

The Questionable Applicability of BDE-175 as an Indicator for Commercial Octabromodiphenyl Ether

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Introduction

It has been well documented in the literature that polybrominated diphenyl ethers (PBDEs or BDEs) have been utilized as brominated flame retardants (BFRs) in a variety of commercial products. PBDEs have historically been produced commercially at three levels of bromination resulting in distinct mixtures: penta-, octa-, and deca-BDE. Due to widespread environmental contamination and health concerns associated with the lower PBDE congeners, the penta- and octa-BDE commercial mixtures were removed from the market in 2004 (La Guardia et al. 2006). The continued presence of PBDEs as environmental contaminants and their potential toxicity has been recognized by the United Nations Environment Programme (UNEP) through the addition of selected PBDE congeners to the Stockholm Convention. Also, the U.S. Environmental Protection Agency recently negotiated an agreement with several companies that will lead to a three year phaseout of deca-BDE.

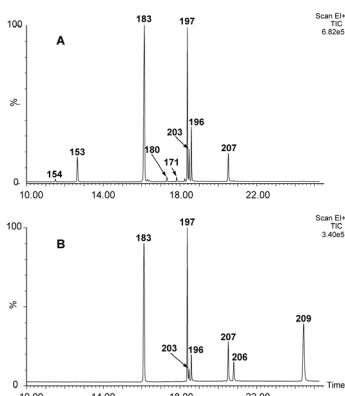


Figure 1. HRMS/LRMS Total Ion Current Chromatograms of A. Great Lakes DE-79™ and B. Bromkal 79-8DE™ on 15 m Restek Stx-500 Column

Technical octa-BDE products are complex mixtures containing PBDEs that range in degree of bromination from pentabrominated to nonbrominated congeners (Figure 1). The complex nature of the octa-BDE product makes the analysis of some congeners by high resolution gas chromatography (HRGC) challenging since congener co-elution can be a problem (Konstantinov et al. 2006). Also, not all 209 possible PBDE congeners are currently available as analytical standards. This hinders the assignment of unknown peaks in environmental samples as well as in technical material. Recently, BDE-175 (2,2',3,3',4,5'-heptabromodiphenyl ether) was added to the Stockholm Convention as an indicator for widely used commercial octa-BDE mixtures such as DE-79™ and Bromkal 79-8DE™ (UNEP, 2009). It was suggested that BDE-175, along with BDE-153, BDE-154, and BDE-183, be used as markers of commercial octabromodiphenyl ether mixtures for enforcement purposes. However, since BDE-175 and BDE-183 co-elute on common HRGC columns such as DB-5, the presence of BDE-175 as a major component in technical octa-BDE mixtures has not been confirmed.

The work presented herein highlights the NMR characterization of BDE-175 and DE-79™ as well as the successful separation of BDE-175 and BDE-183 using HRGC/LRMS.

Materials and Methods

Synthesis of BDE-175

BDE-175 was synthesized at Wellington Laboratories Inc. (Guelph, ON) using unambiguous proprietary methods. The purity and structure of the crystalline material was determined using NMR and HRGC/LRMS analysis.

High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)

Experiments were conducted on an Agilent 7890A GC/5975C MS using a Restek Stx-500 column (15 m x 0.25 mm x 0.15 μm). All injections were done in splitless mode. All experiments were done with the following GC conditions: helium carrier gas flow at 1.0 ml/min, injector temperature 280°C, temperature program set to the following parameters: initial oven temperature 100°C, hold for 2 minutes, ramp at 25°C/minute to 250°C, ramp at 1.5°C/minutes to 260°C, ramp at 25°C/minute to 325°C, hold for 7 minutes. A full scan range of 50-1000 amu was used in positive ion electron impact mode (EI+).

¹H-NMR Experiments

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

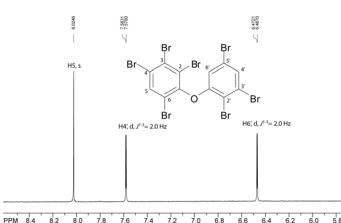


Figure 2. ¹H NMR Spectrum for BDE-175.

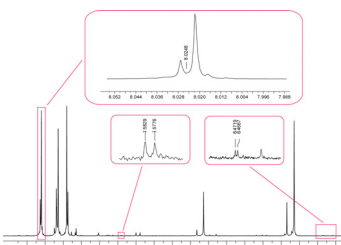


Figure 3. ¹H NMR spectrum for DE-79™. Potential BDE-175 signals are highlighted.

Results & Discussions

The structural assignment of BDE-175 using ¹H-NMR analysis was completed (Figure 2) to confirm the identity of the crystalline material and to determine if any unique chemical shifts could be identified that would facilitate the detection of this congener in the ¹H-NMR spectrum of DE-79™ (Figure 3).

The doublets observed in Figure 2 with chemical shifts corresponding to 6.467 ppm and 7.578 ppm were assigned to the 2,3,5-substituted aromatic ring of BDE-175. The occurrence of similar doublets in the NMR spectrum of DE-79™ does not unambiguously indicate the presence of BDE-175 since these signals could belong to any BDE congener that has a 2,3,5-substitution pattern in one ring. In any event, if each of the doublets is integrated as one proton, their ratio relative to the signals known to arise mainly from BDE-183 is approximately 1:70.

Therefore, although the NMR results are not conclusive regarding the amount of any BDE-175 present, if these doublets in the spectrum of the technical material are indeed attributable to BDE-175, it would only represent a trace level compound.

The successful HRGC/LRMS separation of a 1:1 mixture of BDE-175 and BDE-183 (Figure 4A) allowed us to confirm that this congener was not present in the technical material (Great Lakes DE-79™) in appreciable amounts (Figure 4B). This finding was further verified by analyzing a mixture of BDE-175 and DE-79™ (Figure 4C). Similar results were observed for the Bromkal 79-8DE™ formulation (Figure 5). It is evident from these chromatograms that BDE-175 is not a major component in these particular commercial octabromodiphenyl ether mixtures.

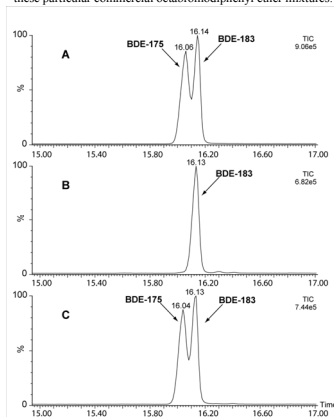


Figure 4. HRGC/LRMS chromatograms illustrating the presence of BDE-175 and BDE-183 in A) a 1:1 mixture (25 μg/ml each), B) 100 μg/ml solution of Great Lakes DE-79™ (BDE-183 has been reported to be present at ~42% (La Guardia et al. 2006) therefore the concentration of BDE-183 in this solution is ~20 μg/ml), and C) Bromkal 79-8DE™ with BDE-175 added (BDE-175 and BDE-183 are each 20 μg/ml).

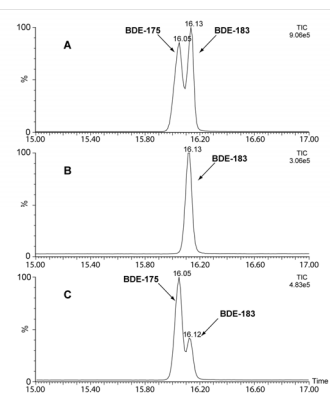


Figure 4. HRGC/LRMS chromatograms illustrating the presence of BDE-175 and BDE-183 in A) a 1:1 mixture (25 μg/ml each), B) 100 μg/ml solution of Bromkal 79-8DE™ (BDE-183 has been reported to be present at ~13% (La Guardia et al. 2006) therefore the concentration of BDE-183 in this solution is ~13 μg/ml), and C) Bromkal 79-8DE™ with BDE-175 added (BDE-175 and BDE-183 are 19 μg/ml and 8 μg/ml respectively).

BDE-153, BDE-154, and BDE-183 are present in the technical octabromodiphenyl ether mixtures at significant levels and, as such, make excellent indicators for its presence in the environment. However, the need to include BDE-175 as an indicator for commercial material is questionable since it seems likely that it is present at very low levels, if at all.

References

La Guardia MJ, Hale RC, and Harvey E. 2006. Environ. Sci. Technol 40:6247.

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