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Identification and quantification of polybrominated diphenyl ethers (PBDEs) in the commercial product Bromkal 70-5 DE

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Abstract

Nine polybrominated diphenyl ethers (PBDEs) have been identified in the commercial PBDE product Bromkal 70-5 DE. The chemical structures of the two major PBDE congeners were confirmed. The PBDE congeners were identified by gas chromatography (GC) by comparison to thirty-one individual PBDE reference compounds. The retention time of each PBDE congener was compared to the retention times of the PBDEs in Bromkal 70-5 DE on four GC capillary columns. The relative retention times of the thirty-one PBDEs versus Dechlorane on the four columns are given. The concentrations of the PBDEs in the commercial product were calculated.

Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities as additive flame retardants in polymers, particularly in electric devices, TV sets, computers, building materials and textiles[1]. PBDEs were first reported in the environment in pike from the river Viskan on the west coast of Sweden in 1981[2]. Today PBDEs are ubiquitous environmental contaminants present in wildlife species[1,3-8], and also in human adipose tissue[9], mothers milk[10] and plasma[11]. There are three main types of commercial PBDE products with varying degrees of bromination, i.e. "pentabromodiphenyl ether", "octabromodiphenyl ether" and "decabromodiphenyl ether". The world production of PBDE was in 1992 estimated to 40 000 tonnes, of which 30 000 tonnes were decabromodiphenyl ether (decaBDE), 6 000 tonnes octabromodiphenyl ether (octaBDE) and 4 000 tonnes pentabromodiphenyl ether (pentaBDE)[1]. However, even though the main product today is decaBDE, the environmental profile, at least in biota, resembles the "pentabromodiphenyl ether" product. This may be due to a previous extensive use of lower brominated products or to

* The PBDE have been given numbers according to the numbering system of PCBs, see ref. 20.

photochemical degradation of decaBDE[12-14]. Also, metabolic degradation has been indicated in rainbow trout dosed with decaBDE[15] and metabolites of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47)* have been determined in experimentally dosed rats.

One of the "pentabromodiphenyl ether" products is Bromkal 70-5 DE, a mixture that have been extensively used as analytical standard due to the lack of reference compounds. The two major PBDE congeners in Bromkal 70-5 DE have previously been identified as BDE-47 and 2,2',4,4',5-pentaBDE (BDE-99)[17]. However, several other minor PBDE congeners are present in the mixture. The aim of the present study was to identify individual PBDE congeners in Bromkal 70-5 DE. The study was performed by comparison of the gas chromatographic retention times of the components in the commercial product with those of pure PBDE congeners.

Experimental Methods

Chemicals

The commercial product analysed was Bromkal® 70-5 DE (Chemische Fabrik Kalk GmbH, Germany). The individual PBDEs (listed in Table 3) have been synthesized by bromination of diphenyl ether, or by coupling of a bromophenolate and a bromoiodonium salt as described elsewhere[18-20]. Dechlorane® 603 (Hooker Chemical Corp.) was used as retention time reference standard. All standard solutions were prepared in isooctane (analytical grade, Merck).

Instruments

Gas chromatography (GC) was performed on a Hewlett Packard 5890 and a Fisons 8000 series instrument equipped with split-splitless injectors and electron capture detectors. Helium (99.995%) was used as the carrier gas and argon/methane as makeup-gas. GC columns and settings are given in Table 1 and 2. Data were collected and processed with a PC based Ezy Chrom v6.6 data system.

Table 1. Gas chromatography column characteristics

Column (manufacturer)	Stationary phase	Dimension (length x I.D.)	Film thickness	Character
CPSil-8 (Chrompac)	5% phenyl-95% dimethylsilicone	50 m x 0.25 mm	0.25 µm	low-polar
HP-1701 (Hewlett Packard)	14% cyano-propylphenyl-86% dimethyl-siloxane copolymer	60 m x 0.25 mm	0.25 µm	medium-polar
SP-2380 (Supelco)	90%-biscyanopropyl-10%-cyanopropylphenyl siloxane	30 m x 0.32 mm	0.20 µm	polar
SB-Smectic (Lee Scientific)	biphenylcarboxylate ester methylpolysiloxane	25 m x 0.32 mm	0.15 µm	medium-polar, structural interactions

Table 2. Instrument parameters used for the GC analyses.

Column	Injector/detector temp (°C)	Injector pressure (kPa)	Temperature program (temp,°C(time, min);rate,°C/min)
CPSil-8	270/325	175	80(2);10-210;3-290(30);3-310(10)
HP-1701	270/325	230	80(2);10-210;3-290(40)
SP-2380	270/325	100	80(2);10-200;3-250(40)
SB-Smectic	270/325	100	80(2);10-180;2-250(30)

Methodological development

The GC parameters were optimized for each column using a solution of Bromkal 70-5 DE (0.4-10 ng/µl), cf. Table 2. The individual PBDE standards (100 pg/µl) were analysed with Dechlorane (260 pg/µl) present as retention time reference and the relative retention times of the PBDEs vs Dechlorane were calculated, cf. Table 3. All PBDE congeners with relative retention times similar to peaks in Bromkal 70-5 DE were added to two solutions of Bromkal 70-5 DE (1 and 10 ng/µl) at levels estimated to be ca. 1.5-3 times the concentration of the compound in Bromkal 70-5 DE. The two solutions were then analysed on the four GC columns and peak shapes were examined for deformities to verify the identification

Results and Discussion

The commercial PBDE product Bromkal 70-5 DE was analysed on four GC columns with low, medium and polar stationary phase, cf. Table 1. One of the columns, SB-Smectic, has a stationary phase that exhibit structural interactions with the analyte. Thirty-one individual PBDE congeners were analysed on the four columns and relative retention times vs Dechlorane were calculated, cf. Table 3. The PBDE present in Bromkal 70-5 DE could then be tentitatively identified and were added to a solution of Bromkal 70-5 DE to verify that the identifications were correct. A few PBDE congeners (BDE-12/-13, BDE-17/-25, and PBDE-51/-71) were found to have similar retention properties, but all PBDEs could be resolved on at least one of the GC columns.

Bromkal 70-5 DE was found to consist of mainly one tetraBDE, three pentaBDE and two hexaBDE, cf. Figure 1. The main tetraBDE and the main pentaBDE have previously been identified as 2,2',4,4'-tetraBDE (BDE-47) and 2,2',4,4',5-pentaBDE (BDE-99), respectively[17]. The two remaining pentaBDE were identified in the present study as 2,2',4,4',6-pentaBDE (BDE-85) and 2,2',3,4,4'-pentaBDE (BDE-100) and the two hexaBDE as 2,2',4,4',5,6'-hexaBDE (BDE-154) and 2,2',4,4',5,5'-hexaBDE (BDE-153). In addition to these, two triBDE, one tetraBDE, one hexaBDE and one heptaBDE were identified, cf. Table 3 and Figure 1. The relative retention times of all the individual PBDE congeners analysed are given in Table 3. Compounds found to be present in Bromkal 70-5 DE are given in bold in Table 3 and with their IUPAC numbers[21] in Figure 1.

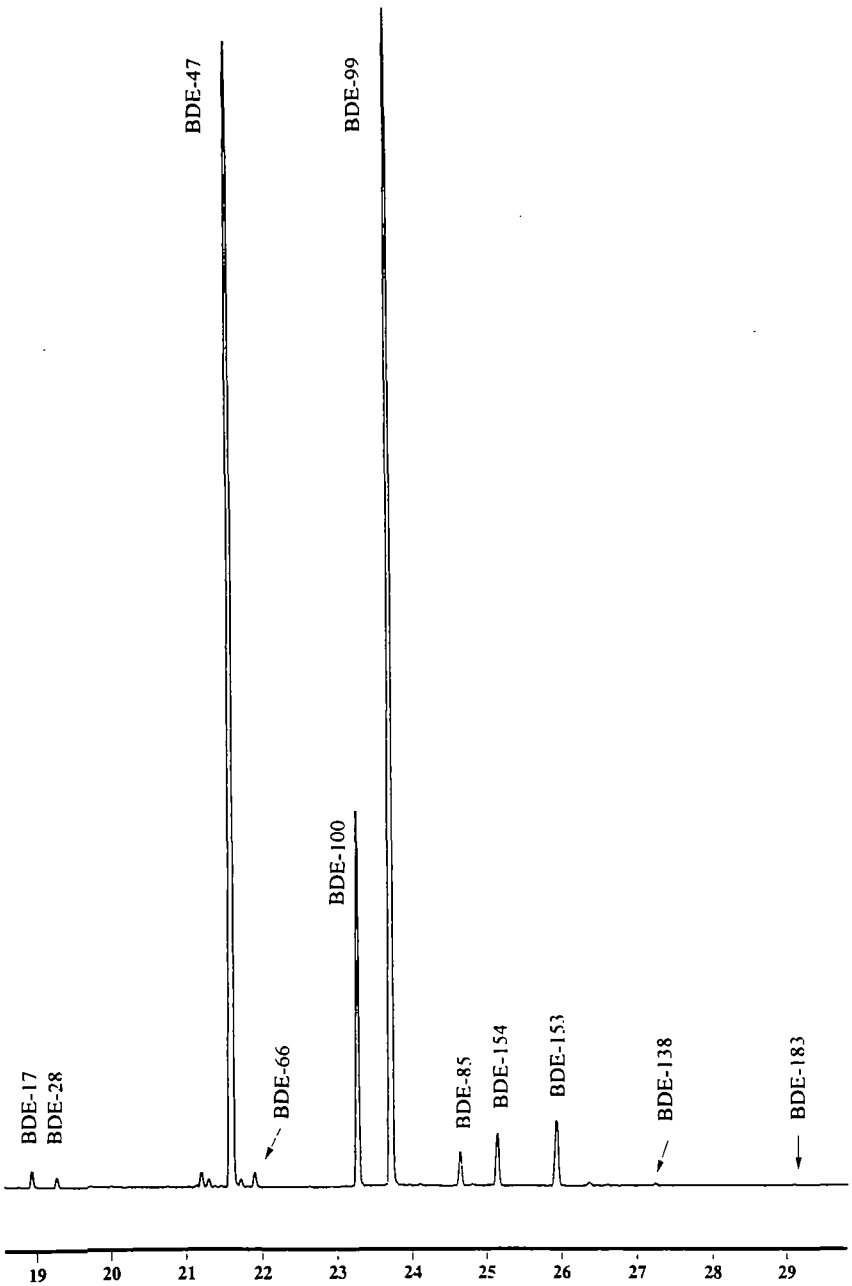

Figure 1. GC chromatogram of Bromkal 70-5 DE. Compounds identified are indicated with their IUPAC numbers[21], cf. Table 3.

Table 3. PBDE congeners analysed and their relative retention times (RRT) vs Dechlorane. Compounds present in Bromkal 70-5 DE are indicated in bold.

IUPAC No.	Structure	CPSil-8 (RRT)	HP1701 (RRT)	SP-2380 (RRT)	SB-Smectic (RRT)
7	2,4	0.400	0.385	0.474	0.437
8	2,4'	0.411	0.400	0.505	0.460
12	3,4	0.415	0.400	0.494	0.420
13	3,4'	0.415	0.402	0.500	0.477
15	4,4	0.424	0.412	0.530	0.530
17	**2,2',4**	**0.506**	**0.496**	**0.629**	**0.598**
25	2,3',4	0.506	0.493	0.616	0.597
28	**2,4,4'**	**0.519**	**0.508**	**0.651**	**0.663**
30	2,4,6	0.468	0.447	0.529	0.494
32	2,4',6	0.496	0.487	0.609	0.567
33	2',3,4	0.520	0.510	0.642	0.622
35	3,3',4	0.528	0.516	0.650	0.655
37	3,4,4'	0.540	0.529	0.677	0.765
47	**2,2',4,4'**	**0.627**	**0.612**	**0.797**	**0.882**
51	2,2',4,6'	0.605	0.594	0.766	0.785
66	**2,3',4,4'**	**0.641**	**0.628**	**0.838**	**0.941**
71	2,3',4',6	0.614	0.602	0.767	0.792
75	2,4,4',6	0.600	0.580	0.723	0.748
77	3,3',4,4'	0.667	0.654	0.886	1.076
85	**2,2',3,4,4'**	**0.787**	**0.794**	**1.128**	**1.407**
99	**2,2',4,4',5**	**0.735**	**0.720**	**0.953**	**1.109**
100	**2,2',4,4',6**	**0.711**	**0.690**	**0.884**	**1.023**
116	2,3,4,5,6	0.750	0.732	0.976	1.161
119	2,3',4,4',6	0.719	0.699	0.897	1.048
128	2,2',3,3',4,4'	1.046	1.148	*	2.150
138	**2,2',3,4,4',5'**	**0.944**	**0.986**	**1.494**	**1.646**
153	**2,2',4,4',5,5'**	**0.864**	**0.869**	**1.182**	**1.354**
154	**2,2',4,4',5,6'**	**0.816**		**1.011**	**1.210**
166	2,3,4,4',5,6	0.954	0.985	*	1.659
183	**2,2',3,4,4',5',6**	**1.061**	**1.107**	**1.546**	**1.673**
190	2,3,3',4,4',5,6	1.232	*	*	2.215

* The compound did not elute within the time of the GC program used.

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