

Development of analytical method for PBDEs and PBDDs/DFs in environmental matrices and some chemical formulations

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Introduction

Brominated flame retardants (BFRs) are environmentally and toxicologically hazardous compounds amongst many of chemicals used to reduce inherent fire hazards in a variety of goods. Polybrominated diphenyl ethers (PBDEs) are widely used flame retardants in textile and plastic materials and their content can be up to 10-30 % of the product weight as is found for polyurethane foams.¹ The technical PBDE products become available at the market as pentaBDE, octaBDE and decaBDE formulation.

A combustion of the wastes containing PBDEs as well as thermal destruction of other BFR-containing materials may lead to the formation of another and considered to be highly toxic compounds such as polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs).²⁻⁵ Some of PBDE congeners were found to be liable for debromination and photodegradation under a real environmental condition but also during chemical laboratory analysis.⁶ Additionally, co-occurrence of PBDDs/DFs and PBDEs can cause interferences during quantitative analysis of PBDFs when using HRGC/HRMS. The objective of this study was to develop a method of perfect separation of PBDDs/DFs from PBDEs and their congener-specific determination using HRGC/HRMS but also to optimize quantification of BDE #209 in environmental samples.

Material and Methods

PBDEs (#47, 77, 99, 100, 105, 126, 153, 183, 190, 209, EO-5003, 5100) and PBDDs/DFs (EDF-4153, -4154, -5059) standard solutions were used to standardize a method of separation of PBDDs/DFs from PBDEs, and for recovery check trials each of PBDE and PBDD/DF congeners through an entire analytical procedure.

The mixture of PBDEs/PBDDs/PBDFs was initially fractionated using activated basic alumina column chromatography and hexane (Fr. 1), 0.5 % DCM in hexane (Fr. 2) and DCM (Fr. 3). Fraction 3, which contained brominated compounds was concentrated down to 200 μ l and further fractionated using a two-dimensional HPLC with the graphitic carbon (Hypercarb) and pyrenyl silica (PYE) columns. A detailed procedure of 2D HPLC fractionation for planar organochlorine compounds was described in detail earlier⁷⁻¹⁰. Separation, detection, identification and quantification of brominated compounds was achieved using DB-5 capillary column (15 m length x 0.25 mm i.d. and 0.10 μ m film) installed in the Hewlett Packard 6890 GC interfaced to the JEOL JMS-700D MS. The mass resolution of the spectrometer was greater than 10^{-4} atomic mass units. The GC oven temperature was programmed from 150 (2 min) to 300 at a rate of 5 /min with a final hold time of 10 min. PBDD, PBDF and PBDE congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster (using molecular ions of octaBDE in BDE #209). To check the quality of data obtained after HRGC/HRMS quantification BDE #209 was also identified and quantified using GC-ECD (Hewlett Packard 6890 series equipped with ⁶³Ni ECD).

Results and Discussion

The method presented on quantification of composite mixture of PBDEs and PBDDs/DFs using 2D HPLC with graphitized carbon and pyrenyl silica (Tables 1 and 2, Fig. 1) enables separation and enrichment of many congeners of bromodiphenyl ether (BDE) as well as bromodibenzo-*p*-dioxin (BDD) and bromodibenzofuran (BDF). In the next step the homologue groups and congeners of BDE, BDD and BDF are further separated using HRGC/HRMS. The method developed enables an accurate and simultaneous quantification of highly toxic PBDDs/DFs and PBDEs without co-elution, what is a fundamental problem even if study commercial PBDEs formulations.

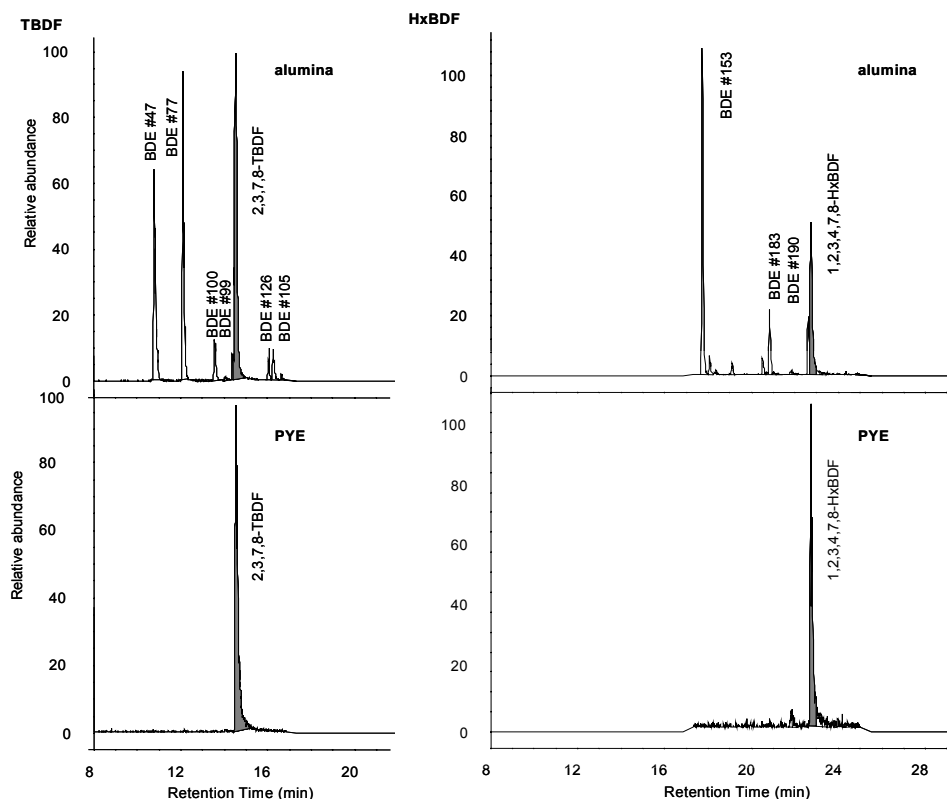


Fig. 1. Chromatogram of tetra- and hexa-BDF and BDEs after alumina column and PYE clean-up.

The quantitative analysis of BDE no. 209 is relatively difficult due to its liable physical properties related to photodegradation and debromination etc. and lower sensitivity of HRGC/HRMS for highly brominated congeners. To solve these problems BDE no. 209 was quantified in parallel by the HRGC/HRMS and GC-ECD and data gained were comparable both for the procedural blanks and a real environmental samples.

Table 1. Separation sequence of PBDEs and PBDDs/DFs on Hypercarb-HPLC

| Fraction | Time (min.) | Eluted compound |
|----------|-------------|---|
| 1 | 0-8 | PBDEs (nos. 47, 77, 99, 100, 105, 153, 183) |
| 2 | 8-28 | PBDEs (nos. 126, 153, 190, 209) Tetra- to octaBDDs/DFs |

Table 2. Separation sequence of PBDEs and PBDDs/DFs on PYE-HPLC

| Fraction | Time (min.) | Eluted compound |
|----------|-------------|--|
| 1 | 0-9.5 | PBDEs (nos. 47, 77, 99, 100, 105, 126, 153, 183, 190) |
| 2 | 9.5-12 | Not eluted |
| 3 | 12-24 | PBDEs (no. 209), 2,3,7,8-tetraBDD/DF |
| 4 | 24-75 | 1,2,3,7,8-PentaBDD/DF, 1,2,3,4,7,8-hexaBDD/DF, 1,2,3,6,7,8-, 1,2,3,7,8,9-hexaBDD, 1,2,3,4,6,7,8- heptaBDF, octaBDD |

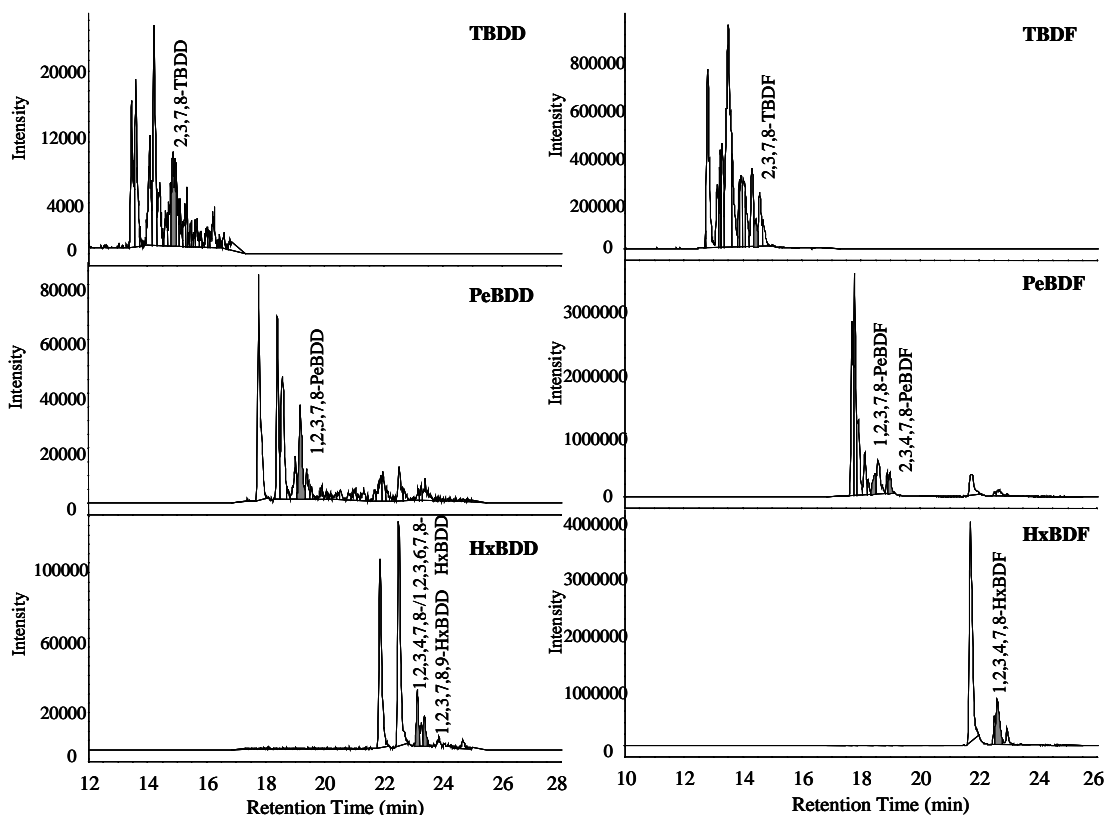


Fig. 2. HRGC/HRMS chromatograms of tetra- to hexa-BDDs/DFs in fly ash (DB-5).

Further, the analytical method developed was applied to quantify brominated aromatic compounds in several environmental matrices including pine needles (passive indicator of troposphere pollution), fly ash, animal matrices and soils. The method presented enabled simultaneous separation of several congeners of bromodiphenyl ether, bromodibenzofuran and bromodibenzo-*p*-dioxin found in environmental samples as shown for fly ash (Fig. 2).

The compounds such as 2,3,7,8-tetraBDD/DF, 1,2,3,7,8-pentaBDD/DF, 2,3,4,7,8-pentaBDF, 1,2,3,4,7,8-hexaBDD/DF, 1,2,3,6,7,8-hexaBDD and 1,2,3,7,8,9-hexaBDD were detected in fly ash from the MSWI. A contamination of the fly ash with PBDFs was greater than with PBDDs but also with PCDFs than PCDDs. The amounts of PBDEs and PBDDs/DFs detected in fly ash were much higher when compared to that found in pine needles sampled around the Tokyo Bay in Japan (see another paper in this communication). The method developed enables not only an accurate and simultaneous quantification of PBDEs/DDs/DFs but also good applicability to low and highly contaminated environmental matrices.

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