

Identification of Minor Components in a DE-71™ Technical Penta-BDE Mix Using ¹H-NMR and GC/MS

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Introduction

Brominated diphenyl ethers (BDEs) are found in various technical mixtures which are used as brominated flame retardants (BFR). The technical pentaBDE products are complex mixtures containing various BDEs ranging mainly from tribrominated to heptabrominated congeners.

The identification of some lower brominated BDEs in environmental samples has aroused interest because they are persistent, bioaccumulate, and there is concern about their potential health hazard. It is therefore important to know which isomers are present in these technical BDE mixtures.

The two major BDEs in one of the technical pentaBDE-mixes, Bromkal 70-5 DE™, were identified as BDE-47 and BDE-99 by using column chromatography and NMR spectroscopy¹. Many other BDE isomers in a pentaBDE-mix were later characterized by using retention time comparisons versus authentic standards². However, there is evidence that several BDEs co-elute on a DB-5 type GC column³, thereby preventing unequivocal assignment of structure using this technique alone. There are also other minor BDEs in penta-BDE mixes that have yet to be identified.

The objective of this work was to confirm the structures of the known BDEs present in Great Lakes DE-71™, to identify other unknown BDEs present and to quantify the components using ¹H-NMR spectroscopy and GC/MS.

Materials and Methods

The BDE reference standards were available in-house. Preparative thin layer chromatography was carried out on DE-71™ using glass plates (20 x 20 cm) spread with Kieselgel G (Merck) silica. The eluting solvent was hexane. Fractions are numbered in order of increasing R_f . Approximately 1.6 mg of DE-71™ was applied per gram of silica.

High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS) Experiments were conducted on a Shimadzu GC/MS-QP2010 using a J&W 30m DB-5 (0.25 mm ID, 0.25 μm film). All injections were done in splitless mode. All experiments were done with the following GC conditions: helium carrier gas flow at 1.0 ml/minute, injector temperature at 250°C, temperature program set to the following parameters: initial oven temperature at 100°C, hold for 5 minutes, ramp at 10°C/minute to 325°C, hold for 40 minutes. A full scan range of 50 to 1000 amu was used in positive ion electron impact mode (EI+).

High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Experiments. DE-71™ was combined with mass-labeled ¹³C₁₂-brominated diphenyl ethers to enable quantitative determination of the various BDEs using HRGC/HRMS and isotopic dilution. Analyses were performed on an Agilent 6890N HRGC coupled to a Waters AutospecUltima HRMS. Separations were conducted on a J&W 30 m DB-5HT (0.25 mm ID, 0.1 μm film) column. The injections were done in splitless mode, with the injector temperature at 250°C, and the helium carrier gas flow constant at 1.0 ml/min. The GC oven was temperature programmed as follows: 100°C (2 min), 10°C/min to 260°C, 1.5°C/min to 300°C, **10°C/min to 316°C, 316°C (5 min)**. The source and transfer line were maintained at 250°C. The mass spectrometer was operated at a resolution of 10,000 in EI+ mode. A 1:1 v/v

mixture of perfluorokerosene-H and 2,4,6-tris(perfluoroheptyl)-1,3,5-triazine was used as an MS calibrant.

Proton NMR analyses were performed on either a 400 MHz or 600 MHz Bruker instrument using dichloromethane- d_2 as a solvent. NMR solvents were purchased from CDN Isotopes.

Results and Discussion

DE-71TM is too complicated a mixture to permit identification of most of the minor BDEs present by ¹H-NMR spectroscopy of the mixture itself. For a more in depth analysis, and identification of minor BDE congeners in the mixture, preparative TLC was used to separate it into six fractions. The total weight recovery of the BDEs after preparative TLC was better than 99%. These isolated fractions were much less complex than the initial mixture, as evidenced by GC/LRMS (see figure 1). This allowed the use of NMR spectroscopy to confirm the structure of many BDEs. The results are summarized in Tables 1 and 2.

Table 1: BDE congeners identified in the various fractions obtained from DE-71TM

Fraction # (a)	Wt%	BDE	
		(b)	(c)
1 (d)	3.5	17/42/47/48/51/85/91/99/102/138	
2	28.7	47/49/99	28/66/85/138
3	49.8	47/99/100/153	66
4 (d)	17.2	99/100/139/153/154	66
5	0.1	100/119/154/155	183
6	0.3	155	183
TOTAL	99.6%		

(a) See figure 1 for the individual GC chromatograms of the six fractions

(b) BDEs identified by GC/LRMS and ¹H-NMR spectroscopy

(c) BDEs identified by GC/LRMS by co-injection with authentic BDE samples

(d) These two fractions were rechromatographed to further simplify the complexity of the BDE isomers present and to permit useful analysis by NMR spectroscopy

Table 2: Weight percentage of the individual BDEs determined in DE-71TM by ¹H-NMR spectroscopy and GC/MS

BDE	Wt % by NMR & GC/LRMS	Wt % by GC/HRMS	Previous work ²	BDE	Wt % by NMR & GC/LRMS	Wt % by GC/HRMS	Previous work ²
			(a)				(a)
183	0.02	0.08	n.r.	99	42.5	44.3	35
156	n.d.	0.06	n.r.	91	0.07	0.11	n.r.
155	0.32	0.39	n.r.	85	3.18	2.50	1.6
154	3.00	3.25	2.5	66	1.02	0.75 (b)	0.22 (b)
153	3.75	3.77	3.9	51	0.02	0.19	n.r.
140	n.d.	0.20	n.r.	49	0.77	0.86	n.r.
139	0.16	0.71	n.r.	48	0.05	0.11	n.r.
138	0.24	0.56	0.41	47	33.00	31.68	37
119	0.002	0.11	n.r.	42	0.02	<0.1	n.r.
102	0.13	0.25	n.r.	28	0.37	0.28	0.11
100	10.90	9.41	6.8	17	0.04	0.09	0.022

TOTAL		99.5%	99.7	87.6
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(a) n.d. = not detected; n.r. = not reported

(b) Signal intensity attributed to BDE-66 only: a small amount of a co-eluant is present

Summary

The structures of all previously known penta-BDE components were confirmed by GC-MS and NMR spectroscopy. Nine new BDE isomers were identified in DE-71TM, the tetra-BDEs 42, 48, 51, and 91, and the penta-BDEs 102, 119, 139, 140, and 155. Eight of these structures were confirmed by ¹H-NMR spectroscopy. NMR spectroscopic evidence was also valuable in reaching the following conclusions:

- The GC signal attributed to BDE-66 actually contains a small amount of a co-eluant, BDE-42. (BDE-42 and -66 are known to co-elute³)
- NMR spectroscopy confirmed that BDE-48, and not BDE-71, is responsible for a GC signal found in fraction #1. (BDE-48 and -71 are known to co-elute³)
- The GC signal assigned to BDE-28 may actually be due to BDE-16 or -33. (BDE-16, -28 and -33 are known to co-elute³).

Quantification of the BDEs in DE-71TM by either NMR or HRGC/HRMS gave similar values. These data are in close agreement with the previously published data² on the quantification of the BDEs in Bromkal 70-5 DETM.

References

1. G. Sundström and O. Hutzinger. 1976. Chemosphere, 3, 187-190.
2. A.Sjodin, E.Jakobson, A.Kierkegaard, G.Marsh and U.Sellstrom. 1998. J. Chromatography A, 822, 83-89.
3. R.P.Kozloski, A.Gelbin and R.Cooper. 2004. Third International Workshop on Brominated Flame Retardants, 359-361.

Figure 1: GC/LRMS chromatographs of technical grade DE-71TM and the six fractions obtained after chromatography