

Liquid Chromatographic – Tandem Mass Spectrometric Techniques for Analysis of Hexabromocyclododecane and Tetrabromobisphenol A Compounds

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Introduction

Brominated flame retardants (BFRs) are a structurally diverse group of chemicals that are incorporated into consumer and industrial products to increase their flame resistance. BFRs are aromatic, aliphatic or cycloaliphatic compounds containing 50-85% bromine by weight. Hexabromocyclododecane [HBCD, C₁₂H₁₈Br₆] is the most widely used aliphatic BFR used primarily in polystyrene foams and thermal insulations in building materials. Secondary applications include use as an additive flame retardant for upholstery textiles. Tetrabromobisphenol A [TBBPA, C₁₅H₁₂Br₄O₂] is the highest volume production BFR on the market, and is a reactive flame retardant used in epoxy, vinyl esters and polycarbonate resins (printed circuit boards). TBBPA is also used in polystyrenes, phenolic resins, paper, and textiles. TBBPA is the parent compound of other commercial flame retardants, including tetrabromobisphenol A bis(allylether) [TBBPA-AE, C₂₁H₂₀Br₄O₂], and tetrabromobisphenol A bis(2, 3-dibromopropyl ether) [TBBPA-DBPE, C₂₁H₂₀Br₈O₂]. TBBPA-AE is an additive BFR in expanded polystyrene foams and paper and textile adhesives and coatings. TBBPA-DBPE is a unique flame retardant containing both aromatic and aliphatic bromine and is used as an additive BFR in polypropylene and styrenic-based resins. Both TBBPA-AE and TBBPA-DBPE are marketed commercially by major North American BFR manufacturers.

We have investigated a range of LC – tandem MS techniques for the determination of HBCD, TBBPA, and the two TBBPA derivatives. In cases where ESI did not afford sufficient ionization efficiency, we investigated alternate techniques including atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI).

Methods

Standards of α -, β -, and γ - HBCD, TBBPA and derivatives, and mass-labeled analogs were supplied by Wellington Laboratories (Guelph, ON). Experiments were conducted on a SciexQTrap hybrid triple quadrupole/linear ion trap mass spectrometer (Concord, ON) operated in negative ion mode. Standards were prepared in methanol and infused into the MS using a Harvard syringe pump at a flow rate of 5 μ L/min. LC separations were performed on an Agilent 1100 Series LC system (Mississauga, ON). HBCD isomers were separated on a Vydac 218MS polymeric reversed-phase HPLC column with a methanol:acetonitrile:water (60:20:20) mobile phase at a flow rate of 250 μ L/min. For the analysis of TBBPA compounds, the mobile phase was methanol:water with 10 mM ammonium acetate at a flow rate of 250 μ L/min.

Results and Discussion

Baseline separation of the HBCD diastereoisomers was achieved on the C₁₈ polymeric LC column. MS-MS detection employed multiple reaction monitoring (MRM) of the [M – H][–] (*m/z* 640.6) \rightarrow Br[–] (*m/z* 79 and 81) transition. [Figure 1]. We have previously applied this methodology for analysis of HBCD in both sediments and biota.^{1,2}

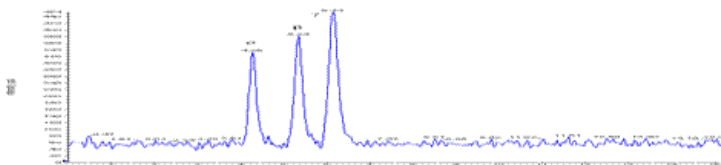


Figure 1. MRM chromatogram of α -, β -, and γ -HBCD separated on C₁₈Vydac column.

TBBPA exhibited excellent response in ESI negative ion mode through formation of the [M-H][–] ion. The MRM transition used for detection was [M – H][–] (*m/z* 542.9) \rightarrow Br[–] (*m/z* 79 and 81). [Figure 2]. This method is similar to that used by St. Louis and Pelletier for determination of TBBPA in sediments and sewage sludge.

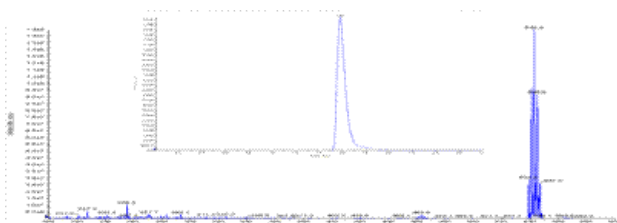


Figure 2. Q1 scan of TBBPA using ESI source in negative ion mode showing precursor ion $[M-H]^-$ and MRM chromatogram (insert) of $[M-H]^-$ (m/z 542.9) \rightarrow Br^- (m/z 79 and 81).

For TBBPA-AE, the predominant precursor ion was the cluster at $[M - C_3H_5]^-$ (m/z 582.9). [Figure 3]. MS-MS analysis monitored the $[M - C_3H_5]^-$ (m/z 582.9) \rightarrow m/z 526.9 transition corresponding to loss of the second allyl group.

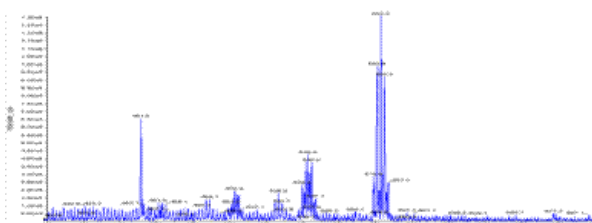


Figure 3. Q1 scan of TBBPA-AE using ESI in negative ion mode.

TBBPA-DBPE exhibited poor response under ESI conditions. Under negative ion APCI conditions, we obtained the precursor ion $[M+CH_3OH]^-$ (methanol adduct); however, we achieved limited sensitivity using MRM. Subsequently, we investigated negative ion APPI for analysis of the TBBPA compounds. This process uses a heated nebulizer to vaporize the sample prior to inducing ionization

by a beam of ultraviolet radiation in the presence of a dopant (toluene) as it passes through the ion source block into the interface region. Negative ion APPI resulted in fragmentation in Q1 to give a predominant ion at m/z 291, ($C_9H_8Br_2O^-$), for TBBPA and both the derivatives. A minor molecular ion was observed, except for TBBPA-DBPE where the molecular ion was not present. [Figures 4-6].

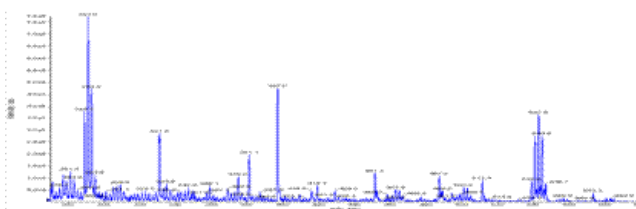


Figure 4. Q1 scan of TBBPA using APPI source in negative ion mode.

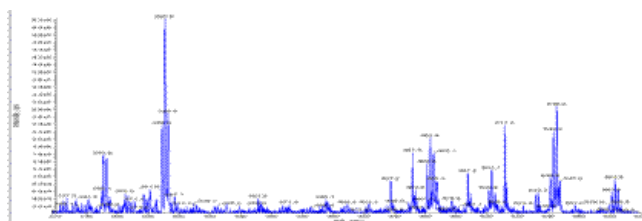


Figure 5. Q1 scan of TBBPA-AE using APPI source in negative ion mode.

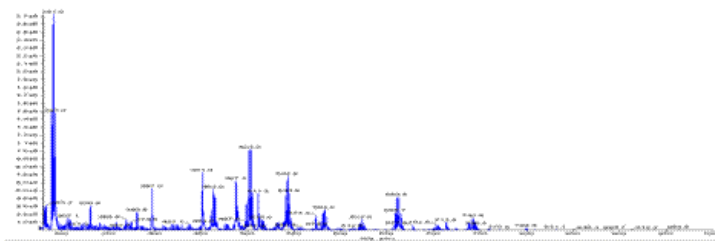


Figure 6. Q1 scan of TBBPA-DBPE using APPI source in negative ion mode.

Despite the physical and chemical similarities of some of the BFRs studied, these results show some compounds can exhibit substantial variations in ionization efficiency using different ionization techniques. We are currently applying these methods to environmental samples in order to assess relative performance, and for investigation of potential matrix effects.

References

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2. Tomy, G.T; Budakowski, W.R.; Halldorson, T.H.J.; Whittle, D.M.; Keir, M.J.; MacInnis, G.; Alae, M. and Marvin, C. (2004) Biomagnification of α - and γ - hexabromocyclododecane isomers in a Lake Ontario food web. *Environ. Sci. Technol.* 38: 2298-2303
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