Improvements to the Analysis of PBDEs in Environmental Matrices: Transitioning from EI Magnetic Sector to GC-APCI TQ MS/MS

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Introduction

The benefits of polybrominated diphenyl ether flame retardants (PBDEs) are outweighed by their risks to human and environmental health, therefore, efforts have been made to ban their production through national regulations and international treaties[1,2]. Due to the serious consequences of non-compliance with these laws, the analytical methods to support this testing were implemented using magnetic sector-based GC HRMS with electron ionization (EI) because of its long history of sensitive, high specificity performance. For over a decade now advancements in atmospheric pressure ionization for GC-MS/MS have proven the ability of GC-APCI to meet or exceed the performance of EI GC HRMS based methods. This work investigates the potential for modernization of PBDE analysis using GC-APCI MS/MS and nitrogen carrier gas.

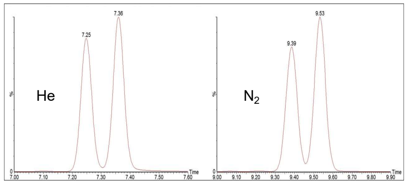

Figure 1. Separation of BDE 49 and BDE 71

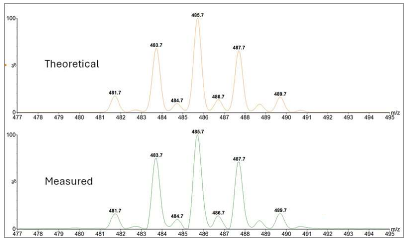

Figure 2. Theoretical and measured isotope ratios for BDE 49

Experimental

Sample and standard preparation was performed at Quebec Laboratory for Environmental Testing (QLET) with aliquots of each sent to Waters' Milford, MA lab for analysis.

MS: Xevo^{TM} TQ Absolute Mass Spectrometer
APGC^{TM} Ionization, positive ion, charge exchange
Corona pin: 1.0 µA   Source: 150 °C
Cone gas: 260 L/hr   Aux gas: 200 L/hr
Makeup gas: 350 L/hr   GC: 8890
Column: Rtx-1614, 15 m x 0.25 mm x 0.10 µm film
Inj: 1 µL @ 260 °C, pulsed splitless, 20 psi 1.2 min

Carrier Gas Program: Nitrogen

Flow Ramp Rate (mL/min/min)	Flow (mL/min)	Hold Time (min)
Initial	0.8	0
0.20	2.1	0
2.0	4.1	20

Temperature Program:

Ramp Rate(°C/min)	Temperature (°C)	Hold (min)
Initial	110	0
30	190	0
3	220	0
20	280	3
30	310	7
		27 min total

Standard and QC Concentrations (ppb):

	SE0	SE1	SE2	SE3	SE4	Low QC	Mid QC	High QC
Tris	0.04995	0.504	5.04	25.08	100.2	1	49.5	99.75
Tetras	0.04995	0.504	5.04	25.08	100.2	1	49.5	99.75
Pentas	0.04995	0.504	5.04	25.08	100.2	1	49.5	99.75
Hexabromobiphenyl	0.0999	1.008	10.1	50.16	200.4	2	99	199.5
Hexas	0.0999	1.008	10.1	50.16	200.4	2	99	199.5
Heptas	0.0999	1.008	10.1	50.16	200.4	2	99	199.5
Octas	0.0999	1.008	10.1	50.16	200.4	2	99	199.5
Nonas	0.24975	2.52	25.2	125.4	501	5	247.5	498.75
Deca	0.24975	2.52	25.2	125.4	501	5	247.5	498.75

Discussion

A potential improvement to the chromatography included in this study was the use of nitrogen carrier gas instead of helium. This change would make the method less susceptible to disruptions caused by recurring He supply chain interruptions and price fluctuations. Although adapting to N_2 carrier often depends on scaling column dimensions, our workflow achieved equivalent separation performance through N_2 carrier gas ramping (Fig. 1), yielding runtimes comparable to the He based reference method. Because increased flowrate decreases the elution temperature for an analyte, this approach also decreases the likelihood of on-column degradation of BDE 209[3]. The last eluting peak, BDE 209, elutes at 24.7 min in the reference method and 21.8 min with good symmetry in the N_2 method. This required N_2 flow of up to 4.1 mL/min which is incompatible with conventional EI GC-MS.

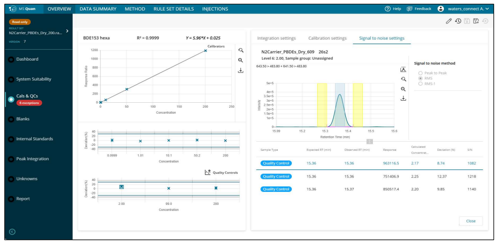

Figure 3. waters_connect for Quantitation results for BDE 153 at 2ppb

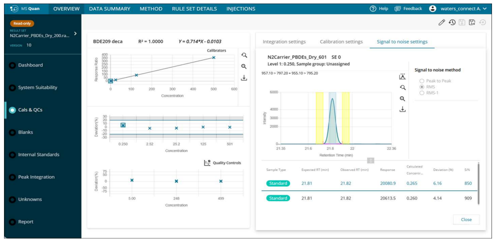

Figure 4. waters_connect for Quantitation results for BDE 209 at 0.25ppb

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Up to 6 MRM transitions per analyte were used. All analytes have multiple naturally occurring isotopic precursor masses of significant relative abundance (Fig 2). The inclusion of multiple MRM transitions results in an acquisition method is potentially more versatile across different sample prep methods and matrices. Furthermore, waters_connect^{TM} for Quantitation Software allows summing of MRMs which can improve signal-to-noise of measurements made near the instrument detection limit (Fig 3, 4). An average r^2 value of >0.999 was achieved for all analytes across >3 orders of magnitude. The 4 labeled recovery standards had an average %RSD <10%. The 6 labeled ISs had an average %RSD of <3%. High, mid and low level QCs (n=3) were prepared and evaluated for precision and accuracy. Precision for all analytes at all levels was within 15% RSD versus a method limit of 20% (Fig 5). All were within <10% after exclusion of outliers (BDEs 196, 197, 206, 207). All calculated concentrations for all QC levels were within method limits, 70 – 130%, with the exception of BDEs 196, 197 and 207 which each fell outside this range in two injections of the lowest level QC.

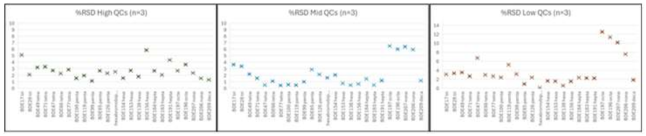

Figure 5. High, Mid and Low concentration QCs precision

Conclusions

- An all-nitrogen GC-APCI TQ configuration was successfully able to perform the analysis of PBDEs within performance criteria established for an EI GC HRMS reference method
- Nitrogen carrier gas flow ramping eliminated the need for column scaling while maintaining the same chromatographic resolution of critical isomer pairs and total runtime
- The faster acquisition rate of TQ versus magnetic sector creates the possibility for future consolidation of PDBE analysis with other (regrettable replacement) halogenated flame retardants without loss of performance

References

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Conflict of Interest Disclosure

The authors declare no competing financial interest.

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