Synthesis and Characterization of Native and Mass Labeled [$^{13}C_{14}$]-Decabromodiphenylethane

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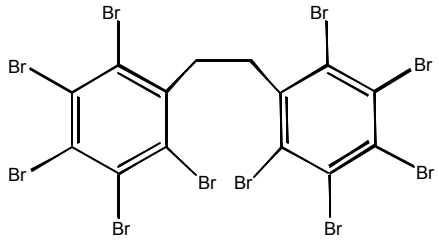
Introduction

Decabromodiphenylethane (DBDPE), containing 82.3% bromine, is a relatively new brominated flame retardant for use in polystyrene and polyolefin-based thermoplastic formulations.



DBDPE

DBDPE was introduced in the early 90's, and is marketed as a non-diphenyl oxide based alternative to brominated diphenyl ethers (BDE)[1]. One study[2] has shown that DBDPE produces no dioxins and only minor quantities of 2,3,7,8-DBDF under pyrolysis conditions.

Although currently DBDPE is not as widely used as BDE-209 (the Br_{10} congener) because of the relatively higher cost, it is predicted that DBDPE will soon become one of the major flame retardants used by the thermoplastics industry. The presence of DBDPE in sediments, sewage sludge and air samples was reported during Dioxin 2004[3]. The levels of DBDPE found ranged from 24 to 42 ng/g dry weight, and its ratio to BDE-209 levels in quantified samples was 0.01 in the sediment and 0.3 to 0.6 in the sewage sludge samples examined.[3]

A lack of surrogate standards for DBDPE definitely poses difficulties in determining levels accurately. This study has two goals: the characterization of mass-labeled DBDPE and an assessment of its utility in determining DBDPE levels in environmental samples.

Materials and Methods

Synthesis. Native and mass labeled [$^{13}C_{14}$]-decabromodiphenylethane were prepared using proprietary methods.

Gas Chromatography/Mass Spectrometry. The analyses were conducted on a Shimadzu GCMS-QP2016 using a 15 m DB-5HT column with 0.25 mm ID and 0.1 µm stationary phase. The injections were done in splitless mode, with the injector temperature at 300°C, and with column flow of 1.50 ml/min maintaining constant linear velocity at 65.5 cm/sec. The following temperature program was used: initial oven temperature: 140°C, hold of 5 min, ramp at 10°C/min to 325°C, hold 20 min. Run times were 43.50 minutes long, and a full scan of 50 to 1000 amu was used.

^{1}H-NMR Experiments. The analyses were performed on 400 MHz Bruker instrument using toluene-d_8 as a solvent.

Results and Discussion

Both native and $^{13}C_{14}$-DBDPE (MDBDPE) were obtained with better then 99% purity, with the MDBDPE surrogate having better than 99% isotopic purity (GC-MSD, HI-RES GC-MS, ^{1}H NMR). DBDPE was obtained in the form of colorless monoclinic crystals with a melting point higher than 360 °C while technical DBDPE (e.g. Firemaster 2100) has a melting point range of 348-353 °C[4]. This higher melting point presumably reflects the absence of contaminants (lower congeners) present in technical material[3].

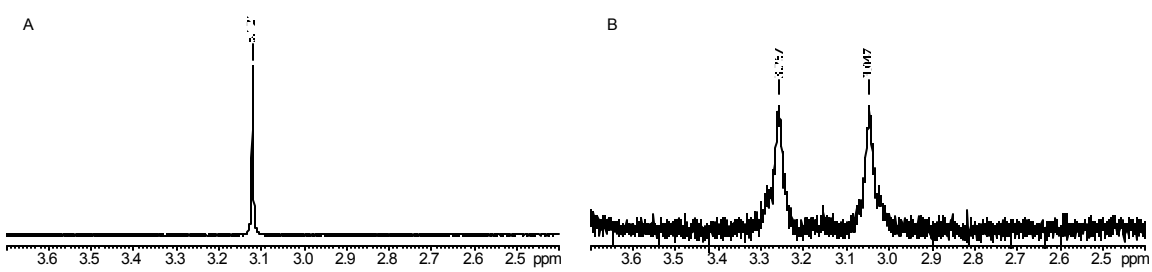


Figure 1. ^{1}H-NMR spectra of A) DBDPE, B) MDMDPE at 400 MHz.

The ^{1}H NMR spectrum of DBDPE consisted of a singlet, corresponding to the protons on the ethane linkage at d 3.12, and of a broad doublet ($^{1}J_{C-H}$ = 138 Hz) at d 3.12 for MDBDPE (Figure 1). The broadness of the doublet for mass labeled DBDPE is due to long-range ^{13}C-couplings.

Decabromodiphenylethane eluted at 23.6 minutes under the conditions mentioned in the experimental section. Figure 2 shows the full scan mass spectrum of DBDPE and $^{13}C_{14}$ -DBDPE .The molecular ion peak was observed at m/z 971.3 (M+ 10) and

m/z 985.3 (M+10) amu for native and mass-labeled DBDPE respectively. The relative intensity of the molecular ion peak was only 10% of the base peak, and we recommend use of the base peak, the pentabromobenzyl fragment, in quantitation experiments.

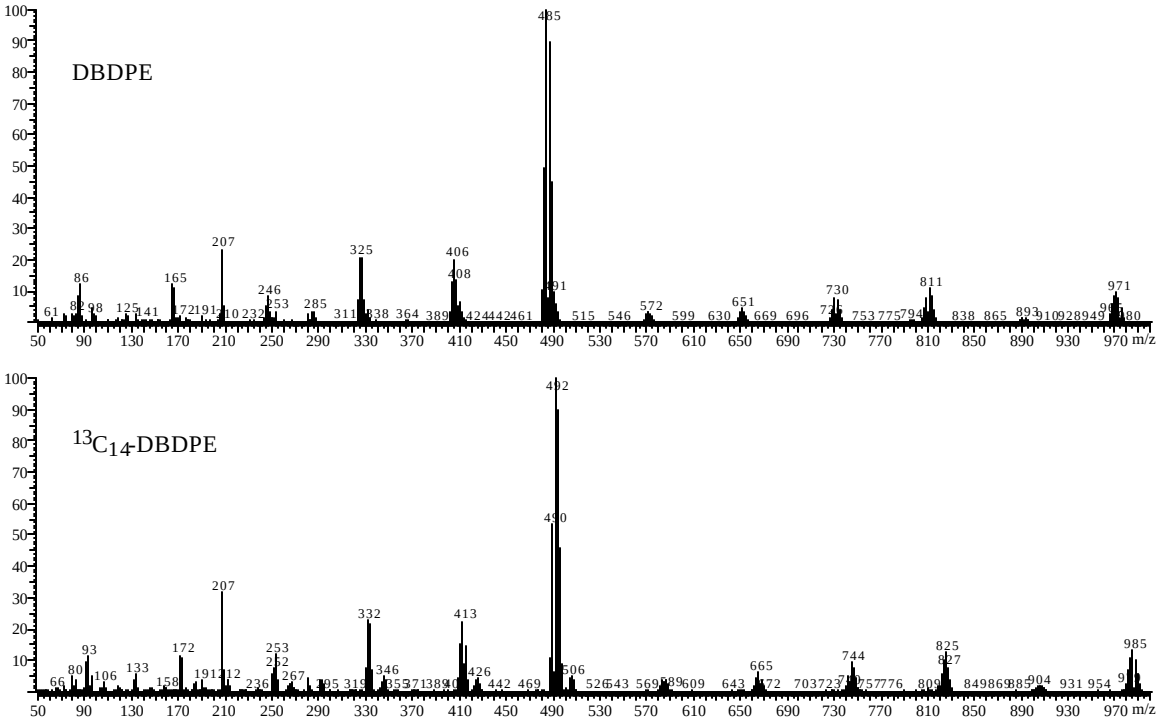


Figure 2. Full-Scan Mass Spectra of DBDPE and MDBDPE.

It should be noted that native DBDPE is similar in mass to mass-labeled [$^{13}C_{12}$]-BDE-209. However, these two fire retardants have different retention times (Figure 3) and very different fragmentation patterns. Even for single ion monitoring, a resolution of 18,000 is sufficient to distinguish DBDPE from [$^{13}C_{12}$]-BDE-209.

Figure 3 shows the result of coinjection of standard solutions of BDE-209 and MDBDPE. A 25 ng sample of each compound was injected onto the column. BDE-209 was integrated at 76% by peak area and at 80% by peak height. The respective values for MDBDPE were 24% for peak area and 20% for peak height. The relative response of DBDPE to BDE-209 is low, about 1 to 4. This observation may be very important for determination of the levels of DBDPE in environmental samples, since the use of BDE-209 as a standard may lead to significantly underestimated results.

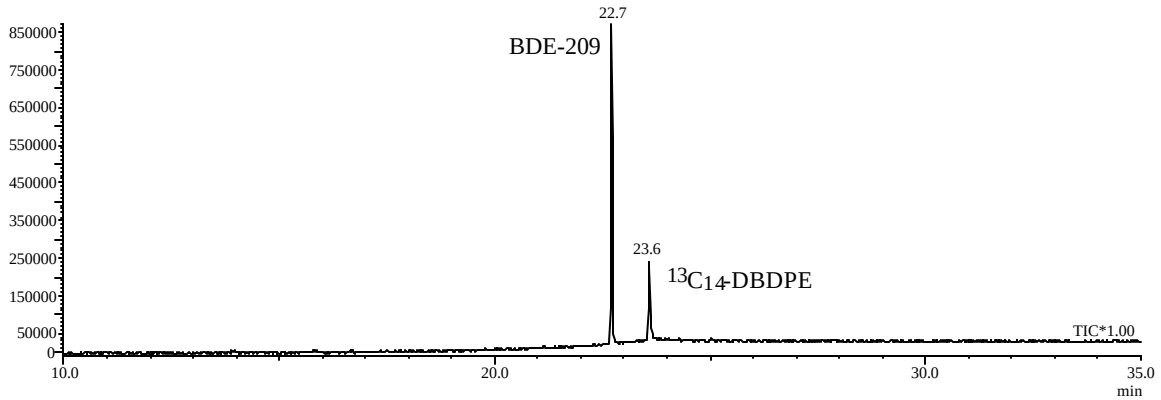


Figure 3. Co-injection of BDE-209 and MDBDPE (25 ng on-column each).

Assessment of DBDPE Levels in Environmental Samples

Presently we are performing analytical work in determining the levels of DBDPE in sewage sludge samples. This work is ongoing and results will be presented at the BFR-2004 workshop.

Conclusions

The large difference in response factors between BDE-209 and DBDPE almost dictates the use of [$^{13}C_{14}$]-decabromodiphenylethane as a surrogate standard to improve the accuracy when determining the levels of DBDPE in environmental samples.

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