Nota de aplicación

Analysis of Brominated Flame Retardants Using the AutoSpec Ultima NT

Clive Robinson, Anthony Newton, Ramesh Rao

Waters Corporation

Abstract

In this application note, brominated flame retardant compounds such as the PBDEs are analyzed using AutoSpec Ultima NT.

Introduction

Brominated flame retardants (BFRs) are the largest group of organic flame retardants currently in use. A key constituent of these materials are PBDEs, polybrominated diphenyl ethers, which are added to plastics to decrease the likelihood and intensity of fire in a wide variety of products, including vehicles, furniture, textiles, carpets, building materials, and electronic circuit boards. PBDEs are additive flame retardant compounds, being mixed (rather than chemically bonded) with polymers as plastics are being made and because they do not bind chemically with the plastic, they leach continuously out of the final product.

PBDEs are both lipophilic (they concentrate in lipids, or fats) and extremely resistant to physical, chemical, or biological degradation making them highly persistent in the environment and bio-accumulative. Environmental contamination occurs due to passive transport of PBDEs via water and air currents, but in addition PBDEs are also actively transported and dispersed because they are a prominent contaminant in sewage sludge, which is sprayed onto farmers' fields.

The toxic effects of PBDEs have not been fully determined, however several studies indicate that commercially obtained penta- and tetra-BDE are endocrine disrupters, which can exert effects on the thyroid system. The effects of penta-BDE on thyroxine and the thyroid gland are considered to be principally due to the induction of liver enzymes, although several mechanisms may operate. Tetra- and penta-BDEs are used in polyurethane and have been found to have high bioconcentration rates, while bioaccumulation of the octa- and deca-BDEs often used in electronics is currently thought to be less significant. The penta brominated diphenyl ether (penta-BDE) formulation will be banned in the European Union (EU) in 2003.

PBDEs now contaminate human milk and have also been found in human fatty tissue and in human blood serum. These compounds have also been found in multiple species of wildlife and in particular marine life, including sperm whales, indicating that the compounds have reached deep ocean waters.

Experimental

The most common BDE congeners found in biological samples are BDE-47 (2,2',4,4'-tetra BDE) and BDE-99 (2,2',4,4',5-penta-BDE), the structures are shown in Figure 1.

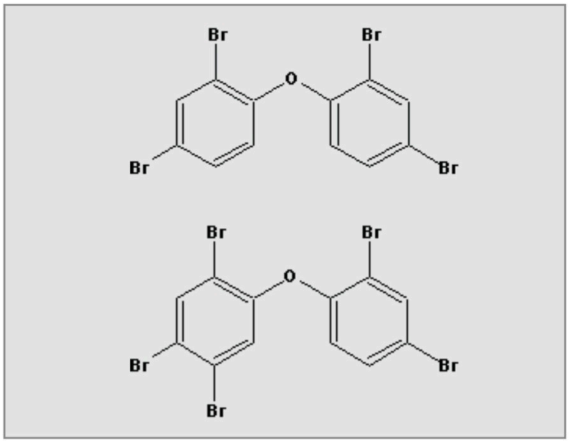


Figure 1. Structures of BDE-47 (2,2',4,4'-tetra BDE) and BDE-99 (2,2',4,4',5-penta BDE).

Analysis of PBDEs and other brominated flame retardant constituents in complex environmental matrices requires a selective, sensitive, and quantitative method of detection. High resolution GC-MS is the analytical method of choice for detection and quantification of PBDEs, elevated resolution being necessary to confirm the identity of individual ion clusters.[1] EI (electron impact) is the preferred ionization method, giving characteristic mass spectra containing M^+, $M\text{-}Br^+$ and $M\text{-}Br^{2+}$ ions. Negative ion chemical ionization (CI^-) is a less favorable approach, as Br^- and HBr dominate PBDE spectra, thus reducing selectivity.

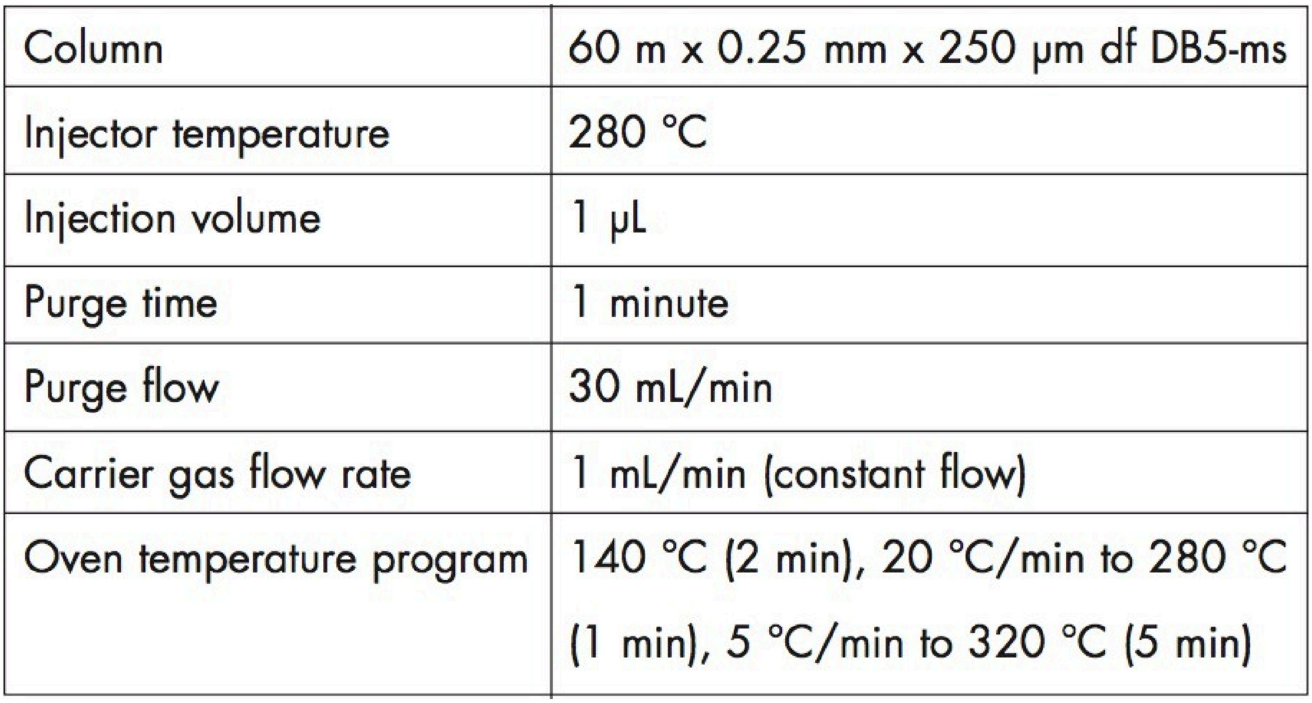
The sample used was a mixture of six PBDE congeners; tetra-brominated BDE 47, 66, and 77 and penta-brominated 85, 99, and 100.

To determine the quantitative linearity and estimate the limits of detection, standards were prepared from 25 fg/µL to 500 pg/µL and injected in triplicate.

Qualitative data was obtained using a 500 fg/µL mixed standard.

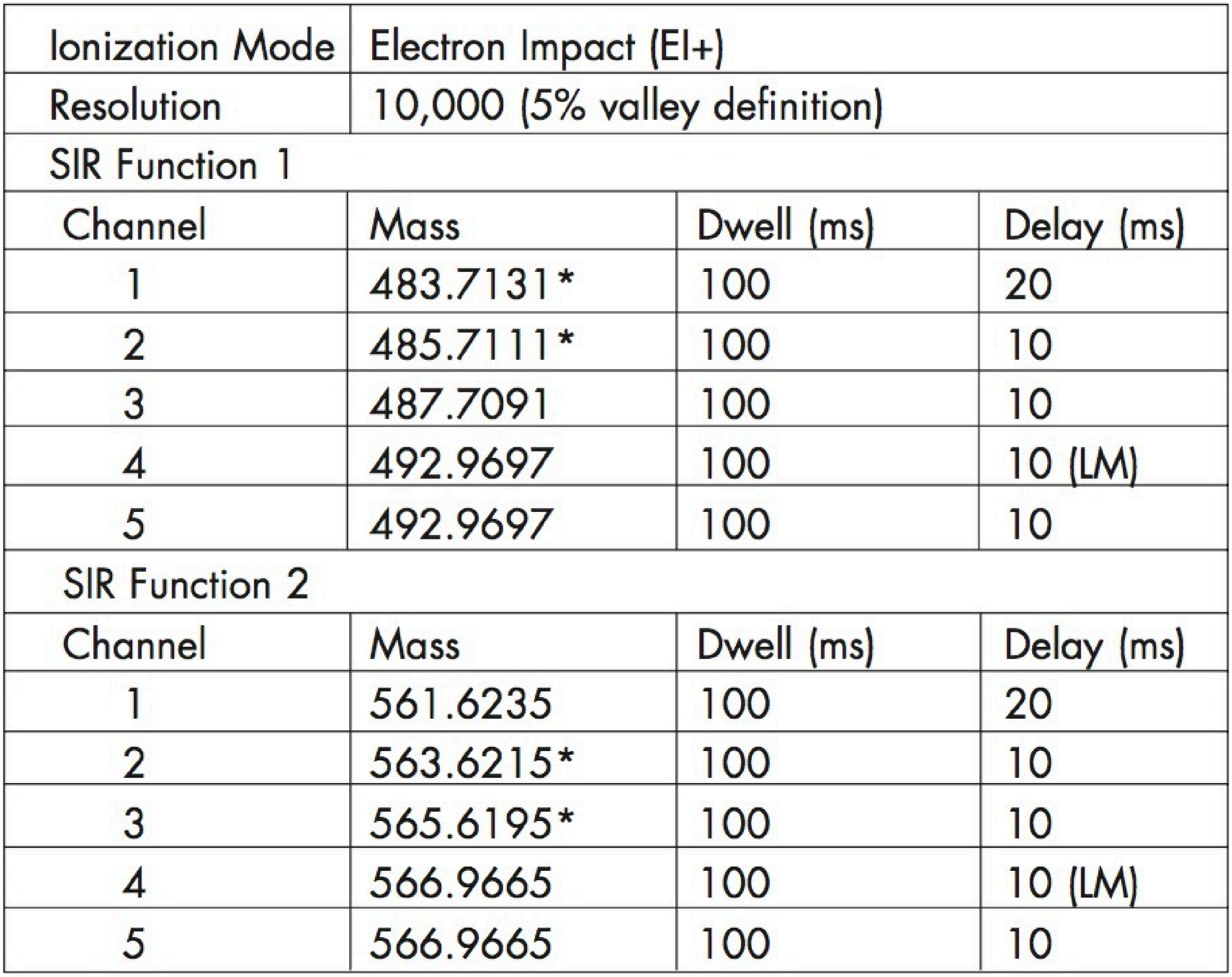
The exact mass measurement capability of the Waters Micromass AutoSpec Ultima NT was then used to confirm the identity of a higher molecular weight deca-brominated BDE using voltage scanning.

GC Conditions



Column	60 m x 0.25 mm x 250 μm df DB5-ms
Injector temperature	280 °C
Injection volume	1 μL
Purge time	1 minute
Purge flow	30 mL/min
Carrier gas flow rate	1 mL/min (constant flow)
Oven temperature program	140 °C (2 min), 20 °C/min to 280 °C (1 min), 5 °C/min to 320 °C (5 min)

MS Conditions

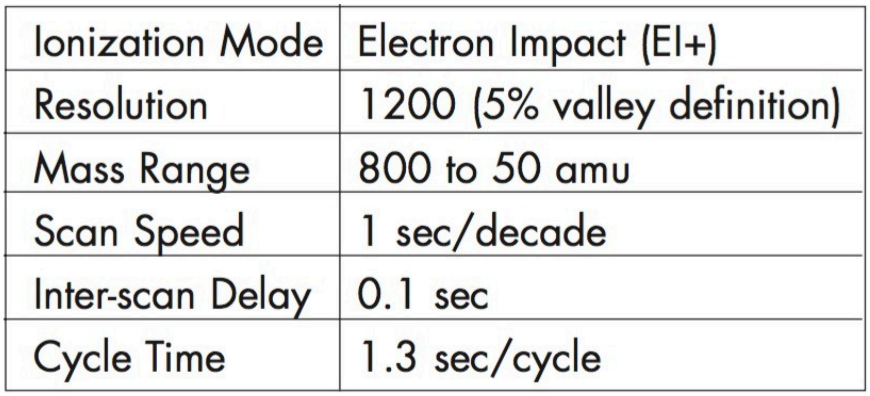


Ionization Mode	Electron Impact (EI+)		
Resolution	10,000 (5% valley definition)		
SIR Function 1			
Channel	Mass	Dwell (ms)	Delay (ms)
1	483.7131*	100	20
2	485.7111*	100	10
3	487.7091	100	10
4	492.9697	100	10 (LM)
5	492.9697	100	10
SIR Function 2			
Channel	Mass	Dwell (ms)	Delay (ms)
1	561.6235	100	20
2	563.6215*	100	10
3	565.6195*	100	10
4	566.9665	100	10 (LM)
5	566.9665	100	10

Quantitative Analysis: using Voltage SIR (Selected Ion Recording)

** indicates major/quantification ions*

Qualitative Analysis: using Magnet Scanning



Ionization Mode	Electron Impact (EI+)
Resolution	1200 (5% valley definition)
Mass Range	800 to 50 amu
Scan Speed	1 sec/decade
Inter-scan Delay	0.1 sec
Cycle Time	1.3 sec/cycle

Results and Discussion

The full scan spectrum of penta-brominated BDE 99 is shown in Figure 1. The spectra of the BDEs all show isotope patterns characteristic of brominated compounds. Figure 2 shows an expanded view of the molecular ion region of the spectrum of BDE 99 (bottom) and the theoretical isotope pattern generated by MassLynx isotope modelling (top). A characteristic of magnetic sector instruments is the mass spectral quality and it can be seen that the isotope ratios in the acquired spectrum are almost identical to the theoretical; Figure 3 shows the same for the tetra-brominated BDE 47.

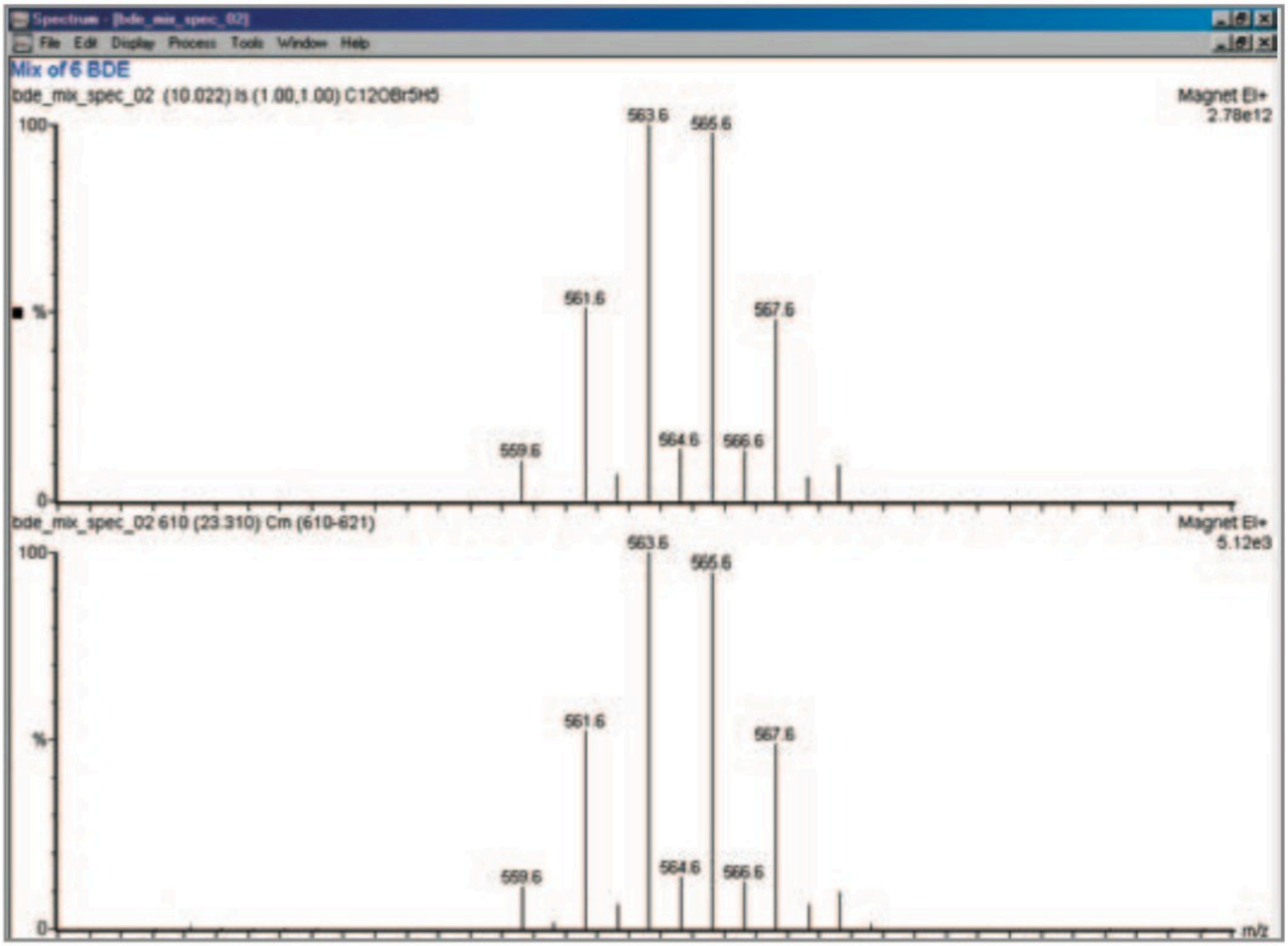


Figure 2. Comparison of acquired and theoretical isotope ratios for BDE 99.

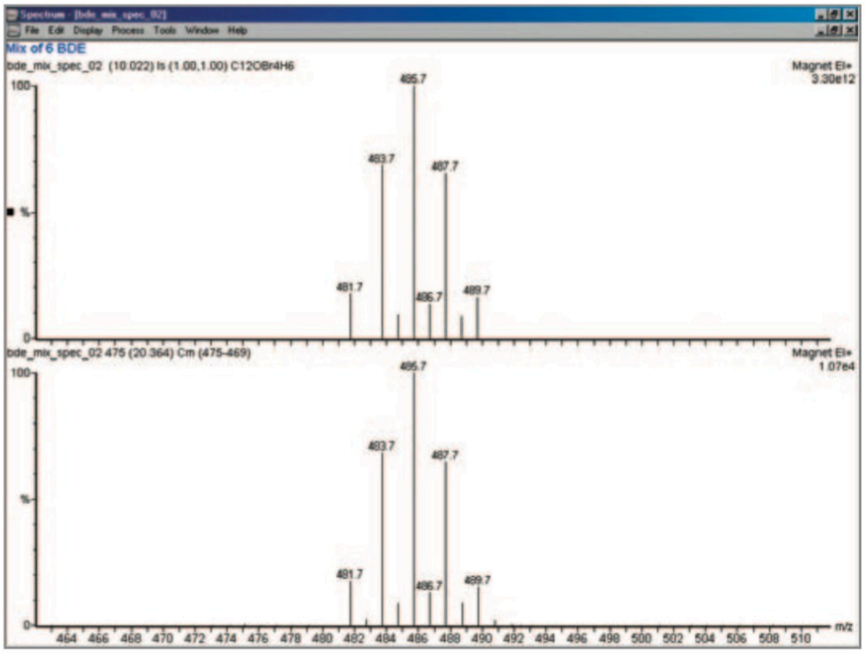


Figure 3. Comparison of acquired and theoretical isotope ratios for BDE 47.

Figure 4 and 5 show the full scan mass spectra of BDE 77 (non-ortho) and BDE 47 (ortho). The spectrum of BDE 47 shows less loss of Br_2 from the molecular ion than BDE 77 due to the spatial separation of the Br atoms in the molecule.

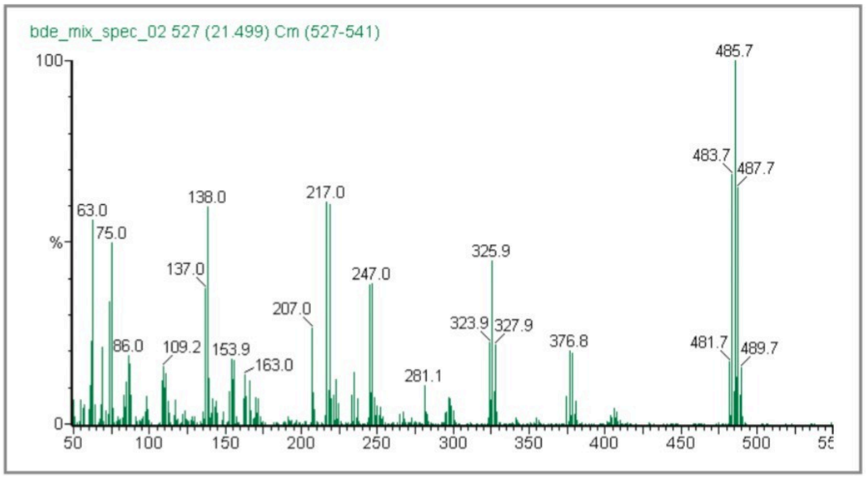


Figure 4. EI+ spectrum of BDE 77 (non-ortho).

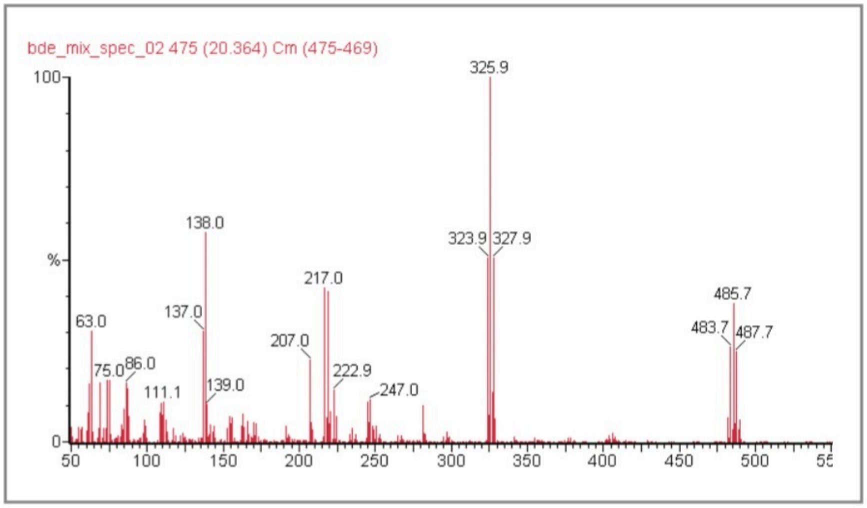
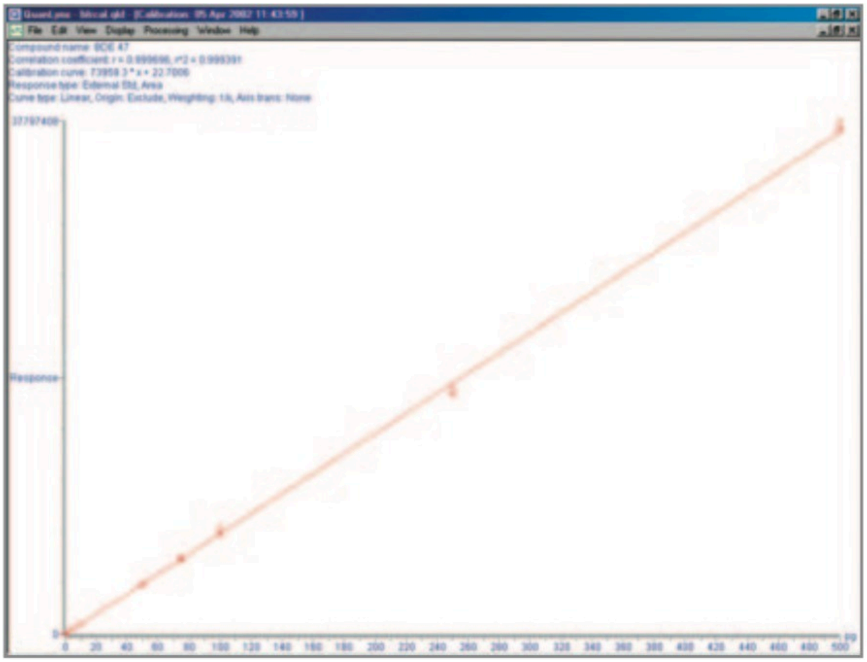


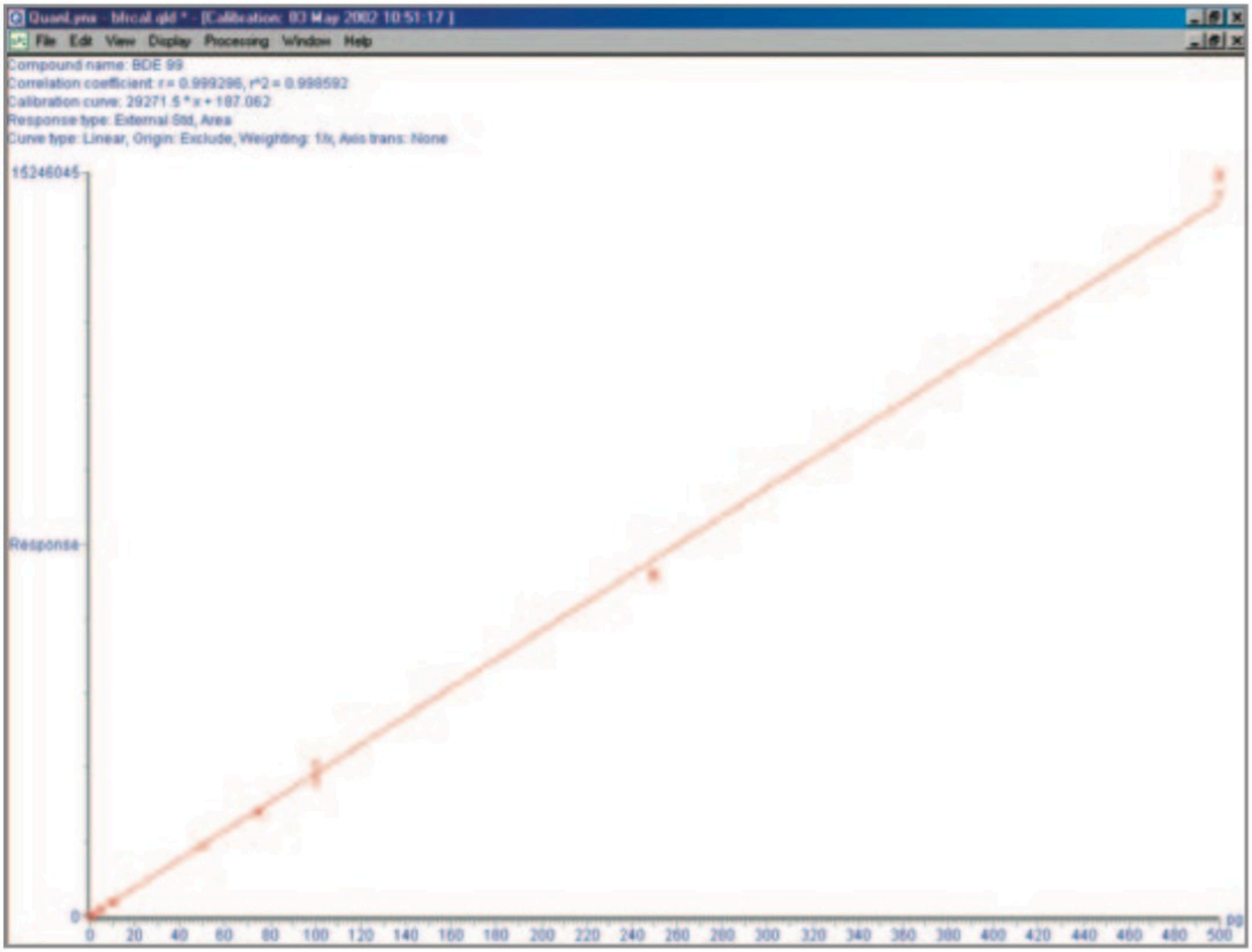
Figure 5. EI+ spectrum of BDE 47 (ortho).

Figures 6 and 7 show calibration curves for BDE 47 and BDE 99 from 25 fg to 500 pg. Excellent sensitivity and linearity was observed for all congeners and all data points met the isotope ratio criteria of ±15% of theoretical on the 2 major ions for each brominated group.



Compound name: BDE 47
Correlation coefficient: r = 0.999696, r^2 = 0.999391
Calibration curve: 73958.3 * x + 22.7006
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

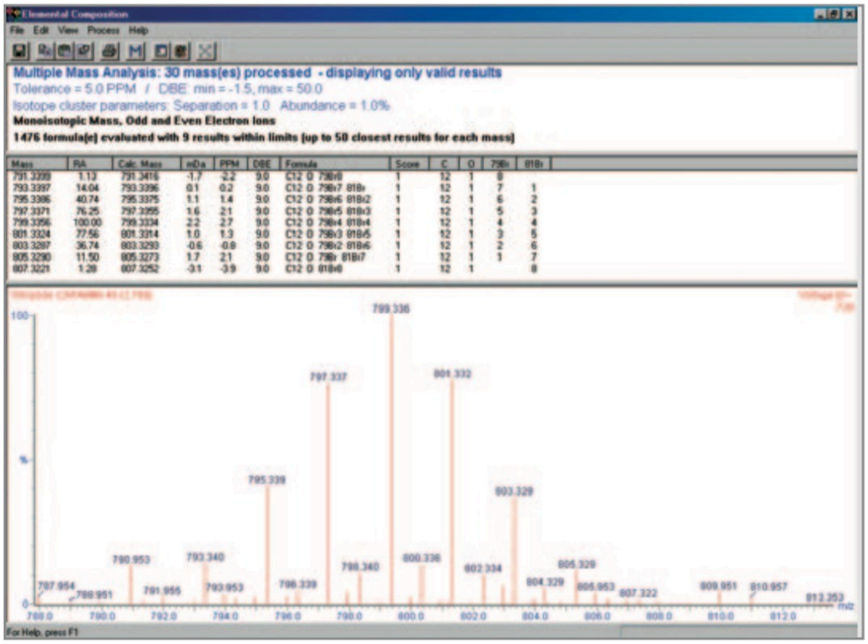
Figure 6. Calibration curve for BDE 47, 25 fg to 500 pg.



Compound name: BDE 99
Correlation coefficient: r = 0.999296, r^2 = 0.998592
Calibration curve: 29271.5 * x + 187.062
Response type: External Std, Area
Curve type: Linear, Origin: Exclude, Weighting: 1/x, Axis trans: None

Figure 7. Calibration curve for BDE 99, 25 fg to 500 pg.

Figure 8 is the molecular ion region of the exact mass spectrum obtained using voltage scanning of decabrominated BDE with the calculated elemental composition of the isotopes. The deca-brominated BDE shows a loss of Br_2, which corresponds to the elemental composition results. The exact mass measurement capability of the AutoSpec Ultima NT is illustrated by the mass accuracy results, which were calculated to be 2.1 ppm RMS.



Multiple Mass Analysis: 30 mass(es) processed - displaying only valid results
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%
Monoisotopic Mass, Odd and Even Electron Ions
1476 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)

Mass	RA	Calc. Mass	mDa	PPM	DBE	Formula	Score	C	O	79Br	81Br
791.3399	1.13	791.3416	-1.7	-2.2	9.0	C12 O 79Br8	1	12	1	8	
793.3397	14.04	793.3396	0.1	0.2	9.0	C12 O 79Br7 81Br	1	12	1	7	1
795.3386	40.74	795.3375	1.1	1.4	9.0	C12 O 79Br6 81Br2	1	12	1	6	2
797.3371	76.25	797.3355	1.6	2.1	9.0	C12 O 79Br5 81Br3	1	12	1	5	3
799.3356	100.00	799.3334	2.2	2.7	9.0	C12 O 79Br4 81Br4	1	12	1	4	4
801.3324	77.56	801.3314	1.0	1.3	9.0	C12 O 79Br3 81Br5	1	12	1	3	5
803.3287	36.74	803.3293	-0.6	-0.8	9.0	C12 O 79Br2 81Br6	1	12	1	2	6
805.3290	11.50	805.3273	1.7	2.1	9.0	C12 O 79Br 81Br7	1	12	1	1	7
807.3221	1.28	807.3252	-3.1	-3.9	9.0	C12 O 81Br8	1	12	1		8

Figure 8. Exact mass measurement of deca-BDE with elemental composition calculations.

Conclusion

Analysis of Brominated Flame Retardant compounds such as the PBDEs requires gas chromatography coupled with the selectivity, sensitivity and dynamic range of high resolution mass spectrometry. The AutoSpec Ultima NT provides unmatched performance for this analysis.

References

1. Alaee, M. *et al*, Determination of Brominated Diphenyl Ethers in Environmental Matrices, Proc. 46th *ASMS Conf. Mass Spectrom*. Allied Topics, Orlando, FL, May 31-June 4, 1998, page 739.

Featured Products

MassLynx MS Software <https://www.waters.com/513662>

720000270, August 2003