in the text. HP Chemstation software (Agilent) was used to control the GC instruments and to acquire data. Raw data files were imported into HyperChrom software (ThermoElectron, Milan, Italy) used for GC × GC data processing, evaluation and visualization. Colour contour plots were produced by Transform software (Fortner Research, Sterling, VA, USA).

2.3. GC × GC–time-of-flight (TOF) MS

The GC × GC–TOF-MS system was built from a TRACE 2D (ThermoElectron) gas chromatograph coupled to a TEMPUS time-of-flight mass spectrometer (ThermoElectron, Austin, TX, USA). A 30 m × 0.25 mm, 0.25 μm DB-1 was used as first-dimension column. The 007-65HT column with dimensions of 1 m × 0.1 mm, 0.1 μm was used as second-dimension column. For specification of both columns, see Section 2.2. The front end of the second-dimension column was coupled directly to the first-dimension column and the back end to a 30 cm × 0.1 mm retention gap mounted in the GC–MS interface. Mini press-fits (Techrom) were used for the connections. Modulation was performed at the beginning of the second column with a modulation period of 8 s. Helium gas (Hoek Loos) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. One microlitre samples were injected manually into a PTV inlet port operated in the constant-temperature splitless mode at 300 °C, with the split opening 2 min after injection. The mass spectrometer was tuned and calibrated in the ECNI mode using heptacosafluorotributylamine (Fluka Chemie, Buchs, Switzerland) as the reference gas according to the recommendations of the manufacturer. Methane (0.5 ml/min) was used as a moderate gas and the source temperature was 210 °C. The mass range of 70–1000 Da was acquired at a data acquisition rate of 40 Hz. The temperature of the GC–MS transfer line was 340 °C and the temperature programme for both columns was 90 °C (2 min), at 20 °C/min to 190 °C, then at 2 °C/min to 340 °C (25 min). Xcalibur software (ThermoElectron) was used to control the GC × GC–TOF-MS instrument and to acquire data. Raw data files were imported into HyperChrom software (ThermoElectron) used for GC × GC data processing, evaluation and visualization.

3. Results and discussion

3.1. Selection of GC × GC column combination

In our previous paper [10], the performance of seven stationary phases in the one-dimensional (1D) GC separation of the 125 BDE congeners was studied. A DB-XLB column was found to give the lowest number of co-elutions, i.e. 55 congeners involved in 22 co-elutions, followed by a DB-1 column with 61 congeners involved in 24 co-elutions. They were, therefore, tested as the first-dimension columns. As regards the second-dimension column, in another recent study [13], six column combinations (DB-1 combined with six second-dimension columns) were tested for the separation of 12 classes of organohalogenated compounds, with the mutual separation of these classes as the principal aim. One of the classes was the mixture of 125 BDE congeners. One main conclusion was that the use of 007-210 or HT-8 as second-dimension column added little to the selectivity of the 1D-GC separation. Much better results were obtained with SupelcoWax-10, LC-50, VF-23ms and 007-65HT. However, with SupelcoWax-10 strong decomposition of penta- and higher substituted BDE congeners was observed. Co-elution data for the other three column combinations, which did not cause any degradation, are presented in Table 2. It shows that the number of co-elutions is essentially the same in all cases. However, the 007-65HT second-dimension column adds most to the selectivity of the first-dimension column, leaving only 35 BDEs being involved in co-elutions. An added advantage of this column is that, in the paper on between-class separations quoted above [13], it was observed that this column can also be recommended for the separation of PBDEs, as a class, from many potentially interfering halogenated co-extractants.

Table 2 also shows the co-elution data for the DB-XLB × 007-65HT column combination. DB-XLB was tested only in combination with 007-65HT because the latter column provides the best results in combination with DB-1, and also because it is the only column which can stand the high temperatures (>300 °C) required to elute nona- and deca-substituted BDEs. The high temperature limit becomes especially important with DB-XLB because all compounds require a ca. 20 °C higher elution temperature compared with the DB-1 column. Table 2 demonstrates that the separation performance of the DB-XLB × 007-65HT combination is similar to that of DB-1 × 007-65HT and that, as far as the separation criterion is considered, these two column combinations are equally suitable for PBDE separation.

3.2. Behaviour of higher brominated BDEs in GC × GC

The higher brominated BDEs (Br > 8) are known to degrade, with the degradation rate increasing with the temperature, the time spent at the elevated temperature and the presence of catalytic sites. 1D-GC chromatograms of these compounds typically show a rising baseline prior to the elution of the compound

Table 2
Co-elution of BDE congeners on four column combinations

	DB-1 × LC-50[a]	DB-1 × VF-23 ms[a]	DB-1 × 007-65HT[a,b]	DB-XLB × 007-65HT[b]
No. of co-elutions	16	16	17	17
No. of co-eluting BDEs	47	41	35	36
Co-eluting pairs	4/7/6, 12/13, 32/26, 17/25, 16/33/28, 20/35, 22/37, 49/68/71/46/48, 74/76/79/58, 66/42, 77/40, 98/119/120, 115/116, 118/97/86/87/108/123, 140/131/158/141/160, 173/190	12/13, 16/33, 20/35, 22/37, 73/69, 46/48, 76/79/58, 66/42, 77/40, 104/103, 101/98/119, 115/124/116, 118/97/108/86/123, 140/131/158/141/160, 173/190, 198/203	12/13, 25/31, 16/33, 20/35, 22/37, 73/69, 62/51, 46/48, 79/58, 66/42, 77/40, 98/119, 118/97, 108/123, 140/131/158, 173/190, 198/203	6/7, 26/29/32, 16/33, 35/20, 37/22, 51/62, 71/46, 58/79, 66/42, 40/77, 98/119, 118/97, 123/108, 140/158/131, 182/128, 173/190, 198/203

[a] Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 335 °C (10 min) for DB-1 × 007-65HT, to 285 °C (45 min) for DB-1 × LC-50 and to 290 °C (40 min) for DB-1 × VF-23 ms.
[b] Temperature programme: 90 °C (2 min), at 20 °C/min to 190 °C, then at 2 °C/min to 335 °C (10 min) for DB-1 × 007-65HT, to 350 °C (10 min) for DB-XLB × 007-65HT.

due to the decomposition products formed during elution, with an immediate drop of the baseline to the original level just after its elution. In addition, Focant et al. [14] when analysing some 10 BDE congeners together with polychlorinated biphenyls (PCBs) and organochlorine pesticides by GC × GC reported unacceptable 'trapping' and consequent peak broadening of hepta- and higher brominated BDEs in the second dimension for all stationary phases tested (50% phenyl-methylpolysiloxane, polyethylene glycol, 14% cyanopropylphenyl-methylpolysiloxane and 8% phenylpolycarborane siloxane). Therefore, the behaviour of the nona-BDEs and deca-substituted BDE 209 was studied on the two column combinations of interest. It is visualized in Fig. 1.

Fig. 1A shows part of a chromatogram obtained after the injection of a mixture of all BDEs enriched with BDE 209 on the DB-1 × 007-65HT column combination. In the first dimension, BDE 209 elutes at 88.9 min and is visible as a vertical yellow band. BDE 209 shows up as a band rather than a spot because of the high concentration that was injected (ca. 100 times more than the octa- and lower brominated BDEs) and the zoom-in visualization used to ensure the visibility of the decomposition products. The second-dimension retention time and peak width of BDE 209 can, however, easily be observed from the zoom-out contour plot and second-dimension chromatogram shown as inserts of Fig. 1. For clearer recognition, its position in the main chromatogram is marked as a black ellipse. One should note that no extreme peak broadening occurs here for any of the compounds. This contrasts with the findings of Focant et al. referred to above. Probably, band broadening in that study was caused by a low temperature of the MS transfer line, which houses significant piece of the second-dimension column. In our MS experiments, the temperature of the transfer line was held at the elution temperature of BDE 209, i.e. at 340 °C.

The next observation of Fig. 1A is that there are some 12–15 lines starting in the top left-hand part of the chromatogram and continuing down to the right-hand part until they arrive at the elution time of BDE 209, when they disappear. These lines cannot be tails of the peaks from which they originate because their intensities increase with the first-dimension retention time—they represent the decomposition products of BDE 209, which are separated in the second dimension. Since the decomposition increases with temperature, so do the line intensities and they, of course, disappear after the elution of the parent compound. The decomposition products now separated in the second dimension can easily be identified using mass spectrometry. This is demonstrated for two of the most intense bands, A and B. As expected, the mass spectra recorded throughout each band were identical; they are shown in Fig. 2 . By comparing them with the spectra of standards (Fig. 2), band A was identified as the nona-substituted BDE 208 and band B as the nona-substituted BDE 207. Actually, even if no mass spectrometer is available or the instrument does not provide enough sensitivity, such bands can be identified if the decomposition product is a congener present in the BDE standard mixture. Identification is possible on the basis of the direction of the decomposition lines because these 'iso-volatility' lines are characteristic for each congener (of course, unless there is iso-volatility co-elution). For instance, the curve marked for clearer recognition by a dotted white line is seen to start at the spot representing the co-eluting octa-substituted pair, BDEs 198 and 203. That is, one decomposition product is either BDE 198 or BDE 203. Other decomposition products that can be identified in a similar way are BDEs 208, 207 and 206. The intensities of the decomposition curves are seen to decrease in the order BDE 207 > BDE 208 > BDE 206. This suggests that the loss of a bromine atom in the meta position is the most, and that from the ortho position the least, favoured elimination. It is not possible to identify the other decomposition products because they start to appear beyond the first-dimension elution times of the most probable target congeners or they are congeners which are missing from our test set. However, based on the curvature of the lines, all decomposition products are octa-substituted BDEs, except for the two which are less curved than the others and are, therefore, hepta-BDEs. In Fig. 1A, they are marked by 7Br.

A significantly different decomposition pattern was observed upon analysis on the DB-XLB × 007-65HT column combination, as is shown in Fig. 1B. The most striking observation is that the peaks of the nona-BDEs and BDE 209 are missing. This is because these four compounds are completely decomposed during the first-dimension run. The direction and curvature of the decomposition lines visible in Fig. 1B provide information

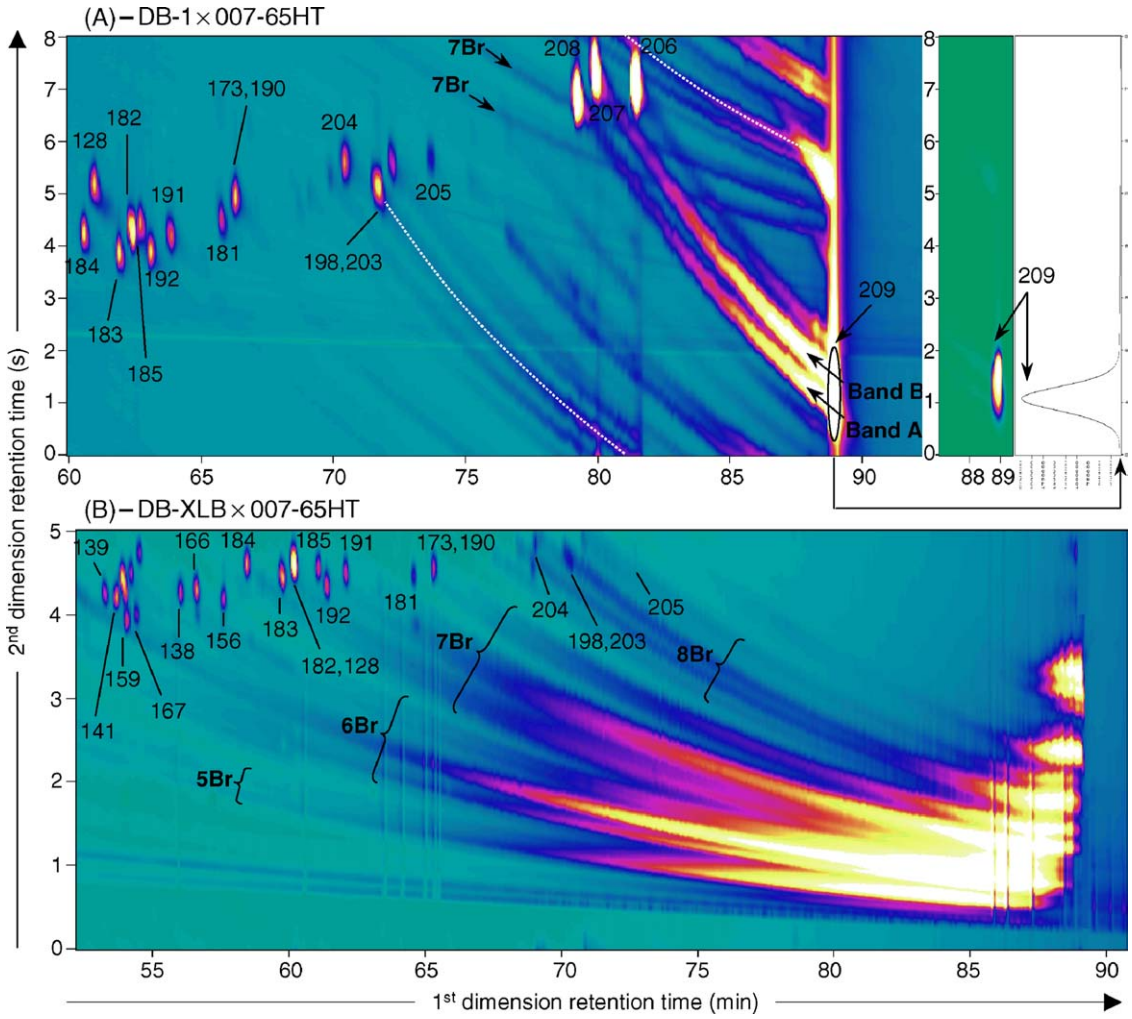

Fig. 1. Part of GC × GC–μECD contour plot of all 125 BDE congeners on (A) DB-1 × 007-65HT and (B) DB-XLB × 007-65HT column combination. Inserts in (A) show zoom-out visualization of part of the contour plot and the second-dimension chromatogram. (A) Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 340 °C (5 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min. (B) Temperature programme: 90 °C (2 min), at 20 °C/min to 190 °C, then at 2 °C/min to 350 °C (10 min). Modulation period, 5 s; constant flow of helium carrier gas, 1.2 ml/min.

about the nature of the decomposition products: hexa-BDEs are the main products, followed by hepta-, octa- and penta-BDEs. This means that on the DB-XLB column and at elevated temperatures, congeners down to hexa-BDEs are being decomposed. In other words, one should avoid to use a DB-XLB column in the first dimension: the preferred column combination for further study is DB-1 × 007-65HT, with which only very little decomposition was observed and, essentially only for the deca-substituted congener.

3.3. Separation of BDEs and related compounds

Fig. 3 shows an apex plot of the 125 BDEs on the preferred DB-1 × 007-65HT combination. The maximum temperature that can be applied is set by the temperature limit of the DB-1 column—325 °C isothermally or 350 °C temperature programmed. As is evident from the figure, this allows to achieve a reasonable run time (<80 min) and permits the second-dimension elution of all but four BDEs within the 8-s modulation period. Wrap-around was observed only for the three nona-substituted BDEs 206–208, and for the deca-substituted congener, BDE 209. The considerable gain in overall resolution, i.e. 17 co-elutions involving 35 congeners as against 22–24 co-elutions involving 55–61 congeners under optimized 1D-GC conditions, can easily be read from Fig. 3. When studying an apex plot, one should keep in mind that the separation or co-elution depends on the distance between apices, which can easily be read from the plot, but also on peak width, which is not shown in apex plots. In order to allow judging the separations in the second dimension, the upper left-hand side inserts show separations of compounds with the same distance of their apices but at different second-dimension retention times ($^2t_{R\ (4'\text{-F-BDE 27/BDE 27})} = 2.5$ s; $^2t_{R\ (\text{BB 153/BDE 154})} = 5$ s) and, thus, different peak widths. It is obvious that, with higher second-dimension retention times, a larger distance between the apices is required to achieve separation.

When analysing real-life samples, the final extract often contains other brominated flame retardants such as PBBs, HBCD, TBBP-A and Me-TBBP-A, and bio-degradation products such as hydroxy- and methoxy-BDEs may also be present [15]. Since

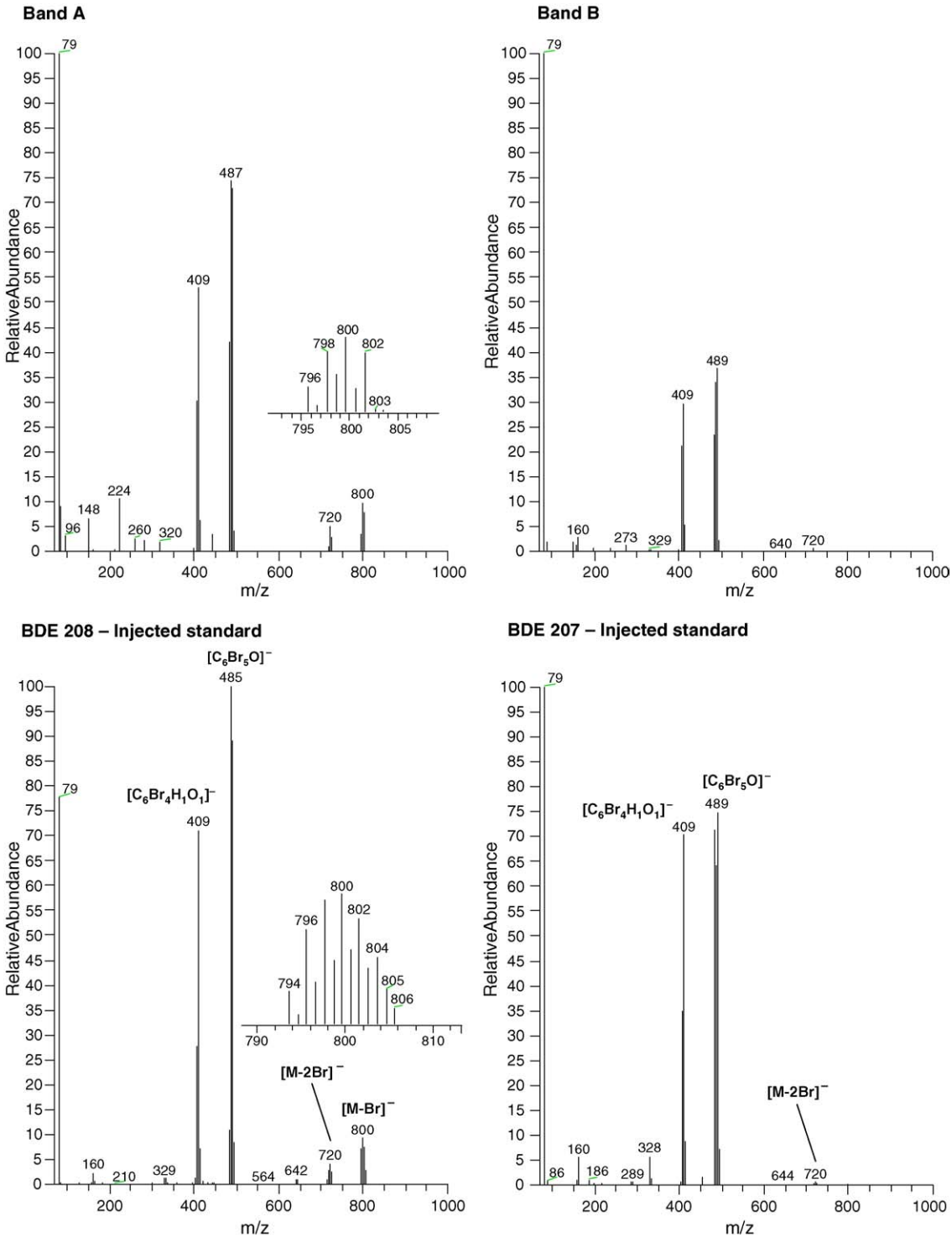

Fig. 2. ECNI mass spectra of (top) bands A and B from Fig. 1 and (bottom) BDE 208 and BDE 207.

they can interfere when ECD or mass-spectrometric detection is used, the position in the GC × GC plane of the, admittedly, still rather limited number of compounds available to us, was evaluated. Their red and blue apex positions are included in Fig. 3. It is obvious, and somewhat disappointing, that no group separation was obtained or, in other words, that all added compounds elute within the 'PBDE band'. This means that the separation or co-elution of other, not yet available congeners of these additional compound classes cannot easily be predicted.

Finally, Fig. 3 clearly shows that the use of the second-dimension column improves the separation of Me-TBBP-A, TBBP-A, BB 169, 6-OH-BDE 47 and 6-MeO-BDE 47. The rest of the added compounds was separated already in the first dimension or remained unresolved despite the added second dimension. The separation of TBBP-A from BDE 153 is valuable

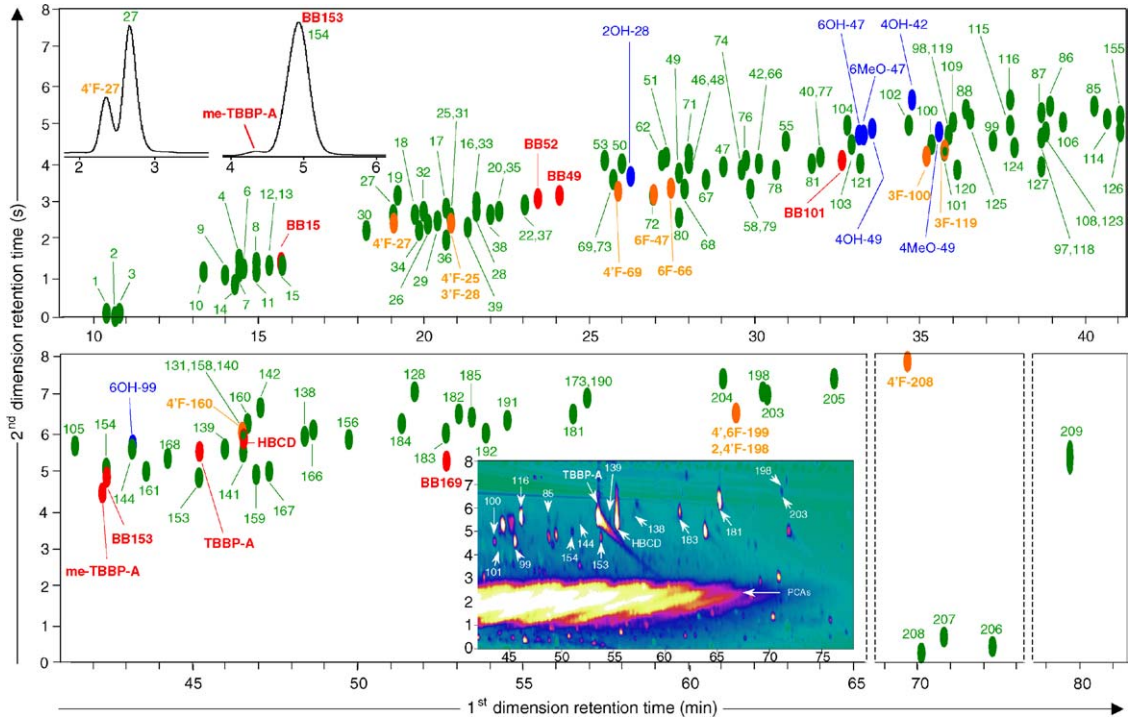

Fig. 3. Overlaid GC × GC–μECD chromatograms on DB-1 × 007-65HT column combination of (●) BDEs, (●) fluorinated BDEs, (●) other brominated flame retardants and (●) BDE metabolites. Temperature programme: 90 °C (2 min), at 20 °C/min to 190 °C, then at 2 °C/min to 325 °C (5 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min. Upper inserts show second-dimension chromatograms for 4′F-BDE 27/BDE 27 (^1t_R = 19.1 min) and BB 153/BDE 154 (^1t_R = 42.4 min). Lower insert shows part of GC × GC–μECD contour plot of dust extract obtained with slightly different temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 335 °C (10 min).

because it enables the quantification of BDE 153 without any interference even if a high concentration of TBBP-A is present, as is the case for the dust sample analysed (lower insert of Fig. 3). The unhampered determination of BDE 153 is of particular interest in the context of on-going degradation studies of BDE 209 [16].

3.4. Fluorinated BDEs as internal standards

^{13}C-Labelled standards generally are the most suitable internal standards because their physico-chemical properties are almost identical to those of the non-labelled analytes. However, the use of ^{13}C-BDEs as internal standards is limited because ECNI-MS and ECD detection, which are required to achieve the desired sensitivity, cannot distinguish the labelled and non-labelled congeners (except for BDE 209 with ECNI-MS detection). Therefore, internal standards, which are chromatographically separated from the parent BDEs but still have similar physico-chemical properties, are required. Recently, fluorinated BDEs were proposed to this end because due to the antagonistic effects of the reduction of London forces and the creation of a permanent dipole moment, fluorine substitution causes only very small changes of the physico-chemical properties of the parent compound [17]. Their suitability in GC × GC–μECD was evaluated by injecting a mixture of 12 fluorinated BDEs and the 125 BDE congeners. Fig. 3, in which the F-BDEs are visualized as orange spots, shows that the second-dimension separation facilitates the use of the F-BDEs as internal standards: all F-BDE congeners which co-elute with their parent compound in the first dimension, are separated in the second dimension, appearing just below the parent congener. Consequently, all F-BDEs except three (6-F-BDE 47, 3-F-BDE 119 and 4′F-BDE 160) which co-elute with another BDE congener, can serve as internal standards with no risk of co-elution with any of the 125 BDEs or any of the other flame retardants or BDE metabolites tested.

4. Conclusions

From amongst the available GC × GC column combinations, the DB-1 × 007-65HT provided the most efficient separation of the 125 BDE congeners in the test set. With this set-up, there were only 17 co-eluting pairs involving 35 congeners as against 22 co-elutions involving 55 congeners in the best available 1D-GC separation. Other flame retardants and, also, hydroxy and methoxy metabolites, were found to elute within the band of PBDEs. Consequently, there is only a limited gain in resolution. However, one rewarding improvement is the separation of TBBP-A and BDE 153: the interference-free determination of BDE 153 is of much interest because of on-going (bio-)degradation studies of BDE 209. In addition, fluorinated BDEs were found to be valuable internal standards because of their very similar physico-chemical properties and excellent separation from the parent BDEs, mainly in the second dimension. GC × GC–TOF-MS and GC × GC–μECD were shown to be excellent tools to study the decomposition of higher brominated BDEs, which occurs during the first-dimension run. On

the selected column combination, the decomposition of nona-BDEs is negligible and although there is some decomposition of deca-BDE, the present GC × GC procedure can be considered most promising for the analysis of all PBDEs in one run. Options to further suppress thermal degradation include the use of a shorter first-dimension column and a lower final temperature.

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