

## Improved Separation of PBDEs and Other Brominated Flame Retardants by Comprehensive Two-Dimensional Gas Chromatography

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in polymers, textiles, electronic boards and various other materials. There are 209 congeners and they are numbered as structurally related PCBs (Ballschmitter 1992). The technical PBDE mixtures are relatively simple and consist of 20–25 congeners. Additional congeners are encountered in environmental samples where processes such as photolytic debromination, microbial debromination in soil, biological debromination or metabolism in higher animals 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.

In the present study, comprehensive two-dimensional gas chromatography (GC×GC), well known for its excellent separation potential (Dallüge *et al.* 2003), 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, 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. The applicability of the approach was demonstrated for a dust extract.

### Materials and Methods

A standard mixture in toluene contained 125 BDEs (for list, see Fig. 1). The BDE crystals were kindly provided by Accustandard (New Haven, CT, USA). For the co-elution studies, three more mixtures were prepared. One was a mixture of the 125 BDEs and nine other flame retardants (BB 15, BB 49, BB 52, BB 101, BB 153, BB 169, HBCD, TBBP-A, Me-TBBP-A), all from Accustandard. The second one was a mixture of the 125 BDE congeners and the two methoxy-BDEs and five hydroxy-BDEs, kindly provided by Prof. Å. Bergman (Department for Environmental Chemistry, Stockholm University, Stockholm, Sweden). The third one was a mixture of the 125 BDE congeners and 12 fluorinated BDEs, kindly provided by Chiron (Trondheim, Norway). A dust sample of household origin was prepared according to a method validated for PCA and PBDE determination by GC–ECNI MS. A brief summary is given in reference (Korytár *et al.* 2005).

The GC×GC system was built from an HP6890 (Agilent Technologies) gas chromatograph equipped with a loop-type carbon dioxide jet modulator (KT2002 CO<sub>2</sub> system; Zoex). Helium gas was used as carrier gas. A 30m×0.25 mm×0.25 µm DB-1 (100% methylpolysiloxane) and DB-XLB (proprietary) fused-silica columns (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, 1.5m×0.10mm×0.1 µm VF-23ms (high cyano-containing polymer) from Varian and 0.8m×0.1 mm×0.1 µm LC-50 (50% liquid crystalline-methylpolysiloxane) from J&K Environmental. The columns were coupled to each other via a modulator loop (1.5m×0.1mm i.d. uncoated fused-silica

deactivated column). Mini press-fits (Techrom) were used for the connections. Raw data files were imported into HyperChrom software (ThermoElectron) used for GC×GC data processing, evaluation and visualization. Contour plots were produced by Transform software (Fortner Research).

## Results and Discussion

### *Selection of GC×GC column combination*

Four column combinations, DB-1×LC-50, DB-1×VF-23ms, DB-1×007-65HT and DB-XLB×007-65HT, were tested for separation of 125 BDE congeners. Column combinations were selected based on the retention data of 125 BDE congeners reported for various stationary phases and column combinations (Korytár *et al.* 2005a, 2005b). Co-elution data for the column combinations tested are presented in Table 1. It shows that the number of co-elutions is essentially the same in all cases. However, the DB-1×007-65HT leaves the least BDE congeners being involved in co-elutions, which makes it clearly the best combination for the separation. Its additional advantage over the DB-XLB×007-65HT combination is significantly lower decomposition of higher brominated BDEs.

Table 1. Co-elution of BDE congeners on four column combinations

	DB-1×LC-50	DB-1×VF-23ms	DB-1×007-65HT	DB-XLB×007-65HT
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

### *Separation of BDEs and related compounds*

Fig. 1 shows an apex plot of the 125 BDEs on the preferred DB-1×007-65HT combination. 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. 1. 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 inserts show separations of compounds with the same distance of their apices but at different second-dimension retention times ( $t_R$  (4'-F-BDE 27/BDE 27) = 2.5 s;  $t_R$  (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 (Marsh *et al.* 2004). Since they can interfere when ECD or mass-spectrometric detection is used, the position in the GC×GC plane of the compounds available to us, was evaluated. Their red and blue apex positions are included in Fig. 1. It 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.

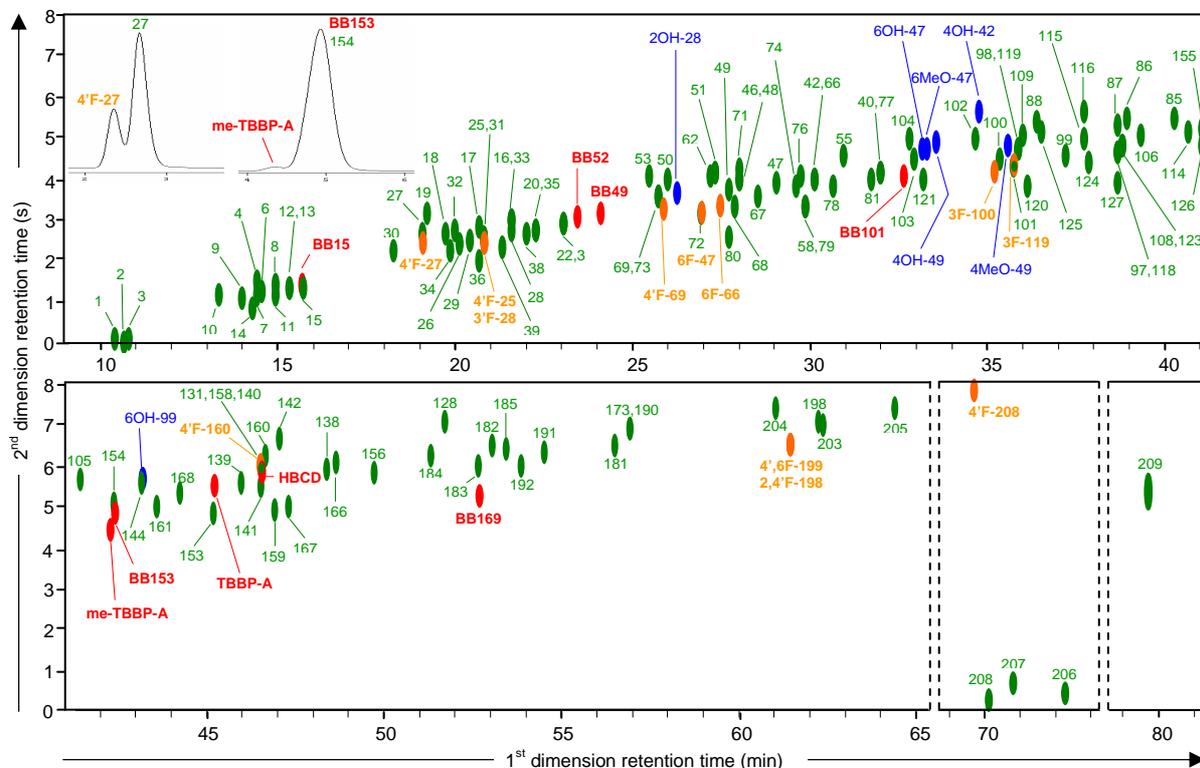


Fig. 1. Overlaid GC×GC–μECD chromatograms on DB-1×007-65HT column combination of (●) BDEs, (●) fluorinated BDEs, (●) other brominated flame retardants and (●) BDE metabolites. Upper inserts show second-dimension chromatograms for 4'F-BDE 27/BDE 27 ( $t_{R} = 19.1$  min) and BB 153/BDE 154 ( $t_{R} = 42.4$  min).

#### Fluorinated PBDEs as internal standards

Fluorinated PBDEs were recently proposed to be used as internal standards in PBDE analysis, because they have very similar physico-chemical properties as PBDEs (Luthe *et al.* 2004). Their suitability for use in GC×GC–μECD was evaluated by injecting a mixture of 12 fluorinated BDEs and the 125 BDE congeners. Fig. 1, 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.

#### Real-life application

A dust extract was analysed to demonstrate applicability of the approach for detection of PBDEs in real-life samples. Fig. 2 shows the GC×GC–μECD chromatogram achieved. By using the standard mixture of 125 BDE congeners, 18 congeners could be identified in the sample and are indicated in Fig. 2. The BDE congeners are well separated from co-extracted polychlorinated alkanes (PCAs) and other matrix constituents: BDEs being observed in the upper part of the chromatogram while PCAs

and matrix constituents occupies lower part of the chromatogram. Excellent separation of TBBP-A and BDE -153 was achieved, which 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. The unhampered determination of BDE 153 is of particular interest in the context of on-going degradation studies of BDE 209 (Parsons *et al.* 2004).

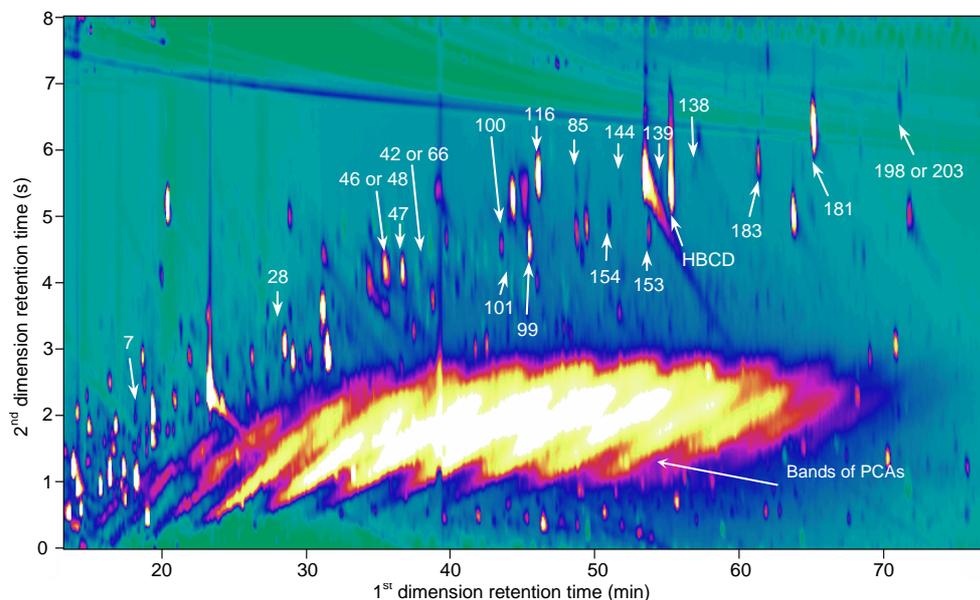


Fig. 2. GC×GC–μECD chromatogram of a dust extract on DB-1×007-65HT column combination for PBDE determination.

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