Native and Mass Labeled [13C14]-Decabromodiphenylethane (DBDPE): Characterization and Use in Determination of DBDPE in Sewage Sludge

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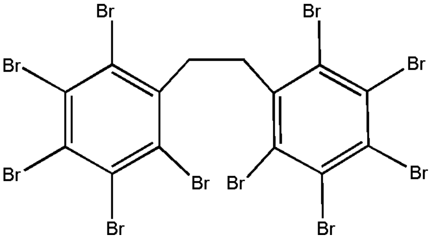
Introduction

Decabromodiphenylethane (DBDPE) 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)[i]. One study[ii] has shown that DBDPE produces no dioxins and only minor quantities of 2,3,7,8-TBDF under pyrolysis conditions.

Although currently DBDPE is not as widely used as decabromodiphenyl ether (BDE-209) because of the 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 2003[iii]. The levels of DBDPE found in sewage sludge ranged from 33 to approximately 100 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.[iii]

The lack of a surrogate standard 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 (MDBDPE) were prepared using proprietary methods.

High Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS). The analyses were conducted on a Shimadzu GCMS-QP2010 using a J&W 15 m DB-5HT column with (0.25 mm ID, 0.1 µm film). The injections were done in splitless mode, with the injector temperature at 300°C, and with a column flow of 1.50 ml/min. 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 minutes. A full scan range of 50 to 1000 amu was used.

High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS). The analyses were conducted on a HP6890 HRGC coupled to a Waters Autospec Ultima HRMS. The column was a J&W 15 m DB-5HT (0.25 mm ID, 0.1 µm film). The injections were done in splitless mode, with the injector temperature at 300°C. The initial column flow was 10 ml/min for 1 min, then decreased at 500 ml/min^2 to 1.0 ml/min. The following temperature program was used: initial oven temperature: 140°C, hold of 5 min, ramp at 10°C/min to 330°C, hold until after DBDPE eluted. The mass spectrometer was operated in the selected ion monitoring (SIM) mode at a resolution of at least 10,000. The transfer line and source were maintained at 300°C. Additional analyses were carried out on a HP5890 HRGC coupled to a VG70SE HRMS with the same column and conditions.

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

Sewage Sludge Sample Extraction and Cleanup. Sewage sludge samples were dried, spiked with MDBDPE and $^{13}C_{12}$-BDE-209 (MBDE-209) and then Soxhlet extracted for 48 hours with a mixture of acetone:toluene (1:4). The extracts were acid digested and then treated with copper to remove sulfur. Additional clean up included hexane elution through an acid silica/silica column, followed by fractionation on a short silica column eluted with hexane and then with dichloromethane/hexane (1:1).

Results and Discussion

Both native and MDBDPE were obtained with better then 99% purity, with the MDBDPE surrogate having better than 99% isotopic purity (HRGC/LRMS, HRGC/HRMS, ^{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[iv]. This higher melting point presumably reflects the absence of contaminants (lower congeners) present in technical material[iii].

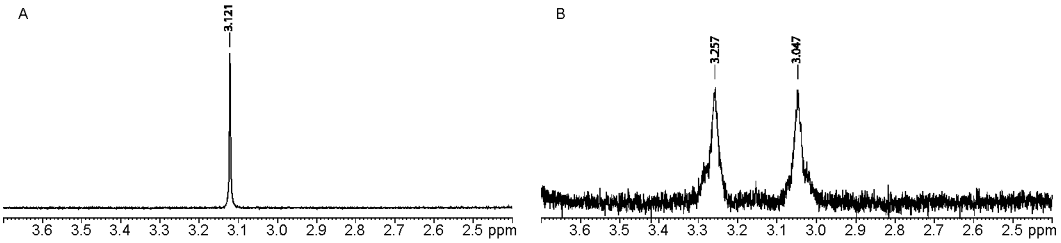


Figure 1. ^{1}H-NMR spectra of A) DBDPE, B) MDBDPE at 400 MHz.

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

The full scan mass spectra of DBDPE and MDBDPE are shown in Figure 2. The molecular ion peaks were observed at m/z 971.3 (M+10) and m/z 985.3 (M+10) amu for DBDPE and MDBDPE, respectively. Quantitation was attempted by using the base peak since its intensity was approximately one order of magnitude greater than that of the molecular ion peak. However, we found that the pentabromophenoxy ethane fragment of DBDPE overlaps with the base peak of the MDBDPE (pentabromobenzyl fragment). Hence, we recommend the use of the molecular ion peaks for quantitation.

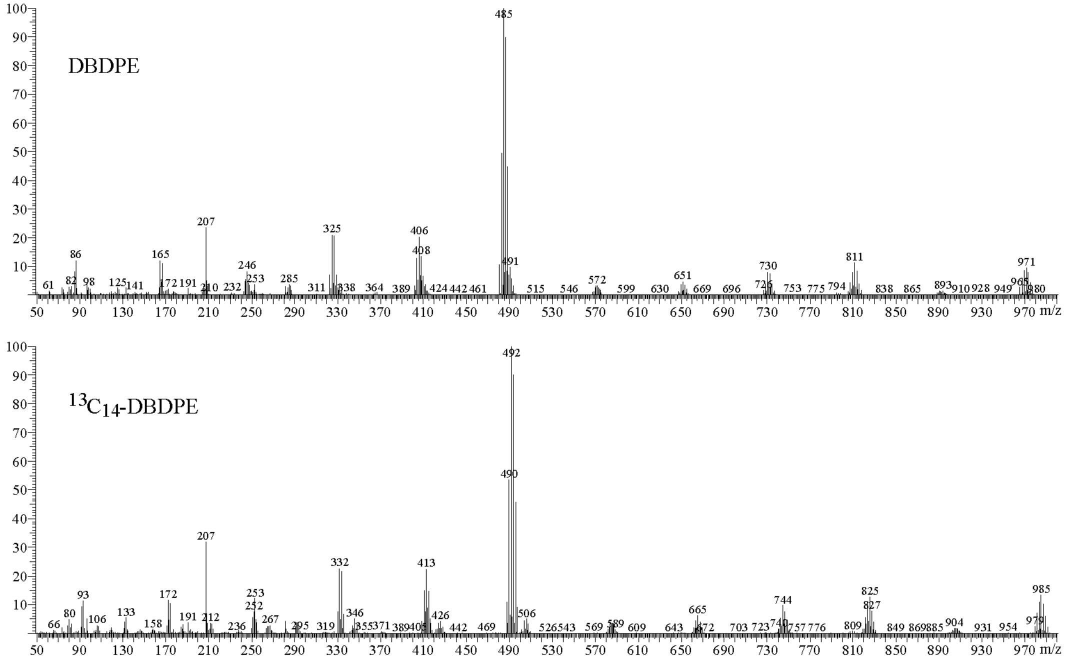


Figure 2. Full-Scan Mass Spectra of DBDPE and MDBDPE (LRMS).

The TIC trace resulting from co-injection of standard solutions of BDE-209 and MDBDPE (25 ng of each; HRGC/LRMS) is shown in Figure 3. Under these conditions, they separate cleanly with MDBDPE eluting after the ether. Notably, the two compounds gave significantly different responses with integrated values (peak area) of 76% and 24% for BDE-209 and MDBDPE, respectively.

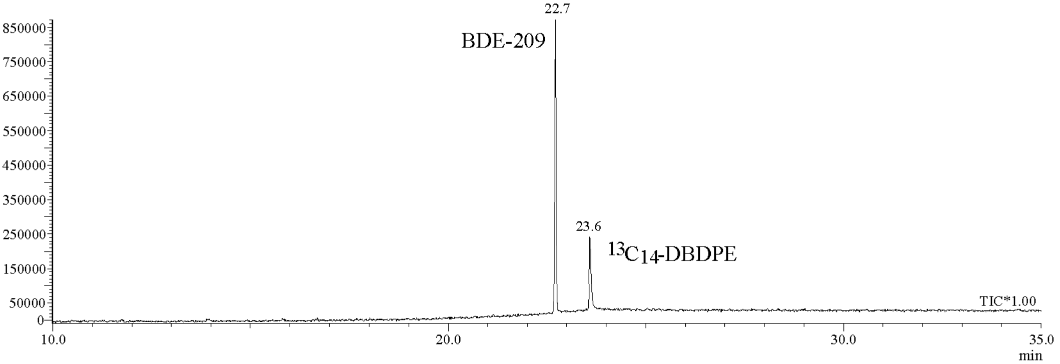


Figure 3. TIC Chromatogram from co-injection of BDE-209 and MDBDPE (1/1 w/w).

Assessment of DBDPE Levels in Environmental Samples

A total of ten samples of sewage sludge from six different locations in Ontario, Canada were examined. During the sample preparation and cleanup, we found that both acid treatment and copper treatment are highly ineffective when toluene is used as a solvent. Better results were obtained using hexane as an extractant, however, the method is still under development.

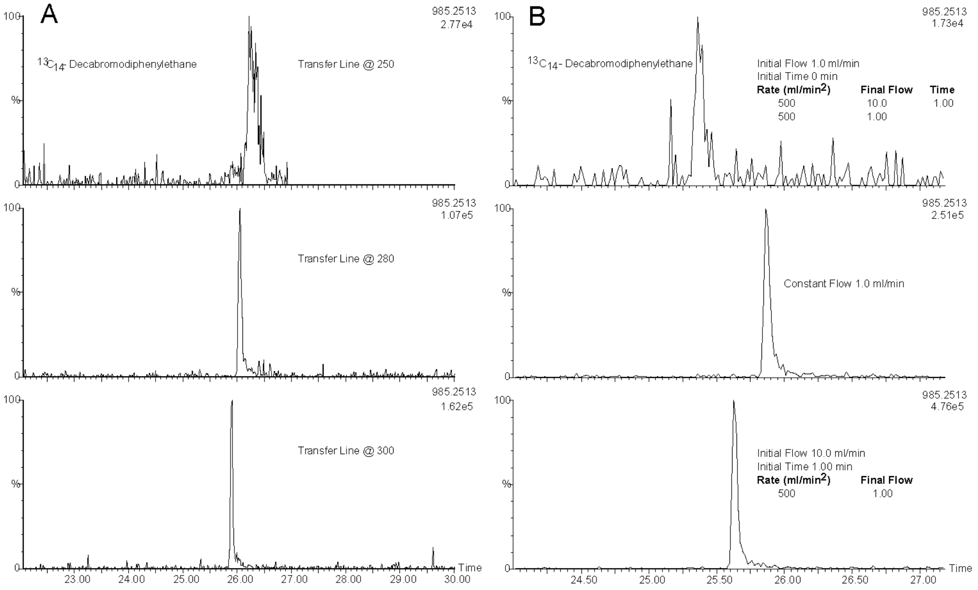


Figure 4. Effects of Transfer Line Temperature (A) and Carrier Gas Flow (B) on HRGC/HRMS Chromatography of MDBDPE

Initial attempts to quantitate DBDPE in sewage sludge samples using HRMS were unsatisfactory using a transfer line temperature of 250°C. We found that an increase of the transfer line temperature to 300°C greatly improves the sensitivity and peak shape (Figure 4 A).

We also investigated the effect of ramping the flow on sensitivity (Figure 4B). The best sensitivity was achieved with the initial flow at 10 mL/min for 1 minute followed by a decrease to 1 mL/min.

It should be noted that native DBDPE (971.2082 amu) is almost identical in mass to mass-labeled [$^{13}C_{12}$]-BDE-209 (971.2043 amu). However, this should not be an issue since they are base line resolvable (see Figure 5).

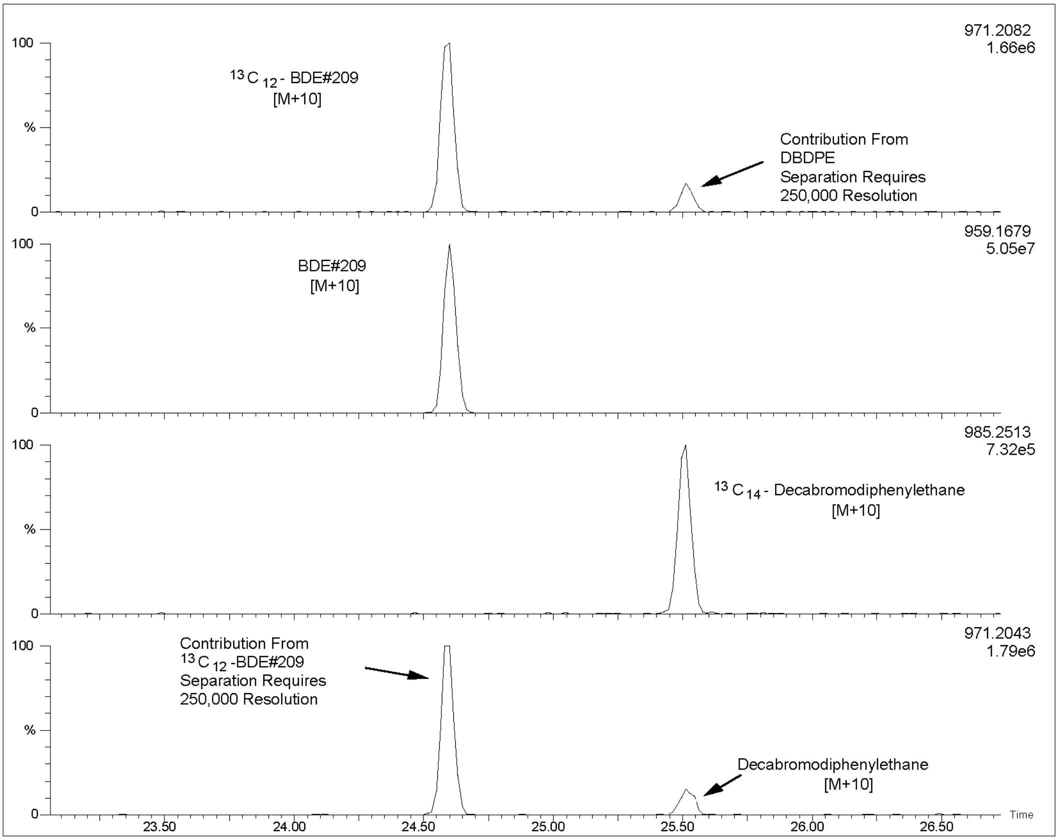


Figure 5. SIM Traces of Sewage Sludge Sample Spiked with MBDE-209 and MDBDPE

With the optimized HRMS conditions, we used 5-point calibrations for DBDPE and BDE-209 to determine their concentration in the sludge samples (see Table 1). The analyses were also repeated for seven of the samples on a VG70SE HRMS coupled with an HP5890 Series II GC using the same column and instrument conditions.

Both BDE-209 and DBDPE were found in all samples analyzed. The concentration of BDE-209 ranged between 0.5 ppm to 1.8 ppm which is comparable with the reported North American concentrations[v]. The levels of DBDPE are slightly lower then those reported elsewhere [iii], although they are in the same range.

During these analyses, it became obvious that the procedures used for sample preparation and the conditions used for HRGC/HRMS analyses were very critical. In this regard, the availability and use of the DBDPE surrogate was invaluable. Our confidence in the accuracy and precision of these results has been bolstered by the use of the DBDPE surrogate.

Table 1. Concentrations of BDE-209 and DBDPE in Sewage Sludge

Sample #	BDE-209 PPB		DBDPE PPB	
	Autospec	VG70SE	Autospec	VG70SE
1	1,860	1,610	31.6	21.4
2	1,150	1,310	10.8	16.1
3	589	444	5.7	10.4
4	661	473	15.0	10.7
5	466	500	15.3	15.5
6	1,470	1,130	8.5	15.2
7	554	467	16.4	16.9
8	1577	-	27.4	-
9	711	-	5.6	-
10	859	-	14.8	-

References

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