

## COMPARISON AND INTERPRETATION OF MASS SPECTRAL DATA OF POLYBROMINATED DIPHENYL ETHER (PBDEs) CONGENERS AND POLYHALOGENATED BIPHENYL CONGENERS

Russell H. Cooper, Richard P. Kozloski, Anke Gelbin, Mohamed Taroua

AccuStandard, Inc. 125 Market Street, New Haven, CT USA 06513

### ***Introduction***

Polybrominated diphenyl ethers (PBDEs) are an important class of compounds for the analytical community to characterize and measure in the environment. As the monitoring community has become increasingly aware that PBDE congeners are a common and widespread environmental contaminant, these compounds are gaining attention similar to that of polychlorinated biphenyls (PCBs) and dioxins. They raise similar toxicity and carcinogenic concerns and are less well documented and understood than the PCB analogues. They appear in flame retardants and have come under increasing environmental scrutiny. Like PCBs, some PBDEs resist degradation and concentrate in adipose tissue affecting endocrine and hepatic functions<sup>1</sup>.

The aim of this paper is to describe and discuss the principal features associated with the mass spectra of some of these PBDEs and compare them to the well known spectra and behavior of PCBs. This may assist in explaining the reactivity and behavior of PBDEs.

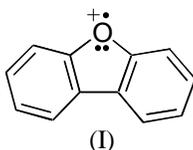
### ***Methods and Materials***

Analysis of PBDE samples was performed using methodology similar to the pioneering PCB work done by Hutzinger, Safe and Zitco<sup>2,3</sup>. Solutions of approximately 1 mg/ml PBDE congener in methylene chloride were prepared and dissolved completely. Samples and methylene chloride reagent blanks were analyzed on a Hewlett Packard GC/MS in electron impact (EI) full scan mode. Separation of the PBDE from any extraneous material was effected on a 30m x 0.25mm narrow bore, 5% phenyl, 95% methyl silicone column programmed from 100° to 300° C at 10°/min. Injector and MS analyzer were maintained at sufficient temperature to keep samples volatilized. 1.0 µl of each solution was injected in duplicate. The total ion chromatogram (TIC) and the resulting mass spectra were tabulated and recorded.

### ***Results and Discussion***

Based on the experimental data of about 130 polybrominated diphenyl ether congeners (synthesized on site), it has been observed that the prominent mass spectral features are:

- Ion clusters with the typical isotope distribution pattern for multiple bromine substitution
- Ion clusters from the parent ion and from the loss of an even number of bromine atoms
- Prominent M-2Br ion clusters of moderate to strong intensity
- Doubly charged M-2Br ions of moderate to strong intensity
- Doubly charged ions of the parent peak cluster that are absent or weak
- M-Br and M-HBr ion clusters of very weak intensity
- Ion clusters of M-C<sub>2</sub>H<sub>4</sub>Br of up to moderate intensity



The prominent M-2Br ion clusters can be explained in terms of the formation of the relatively stable oxonium ion (I) generated by the loss of two bromine atoms in PBDE congeners as demonstrated in figure 1. Its formation, even in the absence of ortho bromines, suggests the facile rearrangement of bromine between the rings after initial ionization. The virtual absence of M-Br

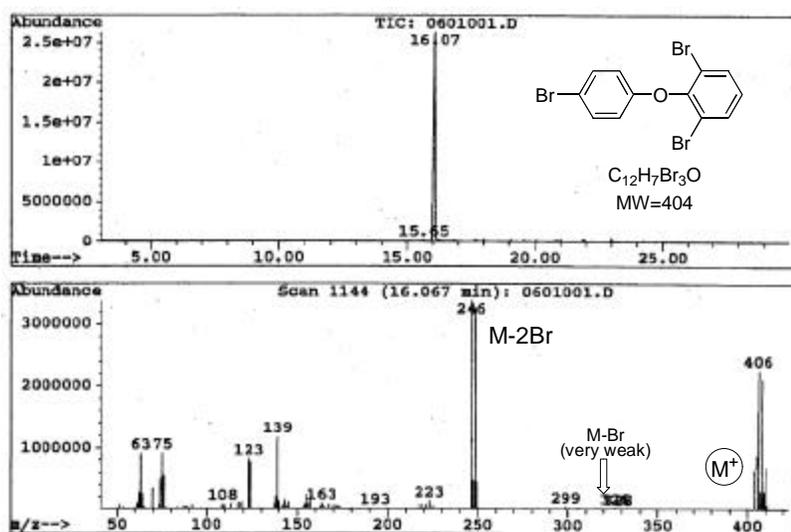


Figure 1: TIC and mass spectrum of 2,4,6-tribromodiphenyl ether

and the M-HBr ion clusters may be attributable to the energy gain in losing an additional bromine atom to form the oxonium ion. The only time significant loss of a single bromine was observed was for the monobromodiphenyl ether.

For 2-bromodiphenyl ether, M-Br was the base peak (see figure 2).

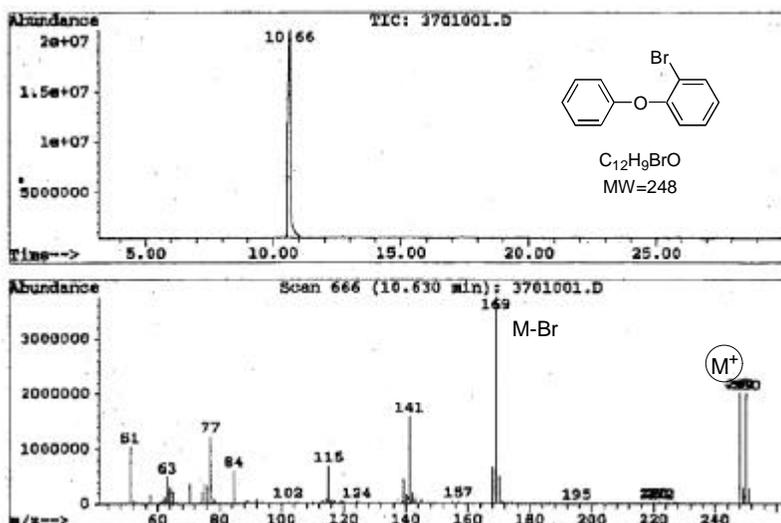


Figure 2: TIC and mass spectrum of 2-bromodiphenyl ether

The greater abundance of the doubly charged ion cluster (M-2Br) as compared to the absent or weak doubly charged ion of the molecular ion may be attributable to the greater degree of unsaturation in the M-2Br ion, thereby giving greater stability to the M-2Br doubly charged ion. Our experience has shown similar results in PCBs and polybrominated biphenyls (PBBs). For mass spectrometers of limited mass range, even the M-2Br ions may be beyond their capability for the more highly substituted ethers. The easily observed M-2Br doubly charged ion cluster can serve to identify the degree of bromination, provided the retention time is consistent with this degree of substitution (figure 3).

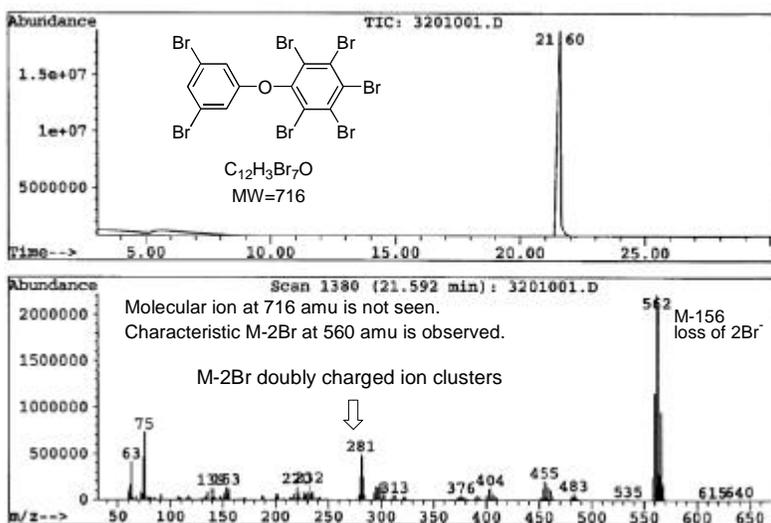
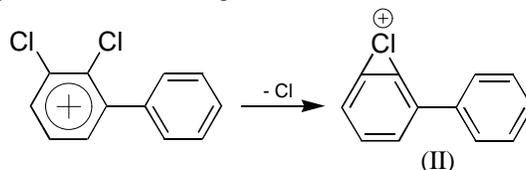


Figure 3: TIC and mass spectrum of 2,3,3',4,5,5'-Heptabromodiphenyl ether

In sharp contrast, PCBs can have prominent M-Cl ion clusters for the congeners having three ortho chlorines or a single ortho chlorine on each ring. The removal of an ortho chlorine atom in these cases can reduce the steric hindrance that prevents the biphenyl rings from becoming coplanar. The energy gained by the increased resonance between the biphenyl rings promotes the loss of a single chlorine atom. A more subtle aspect of this phenomenon is the ability of meta chlorines adjacent to ortho chlorines to enhance this effect. By forming a chloronium ion (II) the molecule is stabilized by the transfer of charge to the chlorine atom.



Since loss of the meta chlorine is equivalent to the loss of an ortho chlorine in these cases, the probability of relieving the steric strain is increased, thereby enhancing the M-Cl ion intensity. This renders the fragmentation pattern in the mass spectrum of most PCBs and PBBs quite distinct from PBDEs. This can also serve to be a useful tool for analytical work.

An  $M-C_2H_4X$  ( $X = \text{halogen}$ ) ion cluster of moderate intensity is found in some PBDEs but not in PCBs. Since an analogous species does not occur in PCB and PBB mass spectra, the oxygen atom in the PBDE must be involved in the charge stabilization of the resulting ion. The intensity of the  $M-C_2H_4Br$  ion cluster tends to be greater when the molecular ion is the base peak and multiple meta bromine atoms are present. The presence of multiple ortho bromine atoms tends to reduce the  $M-C_2H_4Br$  intensity, as well as making  $M-2Br$  the base peak.

### Conclusions

These mass spectral analytical features demonstrate some important similarities and differences in chemical structure between two environmentally important classes of compounds (i.e. PCBs and PBDEs). They also allow the analytical chemist to understand and predict expected spectra and chemical behavior of the less researched and documented polybrominated diphenyl ethers. The analytical chemist is able to postulate the major fragmentation ions expected during GC/MS analysis of most PBDEs congeners. Moreover, for those mass spectrometers with limited mass range capability, (i.e.  $<1000$  amu) this becomes a very valuable tool for identifying the correct PBDE congener by using the strong  $M-2Br$  fragment ion phenomenon described in this paper.

### References

1. Renner, R.; **Increasing levels of flame retardants found in North American environment** *Environ. Sci. Technol. A-pages*; **2000**; 34(21), 452 A-453 A.
2. Hutzinger, O., Safe, S., Zitco, V.; **1974**; *The Chemistry of PCBs*, CRC Lewis Press Publishers
3. Mullins, M., Safe, S., et.al.; **High-resolution PCB analysis: synthesis and chromatographic properties of all 209 PCB congeners** *Environ. Sci. Technol.*; **1984**; 18(6), 468-475.