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

Alexandre Konstantinov1, Brock Chittim1, Dave Potter1, Jeff Klein1, Nicole Riddell1, and Robert McCrindle2

1Wellington Laboratories Inc., Research Division, Guelph, Ontario, N1G 3M5, Canada
2University of Guelph, Chemistry Department, Guelph, Ontario, N1G 2W1, Canada

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 are removed from the market in 2004 (Ga Guanda 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.

The work presented herein highlights the NMR characterization of BDE-175 and DE-79™ as well as the successful separation of BDE-175 along with BDE-153, BDE-154, and BDE-183, be identified that would facilitate the detection of this congener in the 1H-NMR spectrum of DE-79™ (Figure 3).

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 Barak 5 or 500 column (15 m x 0.25 mm x 0.5 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 200°C, temperature program set to the following parameters: initial oven temperature 100°C, hold for 2 minutes, ramp at 25°C/min to 260°C, ramp at 5°C/min to 260°C, hold at 270°C 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 deuteriodimethyl sulfoxide (DMSO-d6) as a solvent. The pulse delay was set to 6 seconds.

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).

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 successful HRGC/LRMS separation of a 1:1 mixture of BDE-175 and DE-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-BDE™ formulation (Figure 5). It is evident from these chromatograms that BDE-175 is not a major component in these particular commercial octabromodiphenyl ether mixtures.

References


Recent, BDE-175 (2,2',6,6'-tetrabromodiphenyl ether) was added to the Stockholm Convention as an indicator for enforcement purposes. However, since BDE-175 and BDE-183 co-elute on common HRGC columns such as DB-5, the presence of BDE-183 does not unambiguously indicate the presence of BDE-175 since these doublets correspond to 6.467 ppm and 7.578 ppm were assigned to the corresponding doublets in the NMR spectrum of DE-79™ does not.

The successful HRGC/LRMS separation of a 1:1 mixture of BDE-175 and DE-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-BDE™ formulation (Figure 5). It is evident from these chromatograms that BDE-175 is not a major component in these particular commercial octabromodiphenyl ether mixtures.