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## Gas chromatographic identification and quantification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE

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### Abstract

Thirty-one brominated diphenyl ether (BDE) standards have been used for identification and quantification of unknown congeners in the technical flame-retardant, Bromkal 70-5DE, using relative retention versus dechlorane and standard additions on four different high-resolution gas chromatography capillary columns with low-polar to very polar properties. Nine new BDE congeners were identified. Eight of these were also quantified as mass percent of the product: 2,2',4,4',6-pentaBDE (6.8%), 2,2',4,4',5,5'-hexaBDE (3.9%), 2,2',4,4',5,6'-hexaBDE (2.5%), 2,2',3,4,4'-pentaBDE (1.6%), 2,2',3,4,4',5'-hexaBDE (0.41%), 2,3',4,4'-tetraBDE (0.22%), 2,4,4'-triBDE (0.11%) and 2,2',4-triBDE (0.022%). The ninth congener was 2,2',3,4,4',5',6-heptaBDE. The two previously identified BDE congeners in Bromkal 70-5DE, 2,2',4,4'-tetraBDE and 2,2',4,4',5-pentaBDE constituted 35% and 37%, respectively, in this batch. © 1998 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are used as additive flame-retardants at levels ranging from 5–30% in polymers and textiles, in such applications as printed circuit boards, computer covers and housings of electrical appliances and carpets [1]. There are three main types of commercial PBDE products with varying degrees of bromination, i.e., “penta-bromodiphenyl ether”, “octabromodiphenyl ether” and “decabromodiphenyl ether”. The annual world consumption of PBDEs has been estimated to 40 000

metric tonnes, of which 75% was “decaBDE”, 15% was “octaBDE” and 10% was “pentaBDE” [2]. PBDEs are industrially produced under catalytic conditions from diphenyl ether and bromine [3], which results in mixtures of BDE isomers and homologues.

The higher brominated diphenyl ethers (with  $\geq 4$  bromine substituents) are highly hydrophobic compounds with low volatility, high molecular masses and they may be characterised as persistent substances. It is thus not surprising that the PBDEs have become ubiquitous environmental contaminants. In 1981, tri- to hexabrominated diphenyl ethers (triBDE–hexaBDEs) were found in fish samples from

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different places along the Swedish River Viskan, where textile industries are located. In fish caught at the same places in 1977, no PBDEs were found, which indicated that these were fairly new pollutants [4]. Due to the lack of pure reference standards, quantification was made using the technical product Bromkal 70-5DE (BK70) and only three congeners could be quantified: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47<sup>1</sup>), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) and 2,2',4,4',6-pentabromodiphenyl ether (BDE-100) (BDE-100 identified in this work). The concentrations of these congeners in fish were high (up to ppm levels on a lipid mass base) and this was confirmed in a later investigation in 1987 where fish caught from about the same locations were analysed [6].

The first finding of PBDEs in samples from remote areas was in 1987, when PBDEs in fish consumers; species such as harbour seal, guillemot and white-tailed sea eagle from the Baltic Sea, the North Sea and the Arctic Ocean were reported [7]. This indicated a world-wide distribution and this has been confirmed by other investigations. PBDEs have since been found in wildlife species from marine, freshwater and terrestrial environments in Sweden and the Arctic Ocean [6,8,9], in Japan [10–12], the Netherlands and the North Sea [13] and in North America [14–16]. PBDEs have also been found in sediment [10–12,17,18] and airborne dust [12].

The concentrations of BDE-47, BDE-99 and BDE-100 in guillemot eggs have increased since the 1970s [6,19]. However during the last decade the trend is more uncertain due to the large between-year variation. Several BDE congeners have been found in human plasma [20] and mothers' milk [21,22]. HexaBDE to decaBDE have been detected in human adipose tissue [23,24]. PBDEs have also been found adsorbed to indoor particles (dust) in modern offices [25].

Until recently, quantitative work has been performed by using technical PBDE products i.e.. BK70, due to the lack of pure reference standards for most BDE congeners. The structures of the major two components in BK70 have previously been identified as BDE-47 and BDE-99, after these two

components were isolated from BK70 and analysed by <sup>1</sup>H nuclear magnetic resonance (NMR) [26]. Since more than 30 BDE congeners now are available it has become possible to analyse for additional BDEs. The aim of the present work has been to identify and quantify as many BDE congeners as possible in BK70. In this way, it will be possible to retrospectively determine abundance and levels of these "new" BDE congeners in previously analysed samples.

## 2. Experimental

### 2.1. Chemicals

The commercial PBDE product, Bromkal 70-5DE was from Chemische Fabrik Kalk (Köln, Germany). Thirty-one PBDE congeners (Table 3) were used as reference compounds in the present study. The methods used for syntheses are described elsewhere [27–29]. Dechlorane 603 (Hooker Chemical, Niagara Falls, NY, USA, today Occidental Chemical, Dallas, TX, USA) was used as a retention time reference and internal standard. Gas chromatography (GC) standards were prepared in glass-distilled 2,2,4-trimethylpentane from Merck, (Darmstadt, Germany).

### 2.2. Instruments

GC was performed using Hewlett-Packard 5890 and Fisons GC 8000 series gas chromatographs. Each instrument was equipped with a split-splitless injector and an electron-capture detector (ECD). Helium (99.995%) was used as carrier gas and a mixture of argon and 10% methane was used as make-up gas. Four different GC columns were used. The column types, manufacturers, stationary phases, dimensions and polarities are given in Table 1. Temperature programs and GC settings are given in Table 2. Data were collected and processed using the data system EZChrom v6.6 (Nordlab, Gothenburg, Sweden).

GC-mass spectrometry (MS) was performed using a Carlo Erba MEGA MFC 500 gas chromatograph connected to a VG Trio-1000 mass spectrometer. Helium (99.995%) was used as carrier gas. The

<sup>1</sup>In this study the PBDEs been given numbers according to the numbering system of PCBs in Ref. [5].

Table 1  
Characteristics of the different GC high-resolution capillary columns used for separation of 31 BDE congeners

Instrument	Column	Manufacturer	Stationary phase	Dimensions (length×I.D.)	Film thickness (µm)	Characteristics
GC–ECD	CPSil-8	Chrompack	(5%)-Phenyldimethylsilicone	50 m×0.25 mm	0.25	Low-polar
GC–ECD	HP-1701	Hewlett-Packard	(14%)-Cyanopropylphenyl-dimethylsiloxane copolymer	60 m×0.25 mm	0.25	Medium polar
GC–ECD	SP-2380	Supelco	(90%)-Biscyanopropyl-cyanopropylphenylsiloxane	30 m×0.32 mm	0.20	Very polar
GC–ECD	SB-Smectic	Lee Scientific	Biphenylcarboxylate ester-methylpolysiloxane	25 m×0.32 mm	0.15	Medium polar/ structural interactions
GC–MS	DB-5MS	J&W Scientific	(5%)-Phenylmethyl-polysiloxane	15 m×0.32 mm	0.25	Low-polar

PBDEs were analysed using the negative ions formed by electron-capture reactions at chemical ionisation (ECNI). Selected ion monitoring (SIM) was used monitoring  $m/z$  79 and 81 for PBDE and  $m/z$  237 and 239 for the internal standard (dechlorane). The ion source temperature was 200°C and the electron energy was 70 eV. Ammonia (99.998%) was used as the reagent gas.

### 2.3. Identification of PBDEs in BK70

The GC parameters were optimised for each column using solutions of BK70 (0.4 and 10 ng/µl). When a satisfactory separation was achieved, the individual BDE standards were analysed (100 pg/µl) with dechlorane (260 pg/µl) present as a retention time reference. The relative retention times (RRTs) on four GC columns were used for identification of unknown BDE congeners. A difference in RRT between each reference standard and the corresponding BK70 component of ±0.001 was accepted for positive identification on CPSil-8 and HP1701 columns and a difference of ±0.015 was accepted on

SP-2380 and SB-Smectic, due to the higher retention time variability, i.e., broader and tailing peaks, with these types of GC columns.

In order to certify the identification, standard additions of the BDEs tentatively identified to be present in BK70 were made. The addition levels were estimated to about 1.5–3-times the amounts in BK70. These solutions were then analysed on all four GC columns and peak shapes were examined for deformities.

### 2.4. Quantification of BDEs in BK70

The concentration range of the BDEs identified in BK70 is large. Therefore, different concentrations of this product were analysed (10, 25, 50, 100, 400 pg/µl) by GC–MS (ECNI) as described above. It is notable that the bromide ions  $m/z$  79 and 81 are so dominating that no other ions can be used for the quantification of PBDEs in the product. Standard solutions of the identified BDEs were prepared at seven levels each and the BDEs in BK70 were quantified against the obtained calibration curves. All

Table 2  
Conditions for the GC separation of BDE congeners

Instrument	Column name	Injector/detector temperature (°C)	Injector pressure (kPa)	Temperature program °C (min)–°C/min–°C (min)	Splitless time (min)
GC–ECD	CPSil-8	270/325	175	80 (2)–10–210–3–290 (30)–3–310 (10)	2
GC–ECD	HP-1701	270/325	230 <sup>a</sup>	80 (2)–10–210–3–290 (40)	2
GC–ECD	SP-2380	270/325	100	80 (2)–10–200–3–250 (40)	2
GC–ECD	SB-Smectic	270/325	100	80 (2)–10–180–2–250 (30)	2
GC–MS	DB-5MS	270	50	80 (2)–12–140–5–280	1.5

<sup>a</sup> Two columns in injector.

solutions (both BK70 and the reference standards) were analysed 2–5 times each. The final quantitative determination of the single BDE congeners was based on the mean values of 4–19 analyses of BK70 (Table 4). The number of analyses was dependent on the concentrations of the single BDE congeners in BK70. For instance, the minor constituents in BK70 were only possible to quantify in the BK70 solutions with the highest concentrations.

### 3. Results and discussion

The BDE congeners present in BK70 were identified by their RRTs vs. dechlorane on four different columns together with results of the standard additions. The RRTs of the 31 analysed BDE congeners are presented in Table 3. The GC columns were chosen to have different polarities or to exhibit interactions related to solute geometry (Table 1). The

Table 3  
BDE congeners analysed and their relative retention times (RRTs) vs. Dechlorane 603

BDE No.	No. of Br	Structure	RRT				Ref. <sup>a</sup>
			CPSil-8	HP-1701	SP-2380	SB-Smectic	
7	2	2,4	0.400	0.385	0.474	0.437	[29]
8	2	2,4'	0.411	0.400	0.505	0.460	[29]
12	2	3,4	0.415	0.400	0.494	0.420	[29]
13	2	3,4'	0.415	0.402	0.500	0.477	[29]
15	2	4,4'	0.424	0.412	0.530	0.530	[29]
<b>17</b>	<b>3</b>	<b>2,2',4</b>	<b>0.506</b>	<b>0.496</b>	<b>0.629<sup>b</sup></b>	<b>0.598<sup>b</sup></b>	[29]
25	3	2,3',4	0.506	0.493	0.616	0.597	[29]
<b>28</b>	<b>3</b>	<b>2,4,4'</b>	<b>0.519</b>	<b>0.508</b>	<b>0.651</b>	<b>0.663</b>	[29]
30	3	2,4,6	0.468	0.447	0.529	0.494	[29]
32	3	2,4',6	0.496	0.487	0.609	0.567	[29]
33	3	2',3,4	0.520	0.510	0.642	0.622	[29]
35	3	3,3',4	0.528	0.516	0.650	0.655	[29]
37	3	3,4,4'	0.540	0.529	0.677	0.765	[29]
<b>47</b>	<b>4</b>	<b>2,2',4,4'</b>	<b>0.627</b>	<b>0.612</b>	<b>0.797</b>	<b>0.882</b>	[27–29]
51	4	2,2',4,6'	0.605	0.594	0.766	0.785	[29]
<b>66</b>	<b>4</b>	<b>2,3',4,4'</b>	<b>0.641</b>	<b>0.628</b>	<b>0.838</b>	<b>0.941</b>	[29]
71	4	2,3',4',6	0.614	0.602	0.767	0.792	[29]
75	4	2,4,4',6	0.600	0.580	0.723	0.748	[29]
77	4	3,3',4,4'	0.667	0.654	0.886	1.076	[29]
<b>85</b>	<b>5</b>	<b>2,2',3,4,4'</b>	<b>0.787</b>	<b>0.794</b>	<b>1.128</b>	<b>1.407</b>	[27]
<b>99</b>	<b>5</b>	<b>2,2',4,4',5</b>	<b>0.735</b>	<b>0.720</b>	<b>0.953</b>	<b>1.109</b>	[27]
<b>100</b>	<b>5</b>	<b>2,2',4,4',6</b>	<b>0.711</b>	<b>0.690</b>	<b>0.884</b>	<b>1.023</b>	[29]
116	5	2,3,4,5,6	0.750	0.732	0.976	1.161	[29]
119	5	2,3',4,4',6	0.719	0.699	0.897	1.048	[29]
128	6	2,2',3,3',4,4'	1.046	1.148	<sup>c</sup>	2.150	[27]
<b>138</b>	<b>6</b>	<b>2,2',3,4,4',5'</b>	<b>0.944</b>	<b>0.986</b>	<b>1.494</b>	<b>1.646</b>	[27]
<b>153</b>	<b>6</b>	<b>2,2',4,4',5,5'</b>	<b>0.864</b>	<b>0.869</b>	<b>1.182</b>	<b>1.354</b>	[27]
<b>154</b>	<b>6</b>	<b>2,2',4,4',5,6'</b>	<b>0.816</b>	<sup>d</sup>	<b>1.011</b>	<b>1.210</b>	[29]
166	6	2,3,4,4',5,6	0.954	0.985	<sup>c</sup>	1.659	[29]
<b>183</b>	<b>7</b>	<b>2,2',3,4,4',5',6</b>	<b>1.061</b>	<b>1.107</b>	<b>1.546</b>	<b>1.673</b>	[29]
190	7	2,3,3',4,4',5,6	1.232	<sup>c</sup>	<sup>c</sup>	2.215	[29]

Compounds present in Bromkal 70-5DE are given in bold.

<sup>a</sup> Literature reference for synthesis.

<sup>b</sup> Concentration in BK70 is too low to calculate a relative retention time.

<sup>c</sup> Did not elute within GC program used (temperature limit of the column).

<sup>d</sup> Missing value.

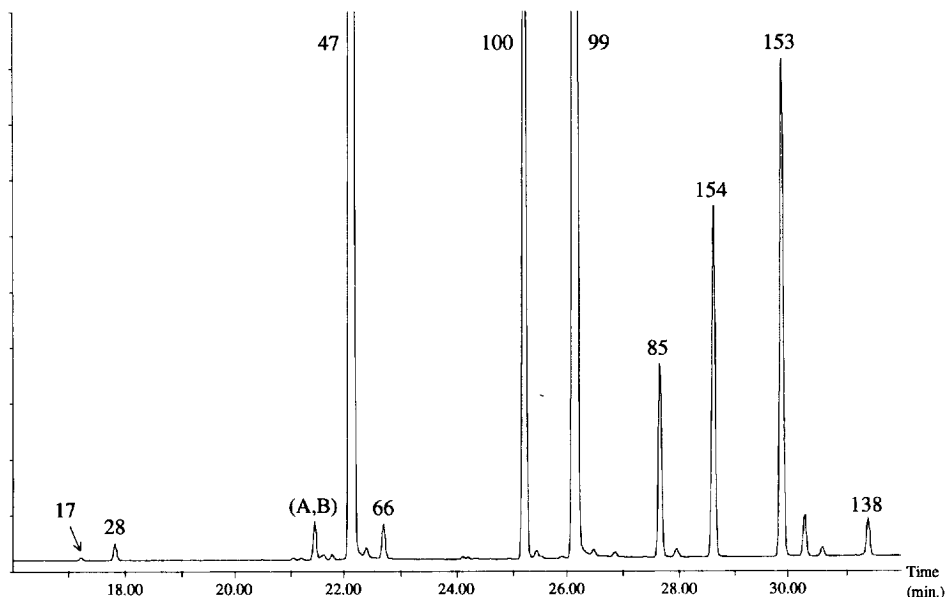


Fig. 1. GC-MS (ECNI) ( $m/z$  79, 81) chromatogram of Bromkal 70-5DE using a DB-5MS column. Identified substances are marked with their BDE numbers [5]. Peak (A, B) could be separated into two peaks on a HP-1701 GC capillary column.

BDE congeners identified as constituents of BK70 are presented in bold in Table 3 and are indicated in the mass chromatogram of BK70 shown in Fig. 1. The two major constituents were, as previously reported, BDE-47 and BDE-99 [26]. Additionally, nine BDE congeners were identified. Peak (A, B) in Fig. 1. could be separated into two peaks only by the HP1701 column. No other coeluting peaks were observed in BK70.

The BDEs identified in BK70 were quantified by GC-MS. The results are given in Table 4 as mass percentage of the product. The two major components, BDE-47 and BDE-99, were found to make up 37% and 35%, respectively. Two more penta-BDEs were quantitatively important; BDE-100 (6.8%) and BDE-85 (1.6%). BDE-153 and BDE-154 contribute with an additional 3.9% and 2.5%, respectively. In addition to these, two triBDEs (BDE-17 and BDE-28), one tetraBDE (BDE-66), one hexa-BDE (BDE-138) and one heptaBDE (BDE-183) were identified (Tables 3 and 4). Together these congeners make up less than 1% of the total BDEs in BK70. The sum of all identified BDE congeners

represent 88% (w/w) of the technical BK70 product. Some of the additional material is brominated compounds. Trace amounts of other brominated substances were detected by GC-MS but their RRTs did not match any of the BDE congeners available. These unidentified brominated compounds most probably do not explain the missing 12%.

The three major peaks in BK70 (BDE-47, BDE-100 and BDE-99) have earlier been found to constitute 41%, 7% and 45%, respectively [26]. In this investigation the corresponding percentages were 37%, 6.8% and 35%. Similar results were reported by de Boer, who found 36% for BDE-47 and 35% for BDE-99 [30]. The discrepancies between the first reported results compared to the present results could be due to differences between batches of BK70.

Among the BDE congeners identified in BK70 several of these compounds can be retrieved in environmental samples. Thus, the dominating tetra-BDE in biota is in general BDE-47 but also BDE-99 and BDE-100, two pentabrominated diphenyl ethers are present in the samples, e.g., in human blood [20] and in marine wildlife [31]. Also the minor PBDE

Table 4

Concentrations (% w/w) of BDE congeners found to be present in Bromkal 70-5DE

BDE No.	Structure	Concentration (%, w/w)	R.S.D. (%)	No. of analyses
47	2,2',4,4'-tetraBDE	37	5.1	16
99	2,2',4,4',5-pentaBDE	35	4.7	15
100	2,2',4,4',6-pentaBDE	6.8	4.6	15
153	2,2',4,4',5,5'-hexaBDE	3.9	5.9	15
154	2,2',4,4',5,6'-hexaBDE	2.5	4.6	19
85	2,2',3,4,4'-pentaBDE	1.6	5.3	16
138	2,2',3,4,4',5'-hexaBDE	0.41	11	13
66	2,3',4,4'-tetraBDE	0.22	5.9	13
28	2,4,4'-triBDE	0.11	6.9	7
17	2,2',4-triBDE	0.022	11	4
183 <sup>a</sup>	2,2',3,4,4',5',6-heptaBDE	n.d.	n.d.	n.d.
Total BDE		88		

The concentrations are given as mean values together with relative standard deviations (R.S.D.s) and the number of analyses. n.d.=Not determined.

<sup>a</sup> The reference standard was not pure enough for quantification purposes.

constituent in BK70, BDE-183, has recently been detected in ambient air, human blood (unpublished) and in fish [32]. The identifications that have been made in the present work will serve as a basis for future in depth studies on the exposure to PBDEs in humans as well as in wildlife and fish.

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