

ANALYSIS AND OCCURRENCE OF NEW BROMINATED FLAME RETARDANTS IN THE ENVIRONMENT

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Introduction

About 75 brominated flame retardants are on the market. Until now, the main focus of human and environmental studies has been on polybrominated diphenyl ethers (PBDEs), and hexabromocyclododecane (HBCD). Flame retardant, such as decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), has recently been found in human and environmental samples^{1,2,3}. DBDPE is being marketed as an alternative to BDEs having similar applications as BDE-209. Levels of BTBPE increased in lake trout of Ontario between 1979 and 1998². In the current study we extended the list of new BFRs and developed a method to determine PBDEs, BTBPE, DBDPE, and octabromo-1-phenyl-1,3,3-trimethylindan (Br Indan) in solid samples simultaneously. Br Indan ($C_{18}H_{12}Br_8$, molecular weight 867, Fig. 1) is a novel additive flame retardant with high bromine content (73%), and the occurrence of Br Indan in human or environmental samples has never been reported. In general, polybrominated phenyl indanes are prepared by mixing phenyl indane and bromine in a solvent with a metal or metal halide Lewis acid. The commercial product name of Br Indan is FR-1808, and the application range is from engineering resins, styrenic substrates, to olefin compositions. Melting point of FR-1808 is in the range of 240-255°C. This compound was designed as an alternative environmentally friendly flame retardant for PBDEs. Testing of the products resulted in levels of 2,3,7,8 congeners of polybrominated dibenzodioxins and dibenzofurans below the limit of detection⁴.

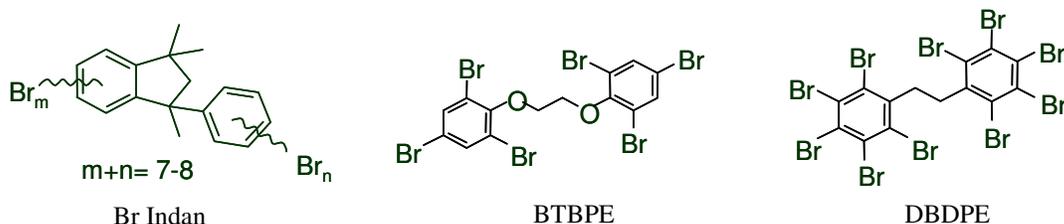


Figure 1: Structure of octabromo-1-phenyl-1,3,3-trimethylindan (Br Indan), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and decabromodiphenyl ethane (DBDPE).

Materials and methods

GC-MS analysis

PBDEs, DBDPE, BTBPE, Br Indan were analysed by gas chromatography (GC) combined with low resolution mass spectrometry (MS). Both GC (e.g. oven temperature, injection mode) and MS parameters (e.g. ion source temperature, ionization gas flow for ECNI) were optimized, and the MS was run in the electron impact (EI) and electron capture negative ionization (ECNI) mode. Impurities in the commercial products were determined. The following optimal settings were used:

Injection temperature 275 °C, injection volume 1 μ L, injection mode pulsed splitless ($P_{\text{initial}} = 18.8$ kPa; pulse pressure = 125 kPa; pulse time = 1.5 min), purge flow = 50.0 mL/min; purge time = 1.50 min

Ramped pressure mode. GC Oven temperature: 90 °C (1.5 min) 30 °C/min 190 °C; 4 °C/min 225 °C; 7°C/min 270 (2min); 10 °C/min 320 °C (10 min). ECNI mode ionization gas methane, flow 2.6 ml.min. Ion source temperature 250 °C, quadrupole temperature 150 °C, transfer line 300 °C.

Clean-up and extraction methods

Four clean-up methods were tested; gel permeation chromatography (GPC), silica gel, sulphuric acid treated silica gel, and solid phase extraction (SPE); for conditions see table 1. Elution profiles and recoveries of the test compounds were determined.

After optimization of the clean-up methods the extraction efficiency of the test compounds was determined using spiked sediment and accelerated solvent extraction (ASE200, 70°C, 2000 psi, 2 cycles) with hexane/acetone (3:1) as extraction solvent. The extract was cleaned with GPC (15-27 min was collected), evaporated to 0.5 ml, further cleaned with SPE, evaporated and a final clean-up step with silica gel was carried out. The final extract was analysed by GC-MS.

Table 1: Experimental conditions of the tested clean-up methods.

GPC	Silica gel	Sulphuric acid silica gel	SPE
Column: PL-Gel 50A 300x25 m (x2) 10µm 50A	1.8 g silica gel, 1.5% water deactivated	5 g silica deactivated with sulphuric acid (66% weight)	OASIS HLB
Mobile phase: dichloromethane 10 mL/min Elution profile: Fractions collected every minute from 14 to 28 min.	Elution profile: F1: 12 ml iso-octane F2: 24 ml 15% (v/v) diethyl ether in iso-octane F3: 16 ml diethyl ether	Elution profile: F1: 35 ml 30% dichloromethane in hexane	Cleaning: 5 mL dichloromethane Conditioning: 5 mL MeOH Washing: 0.5 mL hexane Elution: 5 mL dichloromethane:iso- octane (3:1)

Results and discussion

Analysis

ECNI mass spectrum of Br Indan showed two specific ions corresponding to the molecular ion and losses of a phenyl group and one bromine (m/z 706), and the losses of a phenyl group and two bromines (m/z 626). The EI mass spectrum showed also two specific ions with base peaks at m/z 773 and 407. The commercial product showed a number of small impurities that may be congeners with less bromine (Br_7).

Recoveries of the clean-up methods were satisfactory for all methods (Table 2), except for the sulphuric acid silica gel which showed degradation of BTBPE; recoveries decreased to 54% and bromine containing degradation products were observed in the chromatograms. Br Indan, BTBPE, and DBDPE eluted between 19-20, 18-19, and 21-22 minutes with GPC (Fig. 2).

The developed method consist of an extraction with ASE, a first cleaning of the extract with GPC to remove the bulk of humic acids and sulphur, followed by a SPE clean-up, and finally a silica gel clean-up. The advantage of this three step clean-up method is that the baseline of the chromatogram is clean, which improved the identification and quantification of the compounds. The extraction efficiencies of spiked sediment, including the final clean-up methods (GPC, SPE, and silica gel), were >80% for Br Indan, BTBPE, and DBDPE.

Table 2: Average recoveries (n=3) and relative standard deviations (RSD in brackets) of Br Indan, BTBPE, and DBDPE using silica gel, sulphuric acid treated silica gel, and solid phase extraction.

	Br Indan	BTBPE	DBDPE
Silica gel	103% (5%)	110% (10%)	99% (7%)
Sulphuric acid silica gel	91% (10%)	54% (7%)	101% (1%)
SPE	94% (5%)	128% (4%)	140% (3%)

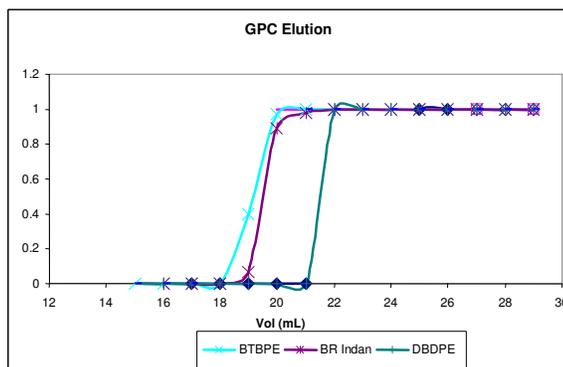


Figure 2: Elution profile of BTBPE, Br Indan, and DBDPE using GPC.

Occurrence of new BFRs in dust and sediment

The occurrence of PBDEs, Br Indan, BTBPE, and DBDPE in two samples of house dust, and two samples of sediment upstream (Schaar van Ouden Doel) and downstream (Terneuzen) collected in 2005 in the Western Scheldt estuary (The Netherlands), were studied. The optimized method was used for the analysis of the solid samples. In both dust samples PBDEs, Br Indan, BTBPE, and DBDPE were identified (Fig. 3). Identification of Br indan was based on the retention time and the selected ions of (m/z 79, 81, and 706) of Br Indan compared to a standard in ECNI and EI mode.

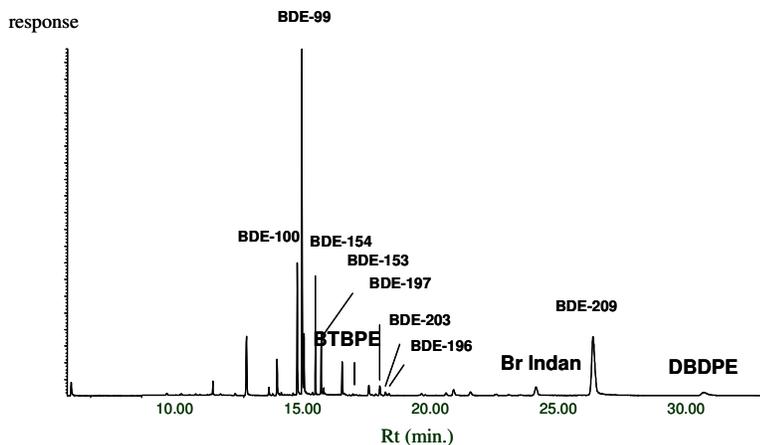


Figure 3: GC-MS (ECNI) chromatogram (m/z 79) of a dust sample. Indicated are BDEs, BTBPE, Br Indan and DBDPE.

PBDEs, DBDPE, BTBPE, and Br Indan were found in the upstream and downstream sediment samples. In the Scheldt area a number of BFRs users are located. High levels of BDE209 in sediment are found in this area. The levels of BDE47, BDE209, PBDEs, DBDPE, BTBPE, and Br Indan are given in Table 3. Levels of DBDPE are more than 10 times lower than BDE209. The ratio of DBDPE:BDE209 (0.01 and 0.02 at Terneuzen and Schaar van Ouden Doel, respectively), are comparable to the ratio found in 2001⁵, which indicates still the higher use of BDE209 than DBDPE. Levels of BDE47, BTBPE and Br Indan are in the same range (low ng/g dry weight). BTBPE found in sediment of the Lake Winnipeg (Canada) food web study⁶ were in the same range as our study (<LOD to 2.7 ng/g dw). Levels of BDE47, BDE209, DBDPE, and Br Indan upstream are about 10 times higher

than downstream. In conclusion, BTBPE, DBDPE, and for the first time Br Indan was identified in sediments and dust samples.

Table 1: Levels (ng/g dry weight) of BDE47, BDE209, DBDPE, BTBPE, and Br Indan in sediment from two locations in Western Scheldt Estuary (The Netherlands). Schaar van Ouden Doel as upstream and Terneuzen as downstream locations.

Compound	Terneuzen	Schaar van Ouden Doel
BDE 47	0.16	1.9
BDE 209	100	560
DBDPE	1.1	10
BTBPE	0.25	0.31
Br Indan	0.11	1.0

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