

Identification of the Minor Components of DE-79™ Technical Mix by Means of ¹H NMR and GC-MS.

Konstantinov A^a, Arsenault G^a, Chittim B^a, McAlees A^a, McCrindle R^b, Potter D^a, Tashiro C^a and Yeo B^a.

^a Wellington Laboratories Inc., Research Division, Guelph, Ontario, Ontario, N1G 3M5, Canada

^b Chemistry Dept., University of Guelph, Guelph, Ontario, N1G 2W1, Canada

* corresponding author. Tel.: +1 519 822 2436; fax: +1 519 822 2849

E-mail address: alex@well-labs.com (A.Konstantinov)

1. Introduction

Brominated diphenyl ethers (BDEs) have been used as brominated flame retardants (BFRs) for many years in a variety of commercial products. The technical octa-BDE products are complex mixtures containing various BDEs ranging mainly from pentabrominated to nonabrominated congeners.

The identification of some BDEs in environmental samples has aroused interest because they are persistent, bioaccumulate, and there is concern about their potential health hazard. These BDEs may be coming directly from use of the technical mixtures. It is therefore important to know the identities of the congeners present in these mixtures.

Four studies¹⁻⁴ have been completed aimed at identifying the major BDEs in the technical octaBDE-mixes, DE-79™. The identification of the BDEs was achieved by either using retention time comparisons versus authentic standards^{1,2}, NMR characterization of the major BDE congeners present in the mixture^{3,4}, and/or assignment based on molecular ion and fragmentation information¹. However, unequivocal assignment of structure using GC/MS techniques alone is not possible because some BDE congeners may co-elute.

The objective of this work was to confirm the structures of the known BDEs present in DE-79™ by ¹H-NMR spectroscopy, to identify other unknown BDEs using HRGC/LRMS and to quantify the components using ¹H-NMR spectroscopy and HRGC/HRMS.

2. Materials and Methods

2.1 Separation

Preparative thin layer chromatography was carried out on DE-79™ (Great Lakes) 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 0.5 mg of DE-79™ was applied per gram of silica.

2.2 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 column (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+).

2.3 High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

DE-79TM 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 Autospec Ultima 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 315°C, 315°C (4 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.

2.4 ¹H-NMR Experiments

¹H-NMR analyses were performed on either a 400 MHz or 600 MHz Bruker instrument using dichloromethane-*d*₂ (CDN Isotopes) as a solvent. The pulse delay was set to 6 seconds.

3. Results and Discussion

DE-79TM is too complicated a mixture to permit identification of most of the minor BDEs present directly by ¹H-NMR spectroscopy. For a more in depth analysis, and identification of the minor BDE congeners in the mixture, preparative TLC was used to separate the DE-79TM technical mixture into four fractions. The total weight recovery of the BDEs after preparative TLC was better than 99% (see Table 1). These isolated fractions were much less complex than the initial commercial mixture, as evidenced by HRGC/LRMS (see Figure 1).

Of the 28 BDE congeners observed by HRGC/HRMS (see Table 2)² in the technical mixture, 23 were identified by comparison with authentic samples and the structures of 17 of them (see Table 1) were confirmed by ¹H-NMR spectroscopy. BDE-128 and -149 are two new BDEs not previously identified in DE-79TM. Other resonances in the NMR spectrum due to further unknown BDE congeners were observed, but structures could not be unequivocally assigned. Work is proceeding to identify these minor unknown BDEs detected by both HRGC/HRMS and ¹H-NMR spectroscopy.

The BDE congeners in DE-79TM were also quantified using isotopic dilution and HRGC/HRMS analysis. DE-79TM was combined with MBDE-MXE (¹³C₁₂-BDE surrogate mixture) and BDE-CVS-E-ISS (¹³C₁₂-BDE-138 injection standard) and analyzed using HRGC/HRMS. The combined mixture was injected in triplicate and quantitated using a five point calibration curve (BDE-CVS-E). The results are shown in Table 2 and compare relatively well with the values calculated from the NMR spectroscopy experiments.

Table 1: BDE congeners identified in the various fractions obtained from DE-79TM

Fraction # (a)	Wt%	BDE (b)
1	0.7	138,149,171,191,197,207
2 (c)	7.0	128,149,138,140,153,171,180,183,191,196,197,206,207
3	73.7	138,153,154,180,183,196,197,203
4	18.6	153,154,183,184,197,201,203,207
TOTAL	100%	

^a See figure 1 for the individual GC chromatograms of the four fractions

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

^c Identification of the individual BDEs were possible after the fraction was rechromatographed to further simplify the complexity of the BDE isomers present and to permit useful analysis by NMR spectroscopy

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Table 2. Weight percentage of the individual BDEs determined in DE-79™ by ¹H-NMR spectroscopy and GC/HRMS

BDE ^{i,ii}	Substitution Pattern	Wt % by NMR	Wt % by GC/HRMS
119	2,3',4,4',6-Pentabromo	Not seen	0.019
99	2,2',4,4',5- Pentabromo	Not seen	0.034
a ⁱⁱⁱ	Unknown Pentabromo	Not seen	0.010
154	2,2',4,4',5,6'-Hexabromo	0.974	0.928
b ⁱⁱⁱ	Unknown Hexabromo	?	0.057
149	2,2',3,4',5',6-Hexabromo	0.148	0.125
153	2,2',4,4',5,5'- Hexabromo	7.34	6.17
139	2,2',3,4,4',6- Hexabromo	Not seen	0.057
140	2,2',3,4,4',6'- Hexabromo	0.002	0.092
138	2,2',3,4,4',5- Hexabromo	0.446	0.496
184	2,2',3,4,4',6,6'-Heptabromo	0.486	0.282
d (128) ^{iv}	2,2',3,3',4,4'-Heptabromo	0.014 ^v	0.158
183	2,2',3,4,4',5',6- Heptabromo	35.6	37.2
182	2,2',3,4,4',5,6'- Heptabromo	Not seen	0.291
191	2,3,3',4,4',5',6- Heptabromo	0.026	0.170
180	2,2',3,4,4',5,5'- Heptabromo	2.15	0.888
171	2,2',3,3',4,4',6- Heptabromo	1.65	0.899
e	Unknown Heptabromo	?	0.020
201	2,2',3,3',4,5',6,6'- Octabromo	1.03	0.675
197	2,2',3,3',4,4',6,6'- Octabromo	19.1	21.6
203	2,2',3,4,4',5,5',6- Octabromo	2.28	4.07
196	2,2',3,3',4,4',5,6'-Octabromo	10.8	9.16
194	2,2',3,3',4,4',5,5'-Octabromo	Not seen	0.044
f	Unknown Octabromo	?	0.105
208	2,2',3,3',4,5,5',6,6'-Nonabromo	0.071	0.134
207	2,2',3,3',4,4',5,6,6'-Nonabromo	14.8	13.7
206	2,2',3,3',4,4',5,5',6-Nonabromo	0.411	0.902
209	Decabromo	(vi)	1.81
TOTAL			100.1%

i IUPAC numbering

ii The BDEs are presented in the order of their elution.

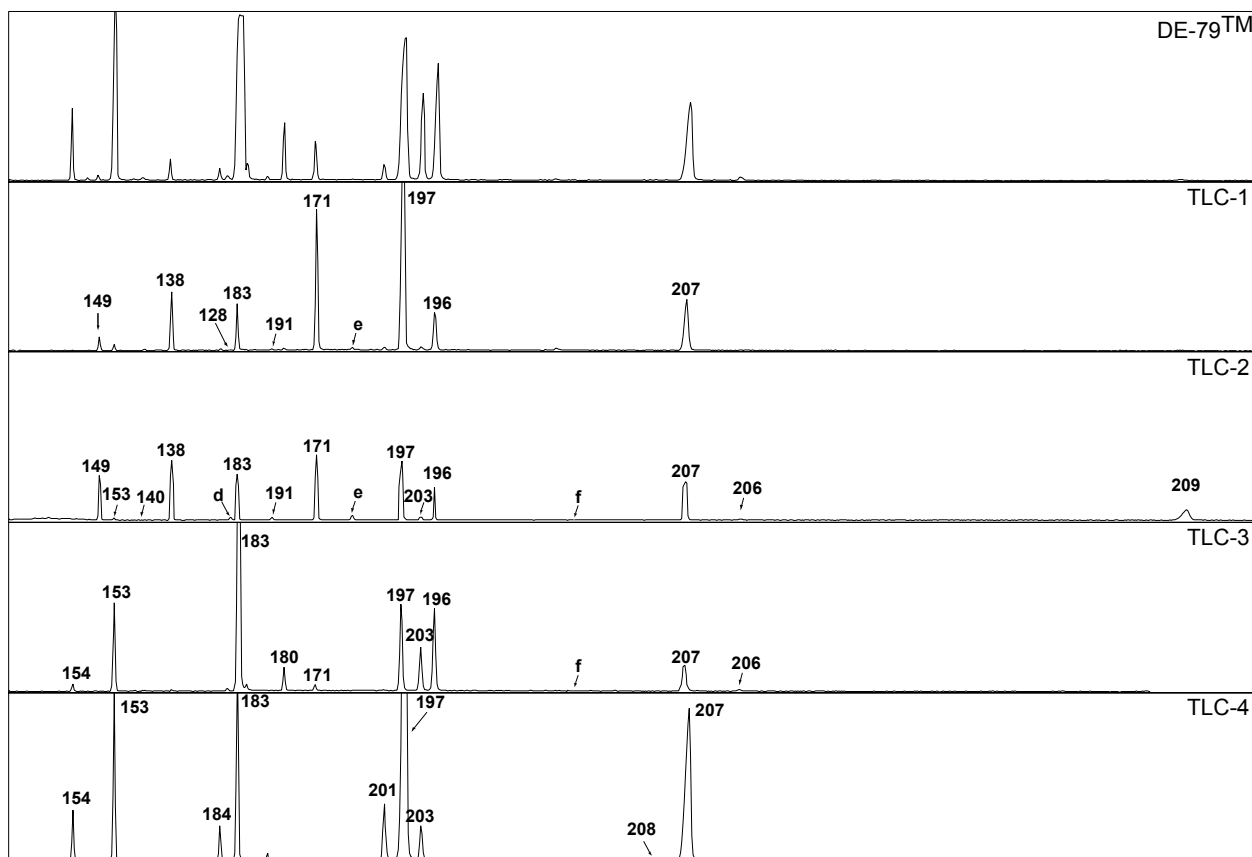
iii Unknowns a and b listed in this Table are not seen by HRGC/LRMS (see Figure 1)

iv NMR spectroscopy identified a minor hexa-BDE that co-elutes with the unknown hepta-BDE.

vi Quantitation of BDE-128 only.

v Can not be seen by NMR. Assume the concentration is 1.8% for the purpose of calculations.

Figure 1: GC/LRMS chromatographs of technical grade DE-79™ and the four fractions obtained after chromatography



References

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