

## ANALYSIS OF LOW BROMINATED PBDD/F - ANALYSIS OF MBDD/MBDF TO T<sub>3</sub>BDD/T<sub>3</sub>BDF ON A SP2331 - COLUMN

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### Introduction

In the last two decades the increased use of brominated organic compounds especially brominated flame retardants (BFR) resulted in the presence of brominated compounds indoor, in the waste stream and in the environment. Some of the BFR, in particular the pentabromodiphenylether, are associated with the presence and the formation potential of brominated dibenzo-p-dioxins and dibenzofurans (PBDD/PBDF). Therefore the analysis of PBDD/PBDF received more attention in recent time.

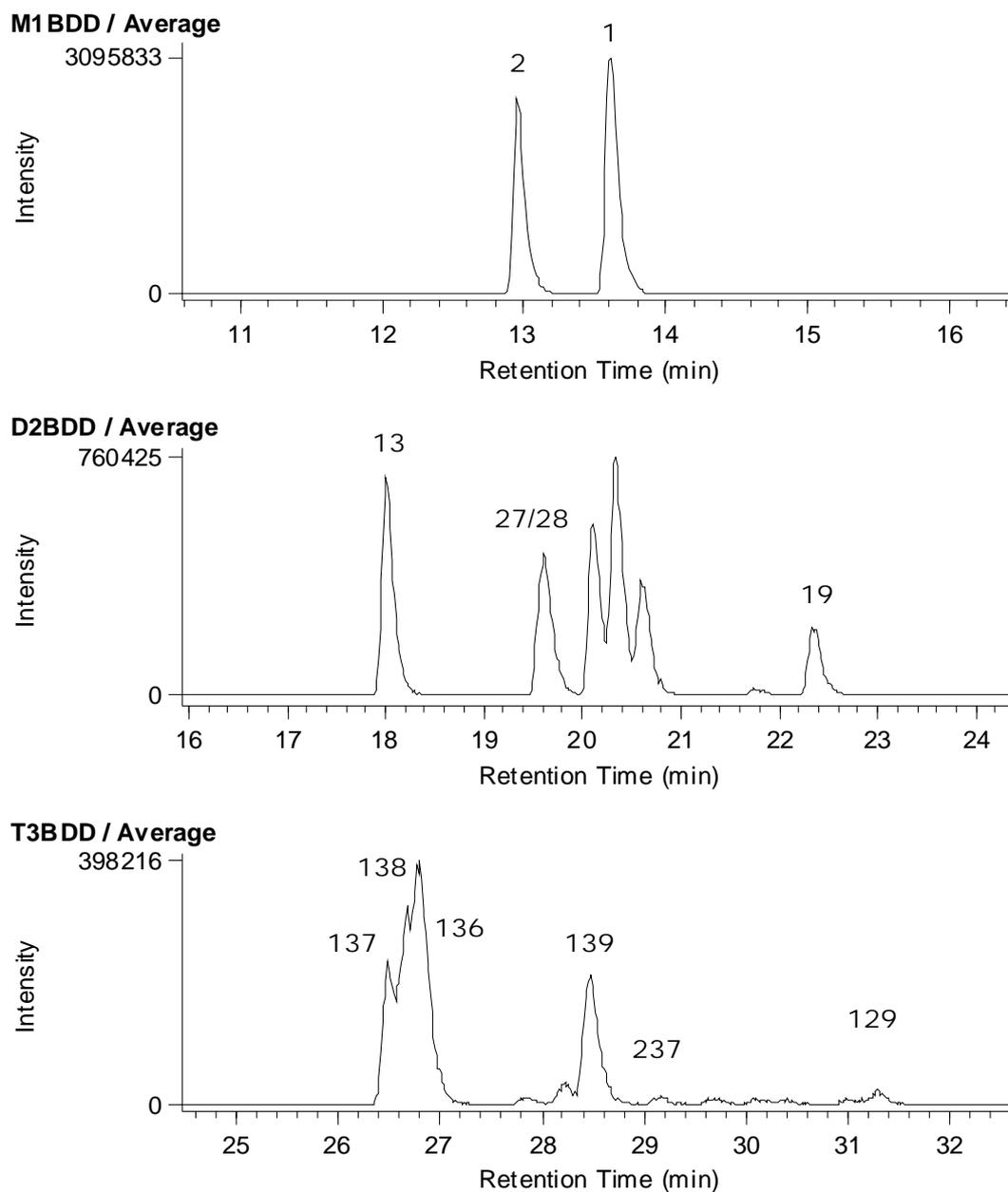
In this respect also the analysis of low brominated PBDD/PBDF homologues might be interesting in some processes and samples: Brominated aromatic compounds are subjected to debromination reaction under various conditions and are dehalogenated more rapidly compared to chlorinated aromatic compounds. Under UV or exposure to sunlight, brominated aromatic compounds can undergo rapid debromination (1). Debromination reactions are also observed during thermal degradation of polybrominated aromatics (2, 3). Furthermore some prominent brominated flame-retardants such as TBBP-A are low brominated aromatic compounds. The thermolysis of these compounds in the presence of a polymer matrix generates preferably low brominated PBDD/PBDF (4, 5). Therefore it might be interesting to have selected samples analysed for low brominated PBDD/PBDF.

For this study we synthesised a low brominated PBDD and PBDF mixture and optimised a temperature program on a SP2331 column.

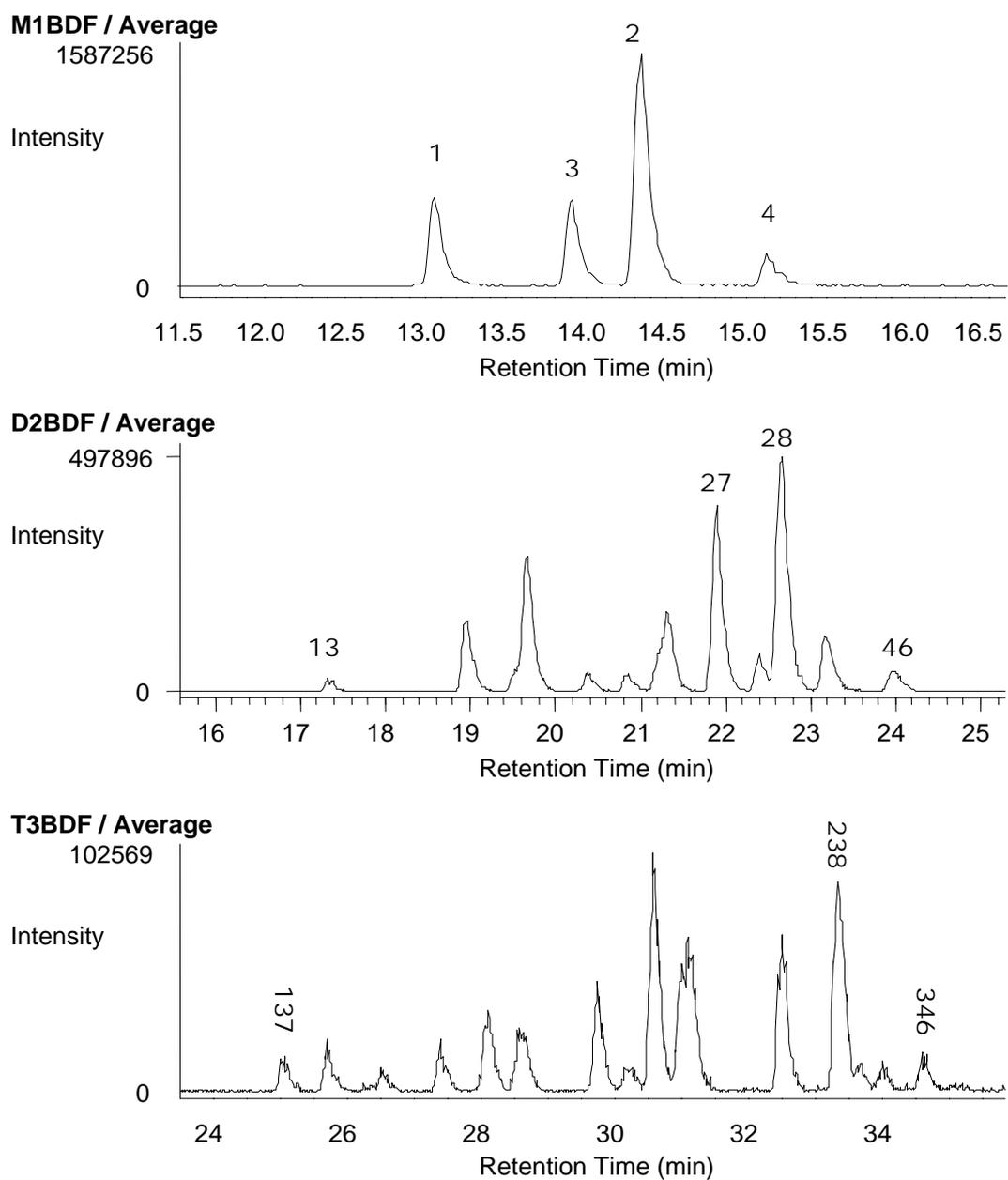
### Materials and Methods

**Standards.** The PBDD standards were synthesized by pyrolysis of bromophenols in Pyrex ampoules. The PBDD was synthesized by condensation of 2-monobromo phenol, 2, 4- and 2, 6-dibromophenol (DBP) and 2, 4, 6-tribromophenol (TBP) at 350°C (30 min). For the PBDF mixture all three monobromophenol isomers, Phenol and 2, 4-DBP were pyrolysed at 370°C (15 minutes) in the presence of trace amounts of CuBr<sub>2</sub>. We obtained commercially 2,7-D<sub>2</sub>BDF, 2,8-D<sub>2</sub>BDF, 2,3,8-T<sub>3</sub>BDF, 2,7/2,8-D<sub>2</sub>BDD, 2,3,7-T<sub>3</sub>BDD.

**GC/MS Analysis.** The analysis was carried out using an HP 5890 II gas chromatograph connected to a JMS-700 mass spectrometer (JEOL Ltd. Japan) (operating at a resolution >10 000). Temperature program used for isomer specific separation of the MBDD/F-T<sub>3</sub>BDD/F on SP2331 column (60m, 0.32mm i.d., 0.20µm,): 120°C, 1 min. isothermal; 20°C/min. to 200°C, 2°C/min. to 260°C, 30min. isothermal. Carrier gas flow rate: He 1.2mL/min. Masses of MBDD/MBDF to T<sub>3</sub>BDD/T<sub>3</sub>BDF are listed in table 1.



**Figure 1:** Chromatogram of M<sub>1</sub>BDD and T<sub>3</sub>BDD on SP2331  
60m, 0.32mm i.d., 0.20µm; 120°C (1 min.), 20°C/min. to 200°C, 2°C /min. to 260°C (30min).



**Figure 2:** Chromatogram of M<sub>1</sub>BDF and T<sub>3</sub>BDF on SP2331  
60m, 0.32mm i.d., 0.20µm; 120°C (1 min.), 20°C/min. to 200°C, 2°C/min. to 260°C (30min).

Table 1: Selected masses (M+) of M<sub>1</sub>BDD/M<sub>1</sub>BDF to T<sub>3</sub>BDD/T<sub>3</sub>BDF for MS detection

M <sub>1</sub> BrDD	261.9629	263.9610	M <sub>1</sub> BrDF	245.9680	247.9661
D <sub>2</sub> BrDD	339.8735	341.8715	D <sub>2</sub> BrDF	323.8785	325.8765
T <sub>3</sub> BrDD	419.7820	421.7800	T <sub>3</sub> BrDF	403.7870	405.7850
T <sub>4</sub> BrDD	497.6925	499.6904	T <sub>4</sub> BrDF	481.6975	483.6955

### Results and Discussion

Figure 1 show the chromatogram of M<sub>1</sub>BDD and T<sub>3</sub>BDD on the SP 2331 column. The use of the 2,4-DBP (resulting in 2- and 3- (7- and 8-) PBDD substitution) and 2,6-DBP (resulting in 1- and 4- (6- and 9-) PBDD substitution) produced a wide range of congeners within the D<sub>2</sub>BDD. However since only 2,4-substituted and 2,4,6-substituted brominated phenols were available preferably the 1,3-substituted congeners (1,3,6-; 1,3,7-; 1,3,8- and 1,3,9-T<sub>3</sub>BDD) were formed within the T<sub>3</sub>BDD resulting only in a limited number of prominent T<sub>3</sub>BDD isomers. However due to isomerisation/bromination reactions also other T<sub>3</sub>BDD isomers were formed in about one order of magnitude lower concentrations.

Figure 2 show the chromatograms of M<sub>1</sub>BDF and T<sub>3</sub>BDF on the SP 2331 column. The use of all three monobromophenols produced a wide range of congeners within the D<sub>2</sub>BDF. Due to the higher pyrolysis temperature and the addition of CuBr<sub>2</sub> the isomerisation/bromination reactions had a significant impact and hence a broad range of T<sub>3</sub>BDF were formed (Figure 2).

On the high polar SP2331-column, all 4 M<sub>1</sub>BDF were separated and also for D<sub>2</sub>BDF and T<sub>3</sub>BDF a reasonable selectivity was achieved (Figure 2). However on the less polar DB5 column even the 4 M<sub>1</sub>BDF were not completely separated (not shown) while the 4 chlorinated M<sub>1</sub>CDF isomers could be separated also on this low polar column. This demonstrates that the selectivity for brominated congeners is smaller compared to the chlorinated congeners.

### References

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