A Detailed Analysis of the Mass Spectrum of Mass-labeled Tetrabromobisphenol A (MTBBPA)

Mehran Alaee[1], Gilles Arsenault[2], Brock Chittim[2], Robert McCrindle[3], Grazina Pacepavicius[1], Dave Potter[2] and BrianYeo[2]

[1] National Water Research Institute, Burlington, Ontario, L7R 4A6, Canada
[2] Wellington Laboratories Inc. Guelph, Ontario, N1G 3M5, Canada
[3] University of Guelph, Chemistry Dept., Guelph, Ontario, N1G 2W1, Canada

Introduction

Tetrabromobisphenol A (TBBPA) is one of the most important flame retardants used currently in use[1]. There has been a growing interest among environmental laboratories in determining the levels of TBBPA in the biota. Mass labeled TBBPA can be used to help quantify the levels of native TBBPA in the environment using GC/MS techniques. It is therefore important that the mass labeled reference standard contain no native contamination.

We recently synthesized the reference standard $^{13}C_{12}$-TBBPA (MTBBPA) in which the carbon atoms on the phenyl rings are labeled and needed to confirm that the mass labeled standard is free of native contaminant. When analyzing the mass spectrum of MTBBPA, it was found that one had to carefully choose the appropriate mass fragments to confirm the absence of any native TBBPA.

This study reports the mass spectrum of the MTBBPA synthesized in our laboratories and discusses how the mass spectral data may be analyzed to determine if native contamination exists in the sample.

Materials and Methods

Chemicals. Native TBBPA was purchased from Sigma-Aldrich and further purified by conventional means. $^{13}C_6$ Benzene (99.1%, Isotec) was used as the starting material for the synthesis of MTBBPA.

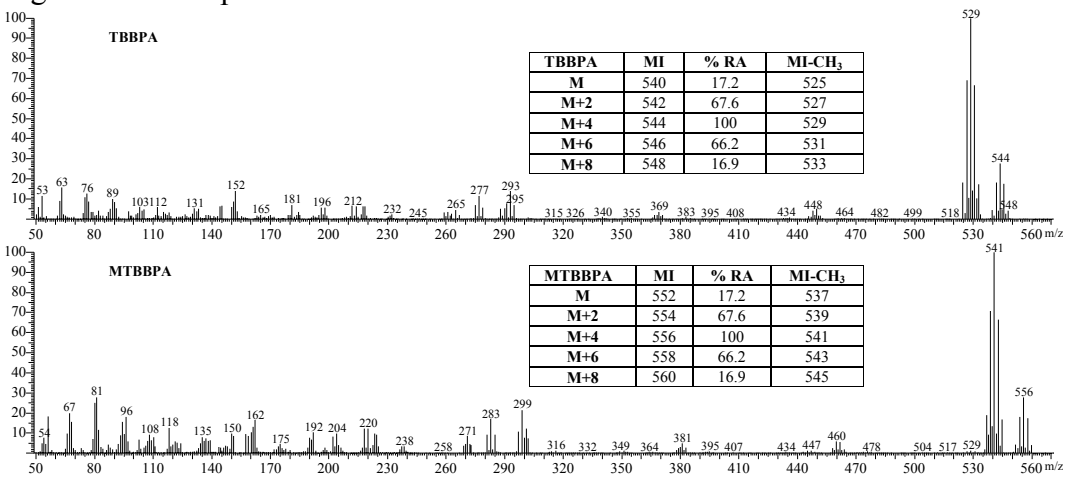
GC/MS Experiments. The HRGC/LRMS experiments were performed on a Shimadzu GC2010:QP2010. Selected Ion Monitoring (SIR) was performed on a HP6890 (HRGC) coupled to a Waters Autospec Ultima mass spectrometer (HRMS) in EI+ mode. The HRGC/HRMS utilized a DB5-HT (15m, 0.25 mm id, 0.1 µm film). The splitless injector was kept at 250 C, while the column program was 100 C (0), 15 C/min to 300. The HRGC was operated at a constant flow of 0.8 ml/min.

Results and Discussions

Full Mass Spectral Analysis of TBBPA and MTBBPA

The full mass spectrum of TBBPA and of MTBBPA are shown in figure 1. The molecular ion (MI) is easily seen but the base peak is due to the fragment from loss of a methyl group. The mass difference between native and mass-labeled for these two signals is 12 amu confirming that the two phenyl groups in MTBBPA contain $^{13}C_6$. The data for the most notable fragments are summarized in Table 1.

Figure 1. Mass Spectra of TBBPA and MTBBPA



TBBPA	MI	% RA	MI-CH_3
M	540	17.2	525
M+2	542	67.6	527
M+4	544	100	529
M+6	546	66.2	531
M+8	548	16.9	533

MTBBPA	MI	% RA	MI-CH_3
M	552	17.2	537
M+2	554	67.6	539
M+4	556	100	541
M+6	558	66.2	543
M+8	560	16.9	545

Table 1. Significant fragments in the mass spectrum of TBBPA and MTBBPA

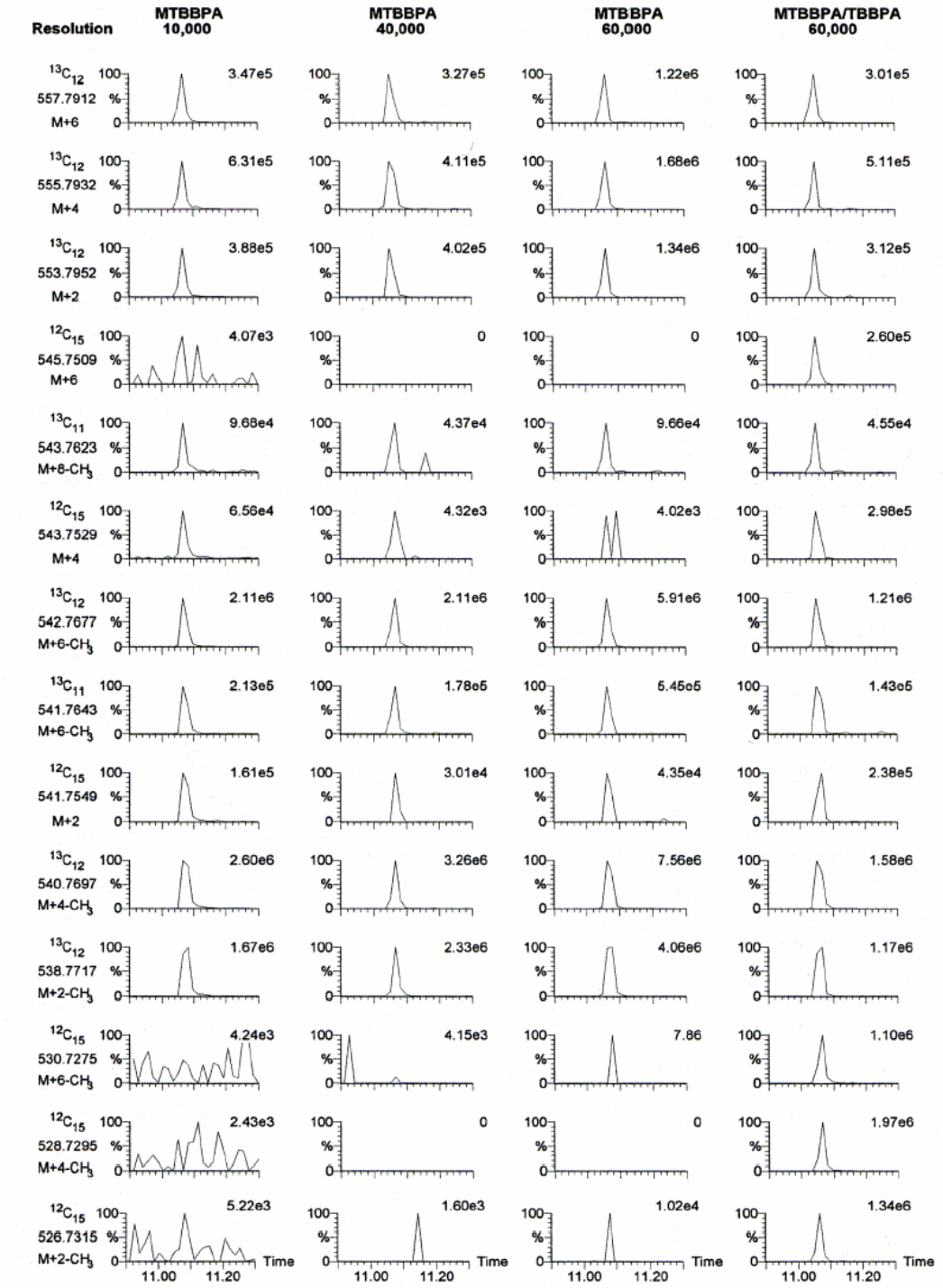
Native m/z	Mass labeled m/z	Explanation
544	556	MI
529	541	MI – CH_3
448	460	MI – CH_3 – Br
293	299	MI – 2,6-dibromophenol

Detailed Analysis of the Mass Spectra Around the Molecular Ion Cluster

Figure 2 reports a detailed analysis of some of the possible values for the MI and MI – CH_3 signals for both TBBPA and MTBBPA.

Verifying that MTBBPA is free from native contamination by simultaneously monitoring the molecular ions of MTBBPA and TBBPA is a difficult if not impossible task even using high resolution mass spectrometry. The MI of TBBPA falls within the MI-CH_3 cluster for MTBBPA. The presence of naturally-occurring ^{13}C in the propyl moiety further complicates the matter, although the contribution is small (2-3%). Thus a resolution of at least 30,000 is required to distinguish the M+2 fragment for TBBPA (541.7549) from that for M+5-CH_3 for MTBBPA (541.7730). The only way of clearly determining if native TBBPA is

Figure 2. HRGC/HRMS Analysis of MTBBPA and a mixture of TBBPA & MTBBPA



present in MTBBPA is by looking for the major native MI – CH_3 signals at m/z 526.7315/528.7295/530.7275. As seen from Figure 1 and 2 this region is free from interfering masses. We know from the full mass spectrum analysis that the MI – CH_3 fragments are the strongest signals for TBBPA.

Signals are observed at 10k resolutions that might be assignable to native MI (m/z 541.7549/543.7529/ 545.7509) in MTBBPA. However, the ratio of the signals is not correct for TBBPA; the observed ratio was 245:100:6 and not the expected 68:100:66. Since we have just confirmed above that there was no native contamination, these signals must be due to some other fragments from MTBBPA. We confirm that these signals are due to the $^{13}C_{11}$-MTBBPA analogues. Knowing that the mass labeled reagent used to synthesize MTBBPA contained 99.1% ^{13}C, and therefore 0.9% ^{12}C, calculations indicate that we should expect to see a ratio of $^{13}C_{12}$-MTBBPA to $^{13}C_{11}$-MTBBPA of 100:11, where the $^{13}C_{11}$ analogues result from the presence of a ^{12}C atom at any position in the benzene rings. This represents a strong contribution. The $^{13}C_{11}$-MTBBPA – CH_3 masses are close enough to the native MI mass that 60k resolutions is required to resolve these signals. We see when we go to 40k resolutions that the signals possibly assignable to native TBBPA at m/z 543.7529 and 541.7549 decrease substantially but that the signals due to $^{13}C_{11}$-MTBBPA – CH_3 at m/z 543.7623 and 541.7643 remain the same relative to the MTBBPA signal at m/z 555.7932. When comparing the relative signal intensity ratio between MTBBPA – CH_3 at m/z 542.7677 and $^{13}C_{11}$-MTBBPA – CH_3 at m/z 541.7643, the ratio is 11% at 10k and 40k, as expected based on the calculations mentioned above.

It should be noted that MTBBPA – CH_4 would give a mass of m/z 541.7599 for the M+6 ion. A resolution of 125k would be required to resolve this signal from $^{13}C_{11}$-MTBBPA – CH_3 at m/z 541.7643. As mentioned above, the strength of the signal measured at m/z 541.7643 indicates that most, if not all, of the signal is due to $^{13}C_{11}$-MTBBPA. However, it can not be said with certainty that there is no contribution form MTBBPA – CH_4 without additional experiments being performed.

Summary

Verification that there is no TBBPA in MTBBPA can be done using selected ion monitoring of the MI-CH_3 fragment ions. The MI fragments possibly due to TBBPA can only be separated from the many fragments occurring in that region due to MTBBPA – CH_3 if the resolution is greater than 60k.

References

1. See for example; i) Hyotylainen, T., Hartonen, K., (2002) Trends in Anal. Chem. 21, 13-27. ii) Bergman, A., (2000) Organohal. Comp. 47, 36- 40. iii) De Wit, C.A., (2002) Chemosphere 46, 583-624.