Fast, ultra-sensitive analysis of PBDEs in food using advanced GC-MS/MS technology

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Keywords

Food safety, polybrominated diphenyl ethers (PBDEs), trace analysis, gas chromatography, triple quadrupole mass spectrometry, selective reaction monitoring (SRM), sensitivity, routine, TSQ 9000, advanced electron ionization (AEI), Chromeleon, isotope dilution

Goal

The aim of the study was to assess the quantitative performance of the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system equipped with the advanced electron ionization (AEI) source for the analysis of polybrominated diphenyl ethers (PBDEs) in food at low concentrations.

Introduction

PBDEs are a class of brominated hydrocarbons with a basic structure containing two phenyl rings linked by an oxygen atom. There are 209 possible PBDE congeners that differ in the number and location of bromine atoms in the phenyl rings.

PBDEs are used as additive flame retardants in different materials such as plastics, textiles, upholstery, and circuitry that can leach into the environment where they persist and bioaccumulate.[1] As a consequence, the use of certain toxic PBDEs with links to cancer (including penta, tetra, and deca BDE) have been banned, and are currently listed in the Stockholm Convention inventory of persistent organic pollutants.[2]

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The major challenges for PBDE analysis are sensitivity and selectivity in complex matrices, chromatographic resolution of critical pairs, degradation of higher brominated compounds, and the cost per sample. Gas chromatography-high resolution mass spectrometry (GC-HRMS) is the analytical technique of choice for PBDE determination in food, and triple quadrupole GC-MS/MS instrumentation in particular has recently become popular for this application due to its high selectivity and sensitivity provided through selective reaction monitoring (SRM) acquisition mode. High selectivity and sensitivity are required to (i) reduce interferences from matrix and background chemical ions that can result in false positive detection and erroneous quantification of PBDEs and (ii) detect ultra-trace levels of these toxic compounds in complex matrices.

The chromatographic resolution of the critical pair (BDE-49 and BDE-71) in PBDE analysis is essential because many of the congeners are isobaric and share common SRM transitions, meaning chromatographic separation is a necessity. For this reason reported methods have low sample throughput with analysis times of up to 45 minutes on costly capillary columns typically of 60 m in length.[3] In this study a new high efficiency, high selectivity 15 m Thermo Scientific™ TraceGOLD™ TG-PBDE capillary column was evaluated for increased sample throughput and reduced cost per sample.

The aim of this project was to evaluate the analytical performance of the TSQ 9000 GC-MS/MS system using the AEI source for the ultra-trace analysis and separation of PBDEs in food matrices. This was attempted using a fast, sensitive, selective method on the high efficiency TraceGOLD TG-PBDE capillary column. The following analytical performance criteria were evaluated: sensitivity, repeatability, linearity, limit of quantification, and the accuracy of measurements in matrix.

The assessment of system robustness and suitability for routine PBDE GC-MS/MS analysis, which was outside the scope of this application note, can be found in a supporting 2018 technical note.

Experimental

Preparation of solvent calibration curve, instrument detection limit (IDL), and limit of quantification (LOQ) standards

Calibration standards containing 27 native PBDE congeners at five concentration levels (Table 1, Appendix), and 16 (^{13}C labeled) PBDEs internal standards (Table 2, Appendix), were acquired from Wellington Laboratories, Inc. (Ontario, Canada).

For the calculation of IDLs and LOQs for individual BDE congeners, the lowest concentration standard was serially diluted with *n*-nonane to 0.5, 0.25, 0.1, 0.075, and 0.05 pg/µL for BDE-209 ready for repeat injections.

Preparation of samples

Sample preparation was performed according to that described in a scientific paper by A. Fernandes et al.[3] The procedure involves sample homogenization/freeze drying, fortification of 10 g of homogenized/freeze-dried sample in 200 mL of *n*-hexane with isotopically labeled ^{13}C PBDE internal standards followed by loading onto a multi-packed silica column containing acidified silica, basified silica, and activated charcoal. PBDEs were then eluted from the multi-packed silica/activated carbon column using 100 mL of *n*-hexane and 400 mL of *n*-hexane/dichloromethane (60:40, v:v) then evaporated to dryness and reconstituted to 0.5 mL in *n*-hexane. The extracts were cleaned further using a silica alumina column and 20 mL of DCM/*n*-hexane (30:70) followed by the addition of ^{13}C-labeled PBDE syringe standards, evaporation, and reconstitution to 25 µL with *n*-nonane prior to analysis.

GC-MS/MS analysis

A TSQ 9000 triple quadrupole GC-MS/MS instrument equipped with an AEI source and coupled with a Thermo Scientific™ TRACE™ 1310 gas chromatograph was used. The AEI source provides highly efficient electron ionization of analytes and a more tightly focused ion beam that leads to an unparalleled level of sensitivity.

Liquid injections of the sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH autosampler, and chromatographic separation was achieved using a TraceGOLD TG-PBDE 15 m × 0.25 mm I.D. × 0.10 µm film capillary column (P/N 26061-0350). Additional details of the instrument parameters are displayed in Tables 3 and 4. Full details of all consumables used are available from the Thermo Scientific™ AppsLab™ Library of Analytical Applications.

Table 3. Gas chromatograph and injector conditions. The full list of consumables and instrument conditions, including SRM transitions, are available from the AppsLab library.

TRACE 1310 GC Parameters	
Injection volume:	2.0 µL
Liner:	PTV 6 baffle liner 2.0 mm × 2.75 mm × 120 mm (Thermo Scientific™ LinerGOLD™ GC Liner) (P/N 453T2845-UI)
Inlet:	65 °C
Inlet module and mode:	PTV, cold splitless
Transfer delay:	0.2 min
Injection time:	0.1 min
Transfer rate:	5.0 °C/s
Transfer temp.:	330 °C
Transfer time:	5 min
Cleaning rate:	14.5 °C/s
Cleaning temp:	330 °C
Carrier gas:	He, 1.5 mL/min
Oven Temperature Program	
Temperature 1:	100 °C
Hold time:	2.0 min
Temperature 2:	340 °C
Rate:	30 °C/min
Hold time:	3 min
Total GC run time:	13 min

Table 4. Mass spectrometer conditions

TSQ 9000 AEI Mass Spectrometer Parameters	
Transfer line:	300 °C
Ion source (Ionization type):	AEI (EI)
Ion source:	300 °C
Electron energy:	50 eV
Emission current:	50 µA
Gain amplification:	×7
Acquisition modes:	Timed-SRM
Q1 & Q3 resolution:	mono-hepta BDE normal (0.7 amu) octa-deca BDE wide (1.2 amu)
Tuning parameters:	AEI SmartTune
Collision gas, pressure:	Argon, 70 psi

Data processing

Data were acquired using timed-SRM mode, processed and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2, which allows instrument control, method development, quantitative/qualitative analysis, and customizable reporting all within one platform (Figure 1, Appendix).[4] This application highlights use of isotope dilution software processing features implemented Chromeleon CDS from version 7.2.9 onwards.

Results and discussion

PBDE chromatography, selectivity, sensitivity in terms of IDLs, LOQs in sample, and linearity were evaluated using solvent-based standards. Extracted food samples were obtained from Fera Science, Ltd., York and were used in the experiments described below.

Chromatography

All target congeners were separated in under 11 minutes including excellent separation of the critical pair BDE-49 and BDE-71 (Figure 2). Resolution of these compounds was 0.6% based on valley height relative to the height of the shortest peak, which is well within the EPA 1614 requirement of less than 40%.[5] Compared with existing GC-HRMS methods (~45 min run times), this will allow for the analysis of up to 100 samples per day (compared to 30 in a published paper) giving an increase in sample throughput of 3× and a significant reduction in cost per sample.[3] Using the TG-PBDE capillary column, good chromatographic peak shape was obtained for all compounds (Figure 2), even for BDE-209, which is particularly challenging for this analysis due to susceptibility to breakdown and peak tailing.

Selectivity

Due to the diversity of matrices with various degrees of complexity, selectivity can be challenging in routine GC-MS analysis. An example of sample complexity is shown in Figure 3 as an overlay of the TIC of fish containing incurred residues (top chromatogram) and of timed SRM (bottom chromatogram) showing target PBDEs.
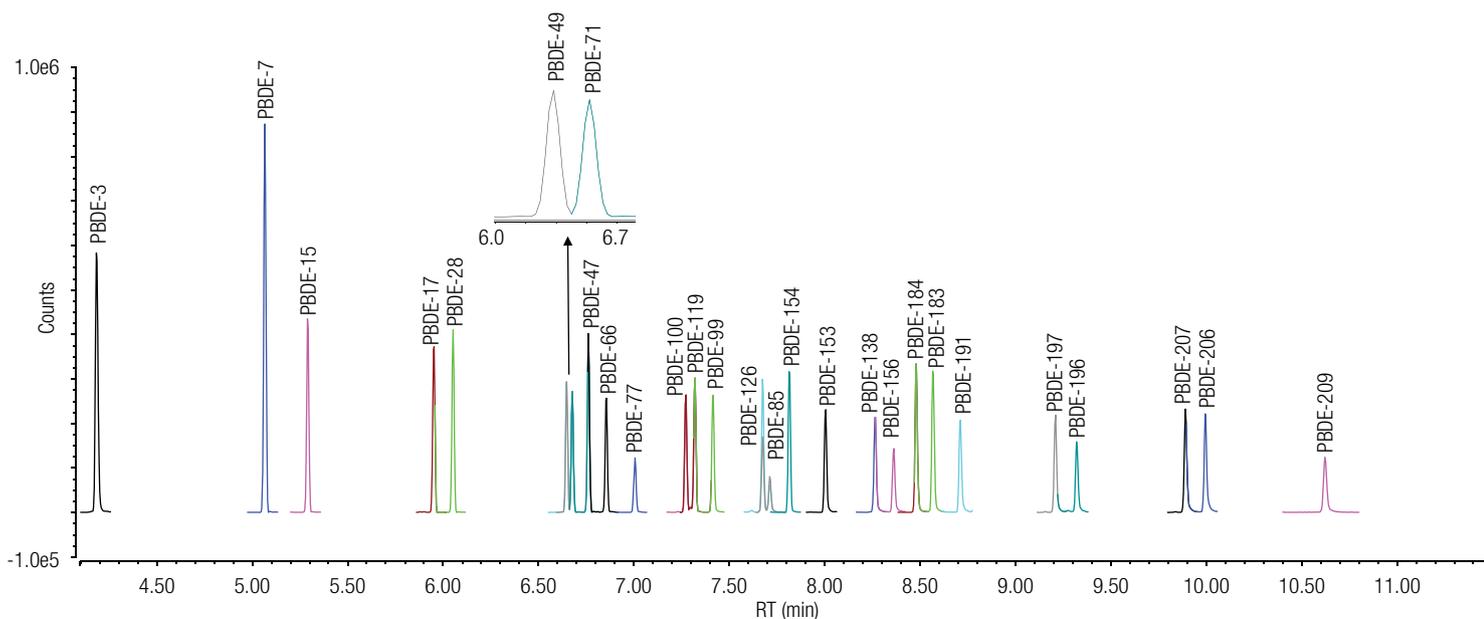

Figure 2. Chromatogram showing the SRM transition (quant ion) for PBDEs in a 1–5 pg/µL solvent standard (CS-1) (equivalent to 2.5–12.5 ng/kg in sample) with excellent chromatographic peak shapes for all compounds. ^{13}C-labeled internal and syringe standards were not displayed to show native peak shapes clearly.
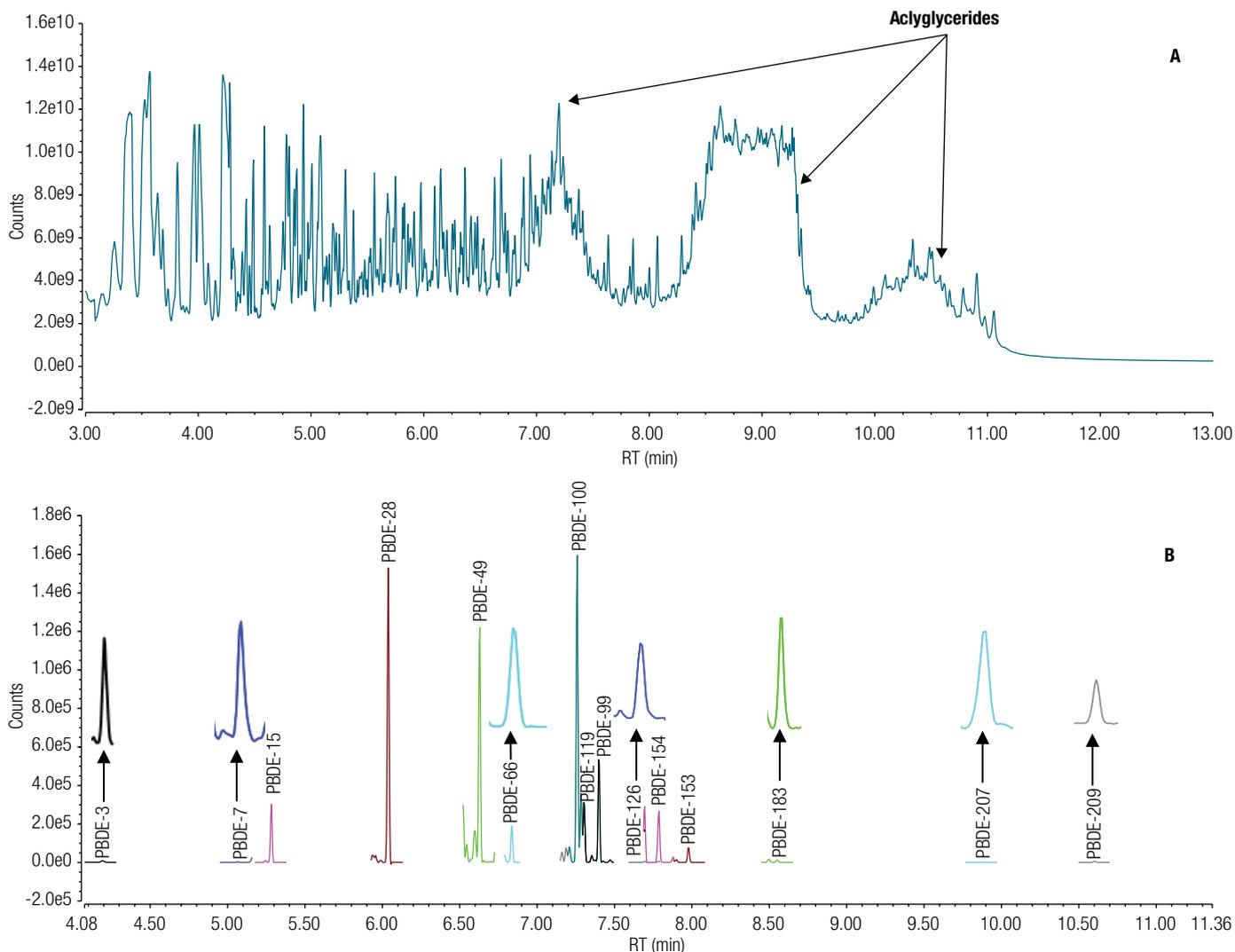
Figure 3. (A) Extracted fish matrix TIC acquired in full-scan containing late eluting acylglycerides (top chromatogram) and (B) corresponding timed-SRM for quant ion of targeted PBDEs (bottom chromatogram)

Carryover assessment

Carryover can be a problem for this application; however, it was found that using a mixed needle wash solvent of dichloromethane/toluene/n-nonane (50:25:25) eliminated this potential problem. In Figure 4 an example SRM transition of the highest concentration injected standard for BDE-209 (2000 pg/µL, 4 ng on column (oc)) (top chromatogram) and the consecutive n-nonane blank (bottom chromatogram) demonstrates that there is no carryover.

Sensitivity: determination of IDLs

The enhanced sensitivity of the new AEI source is demonstrated for the most challenging compound analyzed, BDE-209 (Figure 5). Here a 250 fg/µL (500 fg oc) solvent standard shows excellent signal precision with peak area repeatability <10% RSD at low ppt levels (equivalent to 0.6 ng/kg) in sample extracts). Excellent peak shape was also observed for this high molecular weight compound (MW = 959.2), which is due to the thin film and excellent surface deactivation of the TG-PBDE column coupled with the highly uniform heating profile of the newly designed TSQ 9000 GC-MS/MS system transfer line. These factors result in less peak tailing for low volatility, high boiling compounds such as higher brominated PBDEs and make accurate integration possible.
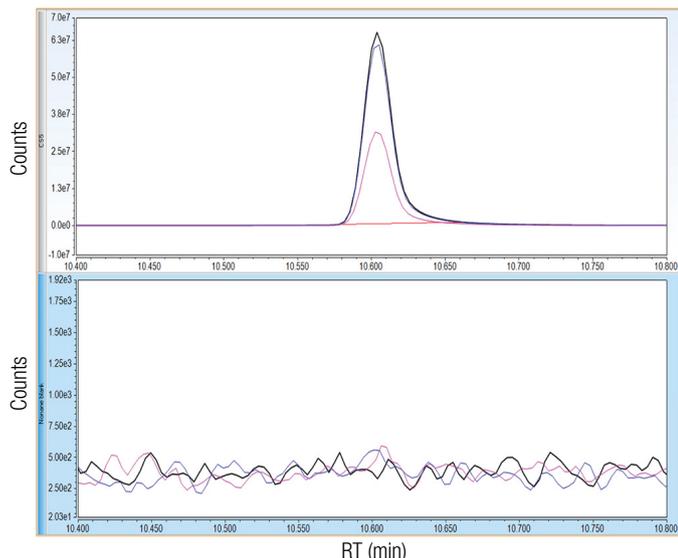
Figure 4. BDE 209 overlaid quantification ion and qualification ions for the highest standard in *n*-nonane/ toluene 2000 pg/µL corresponding to 4 ng on-column (OC) (top chromatogram) and a consecutive *n*-nonane blank (bottom chromatogram). Data is unsmoothed and was acquired in timed-SRM mode.
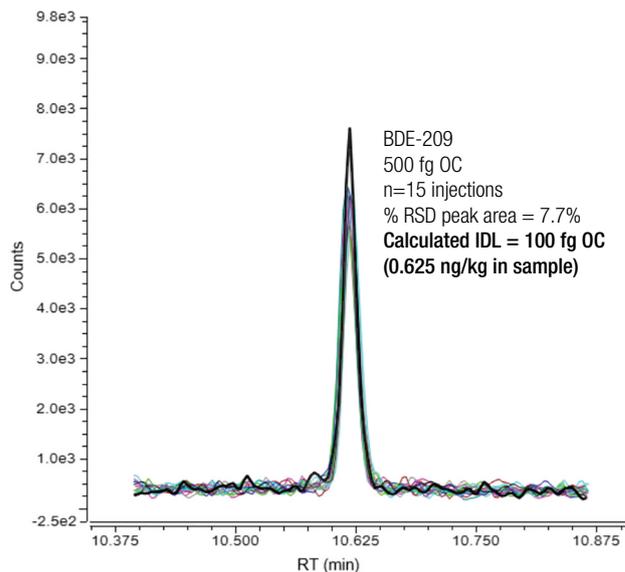

Figure 5. Overlaid quantification SRM transitions (797.3→637.3 *m/z*) from n=15 consecutive injections of a 250 fg/µL BDE-209 solvent standard (corresponding to 0.625 ng/kg in sample). No data smoothing was used and data was acquired in timed-SRM mode.

To practically assess the IDLs n=15 replicate injections of the lowest serially diluted solvent standard with a peak area % RSD of <15% was used. IDLs were then calculated by taking into account the injected amount, peak area % RSD, and t-score of 2.624, corresponding to n=14 degrees of freedom at 99% confidence level (Figure 6). The IDL values calculated ranged from 2 to 100 fg OC (corresponding to 0.003–0.125 ng/kg in sample).

Sensitivity: determination of limit of quantitation (LOQ)

Method LOQs were calculated using serially diluted calibration standards described in the IDL section. Fifteen replicate injections of each of the diluted standards ranging between 0.02 pg/µL and 0.25 pg/µL were performed (equivalent to 0.05–0.63 ng/kg in sample (Table 6).

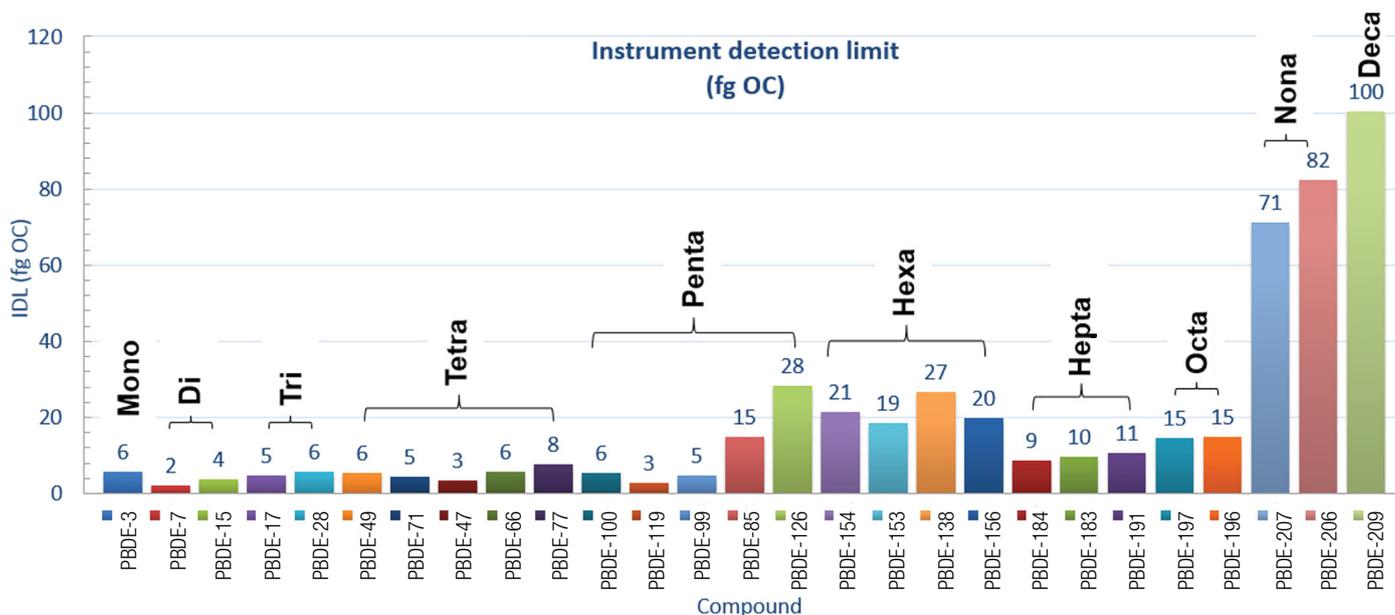Figure 6. Graph showing individual IDLs in fg on column for 27 native PBDEs calculated from n=15 replicate injections of the lowest serially diluted standards

Table 6. Calculated equivalent LOQ concentration in sample from fifteen injections of solvent standards

BDE Number	Bromination No*	Quantification Transition	Amount Injected (pg OC)	Target Ion Ratio %	Mean Measured Ion Ratio (Average) %	Peak Area % RSD	LOQ (pg OC)	LOQ (ng/kg)
BDE-3	Mono	250→115	0.04	60	62	5.6%	0.04	0.05
BDE-7	Di	326→139	0.04	15	15	3.6%	0.04	0.05
BDE-15	Di	326→139	0.10	48	49	3.6%	0.10	0.13
BDE-17	Tri	406→139	0.04	95	93	5.9%	0.04	0.05
BDE-28	Tri	406→139	0.04	79	78	6.4%	0.04	0.05
BDE-49	Tetra	484→217	0.10	34	34	3.3%	0.10	0.13
BDE-71	Tetra	484→217	0.10	33	34	4.1%	0.10	0.13
BDE-47	Tetra	484→217	0.10	36	36	4.3%	0.10	0.13
BDE-66	Tetra	484→217	0.10	30	31	5.0%	0.10	0.13
BDE-77	Tetra	484→217	0.10	115	112	7.0%	0.10	0.13
BDE-100	Penta	564→404	0.10	85	74	4.1%	0.10	0.13
BDE-119	Penta	564→404	0.10	48	48	3.8%	0.10	0.13
BDE-99	Penta	564→404	0.10	62	57	3.0%	0.10	0.13
BDE-85	Penta	564→404	0.10	60	56	5.7%	0.10	0.13
BDE-126	Penta	564→404	0.20	122	131	7.1%	0.20	0.25
BDE-154	Hexa	642→482	0.20	66	64	8.1%	0.20	0.25
BDE-153	Hexa	642→482	0.20	65	57	7.3%	0.20	0.25
BDE-138	Hexa	642→482	0.20	68	63	8.0%	0.20	0.25
BDE-156	Hexa	642→482	0.20	70	74	8.7%	0.20	0.25
BDE-184	Hepta	721→564	0.20	46	46	6.3%	0.20	0.25
BDE-183	Hepta	721→564	0.20	47	49	4.3%	0.20	0.25
BDE-191	Hepta	721→564	0.20	48	47	5.0%	0.20	0.25
BDE-197	Octa	642→482	0.20	48	48	4.0%	0.20	0.25
BDE-196	Octa	642→482	0.20	61	64	5.8%	0.20	0.25
BDE-207	Nona	879→721	0.50	52	53	5.4%	0.50	0.63
BDE-206	Nona	879→721	0.50	60	49	6.3%	0.50	0.63
BDE-209	Deca	797→637	0.50	100	96	7.7%	0.50	0.63

The criteria used to assess individual PBDE LOQs were:

- Ion ratios within ±30 % of the expected values calculated as an average across a calibration curve ranging from 5 to 2000 pg/µL (BDE-209) (corresponding to 12.5–5000 ng/kg in extracted fat)

- Peak area repeatability of <15 % RSD

- Relative response factor (RRF) within ± 30% of that calculated from the average of the calibration

Linearity

Linearity was determined using solvent standards at concentrations 1–400 pg/µL for mono-penta PBDEs, 2–800 pg/µL for hexa-octa PBDEs, and 5–2000 pg/µL nona-deca PBDEs. The calibration of each PBDE was performed using average calibration factor (AvCF) and isotopic dilution functions in Chromeleon CDS with triplicate injections at each concentration (Figure 8).

All compounds show excellent linear responses with coefficients of determination R^2 >0.98, and average RRF % RSD across the calibration range being <10% (Table 7).
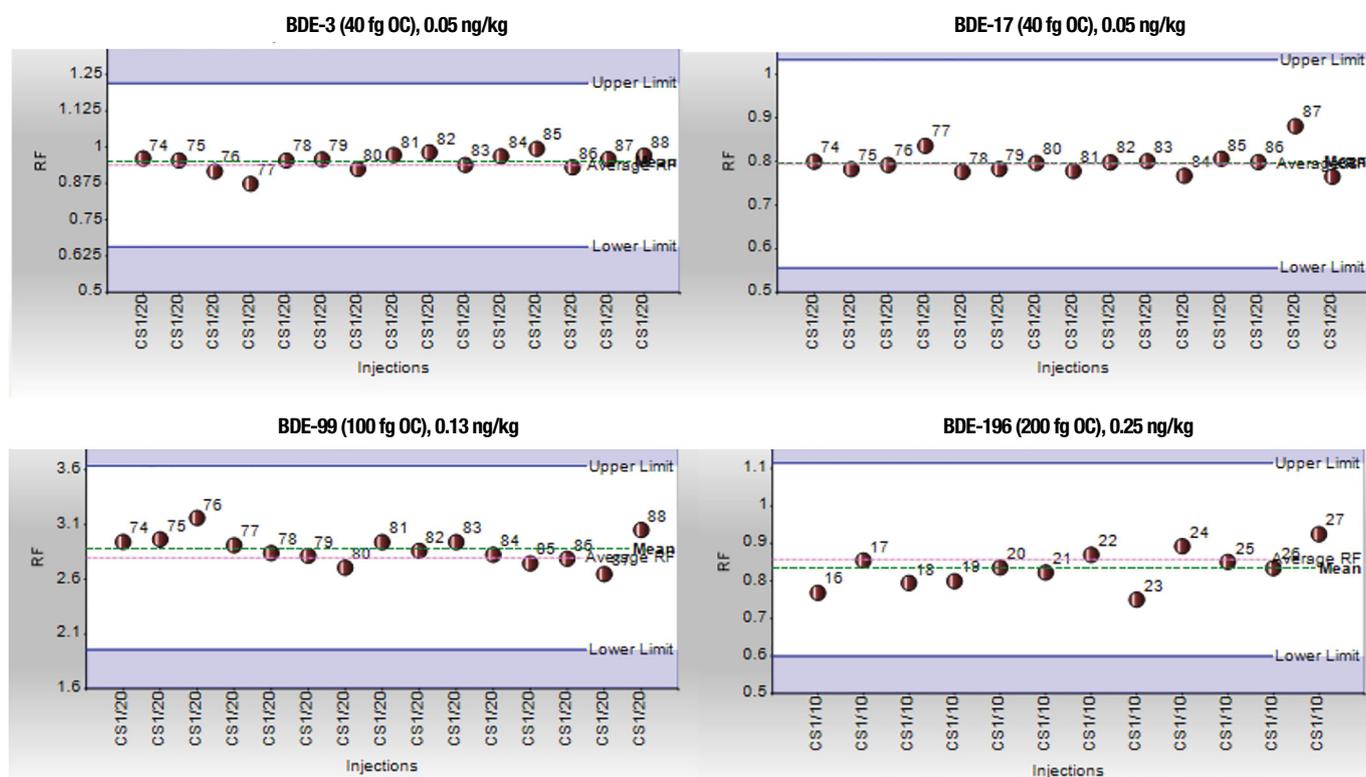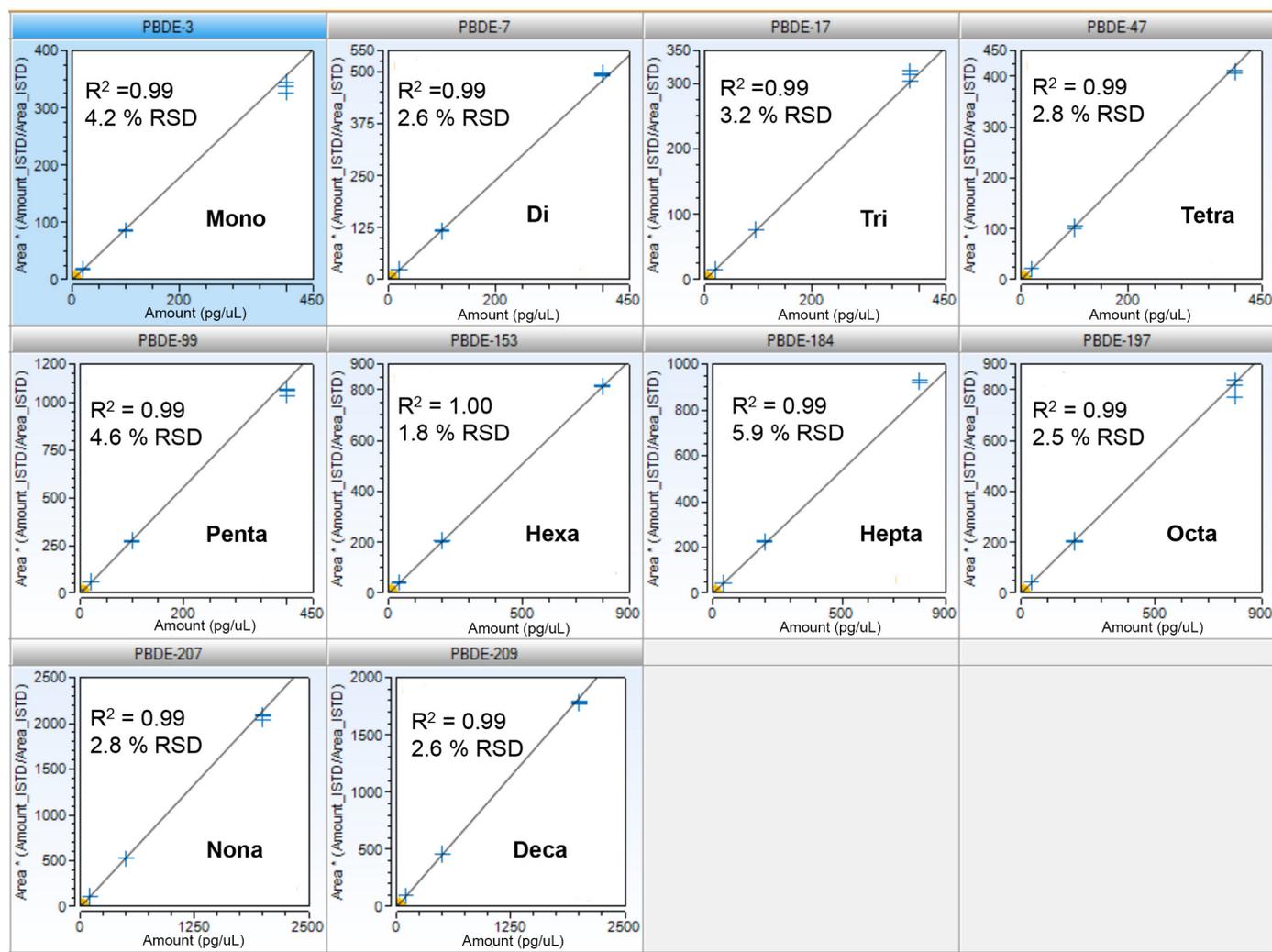

Figure 7. Graphs showing RRF consistency for selected PBDEs over n=15 replicate injections at the LOQ level. The average RRF calculated from the calibration range is displayed as a pink dotted line in the center. The ±30% upper and lower RRF tolerance windows are also defined, and for all PBDEs the RRFs for injections were within specification. This also illustrates how using Chromeleon CDS interactive charts allows the user to easily handle and interpret MS data
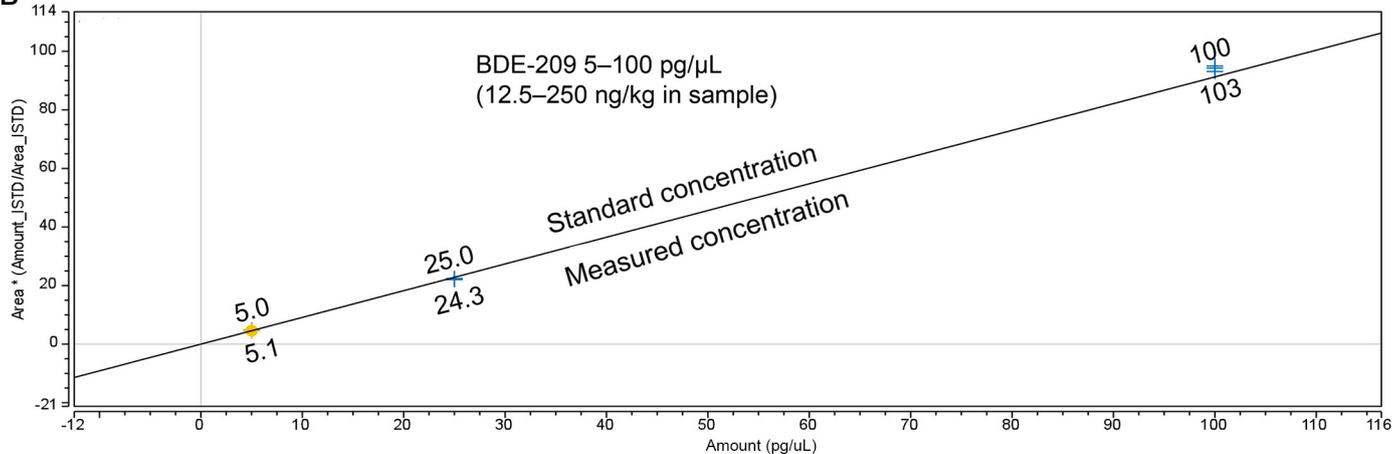
A

B

Figure 8. (A) Linearity of PBDEs demonstrated using a solvent-based calibration curve ranging from 1.0 to 2000 pg/μL in the case of BDE-209 (corresponding to 2.5–5000 ng/kg in food). Average calibration factor (AvCF) function was used in Chromeleon CDS with three replicate injections at each concentration and internal standard adjustment was conducted. Coefficient of determination (R^2) and average RRF % RSD are displayed. (B) Expanded region of calibration for BDE-209 from 5 to 100 pg/μL is shown (corresponding to 12.5–250 ng/kg in extracted fat) demonstrating excellent accuracy and precision for triplicate injections per point.

Table 7. Coefficient of determination (R^2) and RRF % RSD

Compound	R^2	RRF % RSD	Compound	R^2	RRF % RSD
BDE-3	0.9941	4.2	BDE-126	0.9980	2.8
BDE-7	0.9987	2.6	BDE-154	0.9923	5.1
BDE-15	0.9987	2.9	BDE-153	1.0000	1.8
BDE-17	0.9980	3.2	BDE-138	0.9976	2.7
BDE-28	0.9999	1.5	BDE-156	0.9795	9.9
BDE-49	0.9995	3.8	BDE-184	0.9927	5.9
BDE-71	0.9953	4.2	BDE-183	0.9992	1.8
BDE-47	0.9991	2.8	BDE-191	0.9879	7.6
BDE-66	0.9970	4.4	BDE-197	0.9976	2.5
BDE-77	0.9959	6.6	BDE-196	0.9823	9.3
BDE-100	0.9994	1.7	BDE-207	0.9982	2.8
BDE-119	0.9921	5.1	BDE-206	0.9988	2.6
BDE-99	0.9952	4.6	BDE-209	0.9991	2.6
BDE-85	0.9975	7.3			

PBDE quantification in food samples and comparison to GC-HRMS data

Several food samples were tested for the PBDE content and examples of sensitivity, selectivity, and accuracy of measurements are highlighted below (Figures 9 and 10).
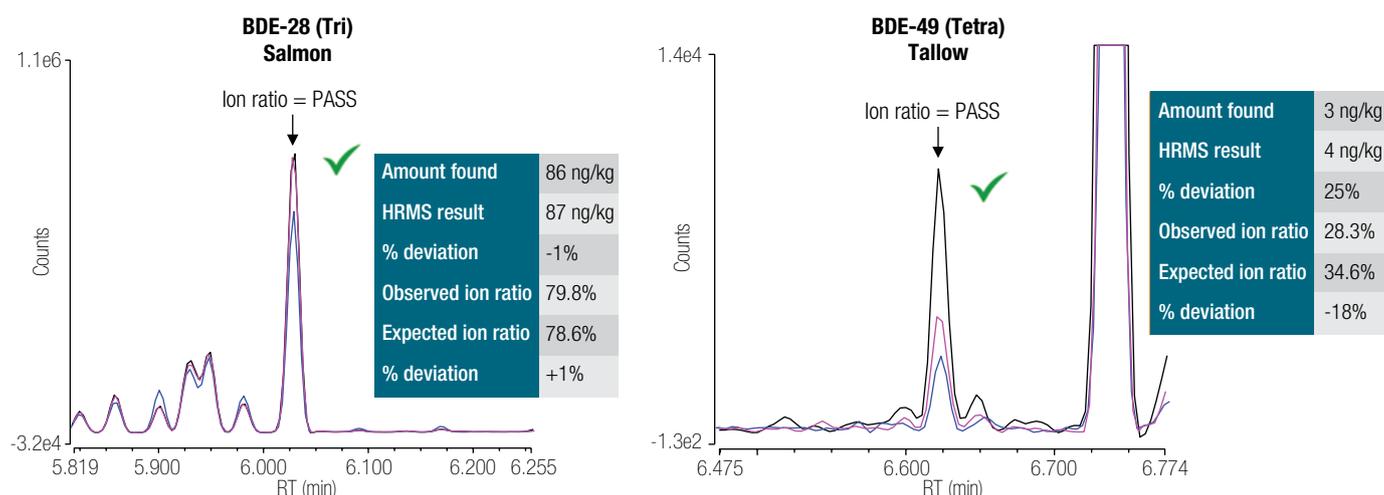

Figure 9. Examples of SRMs chromatograms (quantification in black, and confirmation ions in pink and blue) for BDE-28 in salmon (left chromatogram) and BDE-49 in tallow (right chromatogram); visit the AppsLab Library for full SRM transitions. Below each of the chromatograms the following is shown: (i) amount found in sample in ng/kg, (ii) HRMS (magnetic sector data) result provided from Fera Science, Ltd. in ng/kg, (iii) % deviation from Fera Science, Ltd. result, (iv) observed ion ratio between quantification and primary confirmation ion, (v) expected ion ratio calculated from the average of the calibration, and (vi) % deviation of observed ion ratio versus the expected ion ratio.
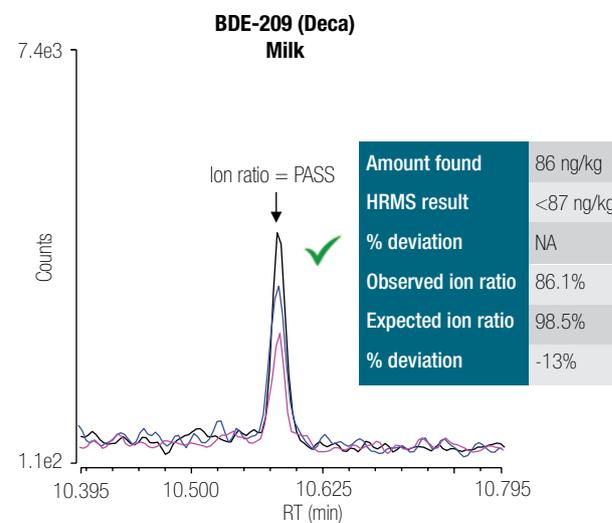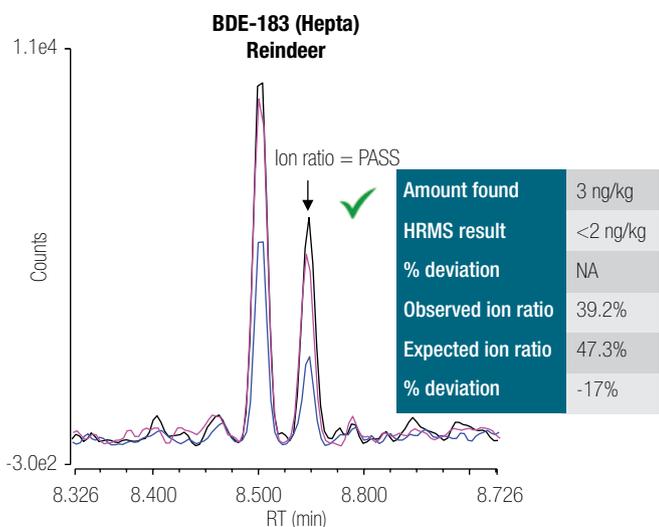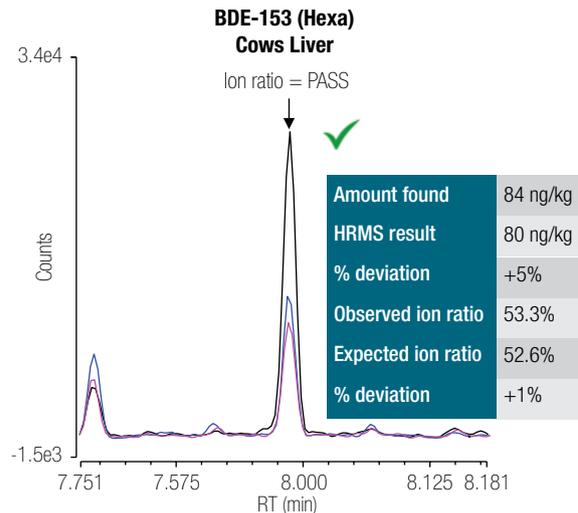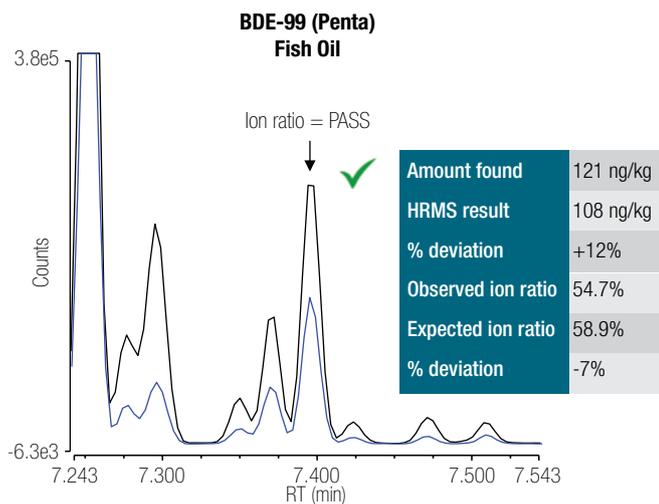
Figure 10. The two chromatograms show the overlaid selective reaction monitoring transitions (quantification in black, and confirmation ions in pink and blue) for BDE-99 in fish oil (top left chromatogram), BDE-153 in cows liver (top right chromatogram), BDE-183 in reindeer (bottom left chromatogram), and BDE-209 in milk (bottom right chromatogram).

In summary, the results comparison for triple quadrupole technology versus GC-HRMS shows very close agreement. The low limits of quantification that are achievable using triple quadrupole technology are clearly demonstrated in the case of BDE-49 in tallow and BDE-183 in reindeer; in both cases low ppt (ng/kg in extracted fat) results were reported with ion confirmation within the ±30% tolerance of the averaged ion ratio across the calibration. In the case of the complex fish oil matrix, the power of the mass spectrometer and TG-PBDE column combination become apparent in their ability to selectively resolve complex matrix interferences and congeners with the deviation in measured ion ratio versus the calibration of only 7%.

Conclusions

The purpose of these experiments was to assess the quantitative performance of the TSQ 9000 GC-MS/MS system for increased sample throughput. Additionally, the results obtained were compared with those from GC-HRMS to assess the measurement accuracy.

- All 27 native BDE congeners were chromatographically separated in <11 min, allowing an increase in sample throughput of 3X compared to existing GC-MS methods.[3]

- The levels of sensitivity obtained allowed IDLs ranging from 2 to 100 fg OC (corresponding to 0.003 to 0.125 ng/kg in extracted fat).

- LOQs (derived from solvent standards) were equivalent to 0.05 to 0.63 ng/kg in extracted fat calculated from n=15 repeat injections of the lowest serially diluted standard that satisfied the acceptance criteria defined below:

  – Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 5 to 2000 pg/μL (corresponding to 10–5000 ng/kg in extracted fat).

  – Peak area repeatability of <15% RSD.

  – RRFs were within ±30% of that calculated from the average of the calibration.

- Excellent linearity was achieved across a calibration of 1–2000 pg/μL (corresponding to 2.5–5000 ng/kg in extracted fat) with all RRF % RSDs <10% and R^2 values >0.98.

- The overall quantitative performance of the TSQ 9000 GC-MS/MS system was demonstrated by the ability to easily detect and confirm (using ion ratio values) low levels of PBDEs even in most critical sample types such as fish oil.

- The results obtained from the TSQ 9000 GC-MS/MS system experiments were in close agreement with HRMS (magnetic sector) data provided from Fera Science, Ltd., York was achieved even at very low concentrations.

Taken together these results demonstrate that the TSQ 9000 GC-MS/MS system configured with the AEI source provides unparalleled levels of quantitative performance making it an ideal analytical tool for routine food safety testing laboratories.

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Appendix

Table 1. Details of 27 native PBDE congeners analyzed, including BDE number, chemical formula, CAS number, and calibration range

BDE Number	Native BDEs	Chemical Formula	CAS Number	Calibration Range (ng/mL)
3	4-Bromodiphenyl ether	$C_{12}H_9BrO$	101-55-3	1.0 to 400
7	2,4-Dibromodiphenyl ether	$C_{12}H_8Br_2O$	171977-44-9	1.0 to 400
15	4,4'-Dibromodiphenyl ether	$C_{12}H_8Br_2O$	2050-47-7	1.0 to 400
17	2,2',4-Tribromodiphenyl ether	$C_{12}H_7Br_3O$	147217-75-2	0.96 to 384
28	2,4,4'-Tribromodiphenyl ether	$C_{12}H_7Br_3O$	41318-75-6	1.0 to 400
47	2,2',4,4'-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	5436-43-1	1.0 to 400
49	2,2',4,5'-Tetrabromodiphenyl ether	$C_{12}H6Br_4O$	243982-82-3	1.0 to 400
66	2,3',4,4'-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	189084-61-5	1.0 to 400
71	2,3',4',6-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	189084-62-6	1.0 to 400
77	3,3',4,4'-Tetrabromodiphenyl ether	$C_{12}H_6Br_4O$	93703-48-1	1.0 to 400
85	2,2',3,4,4'-Pentabromodiphenyl ether	$C_{12}H_6Br_5O$	182346-21-0	1.0 to 400
99	2,2',4,4',5-Pentabromodiphenyl ether	$C_{12}H_6Br_5O$	32534-81-9	1.0 to 400
100	2,2',4,4',6-Pentabromodiphenyl ether	$C_{12}H_6Br_5O$	189084-64-8	1.0 to 400
119	2,3',4,4',6-Pentabromodiphenyl ether	$C_{12}H_6Br_5O$	189084-66-0	1.0 to 400
126	3,3',4,4',5-Pentabromodiphenyl ether	$C_{12}H_6Br_5O$	366791-32-4	1.0 to 400
138	2,2',3,4,4',5-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	446254-95-1	2.0 to 800
153	2,2',4,4',5,5'-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	68631-49-2	2.0 to 800
154	2,2',4,4',5,6'-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	207122-15-4	2.0 to 800
156	2,3,3',4,4',5-Hexabromodiphenyl ether	$C_{12}H_4Br_6O$	405237-85-6	2.0 to 800
183	2,2',3,4,4',5',6-Heptabromodiphenyl ether	$C_{12}H_3Br_7O$	207122-16-5	2.0 to 800
184	2,2',3,4,4',6,6'-Heptabromodiphenyl ether	$C_{12}H_3Br_7O$	117948-63-7	2.0 to 800
191	2,3,3',4,4',5',6-Heptabromodiphenyl ether	$C_{12}H_3Br_7O$	446255-30-7	2.0 to 800
196	2,2',3,3',4,4',5,6'-Octabromodiphenyl ether	$C_{12}H_2Br_8O$	446255-39-6	2.0 to 800
197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	$C_{12}H_2Br_8O$	117964-21-3	2.0 to 800
206	2,2',3,3',4,4',5,5',6-Nonabromodiphenyl ether	$C_{12}HBr_9O$	63936-56-1	5.0 to 2000
207	2,2',3,3',4,4',5,6,6'-Nonabromodiphenyl ether	$C_{12}HBr_9O$	437701-79-6	5.0 to 2000
209	Decabromodiphenyl ether	$C_{12}Br_{10}O$	1163-19-5	5.0 to 2000

Table 2. Details of 16 ^{13}C-labeled PBDEs internal standards, including BDE isomer number, chemical formula, CAS number, and concentration (suffix "L" indicates mass-labeled)

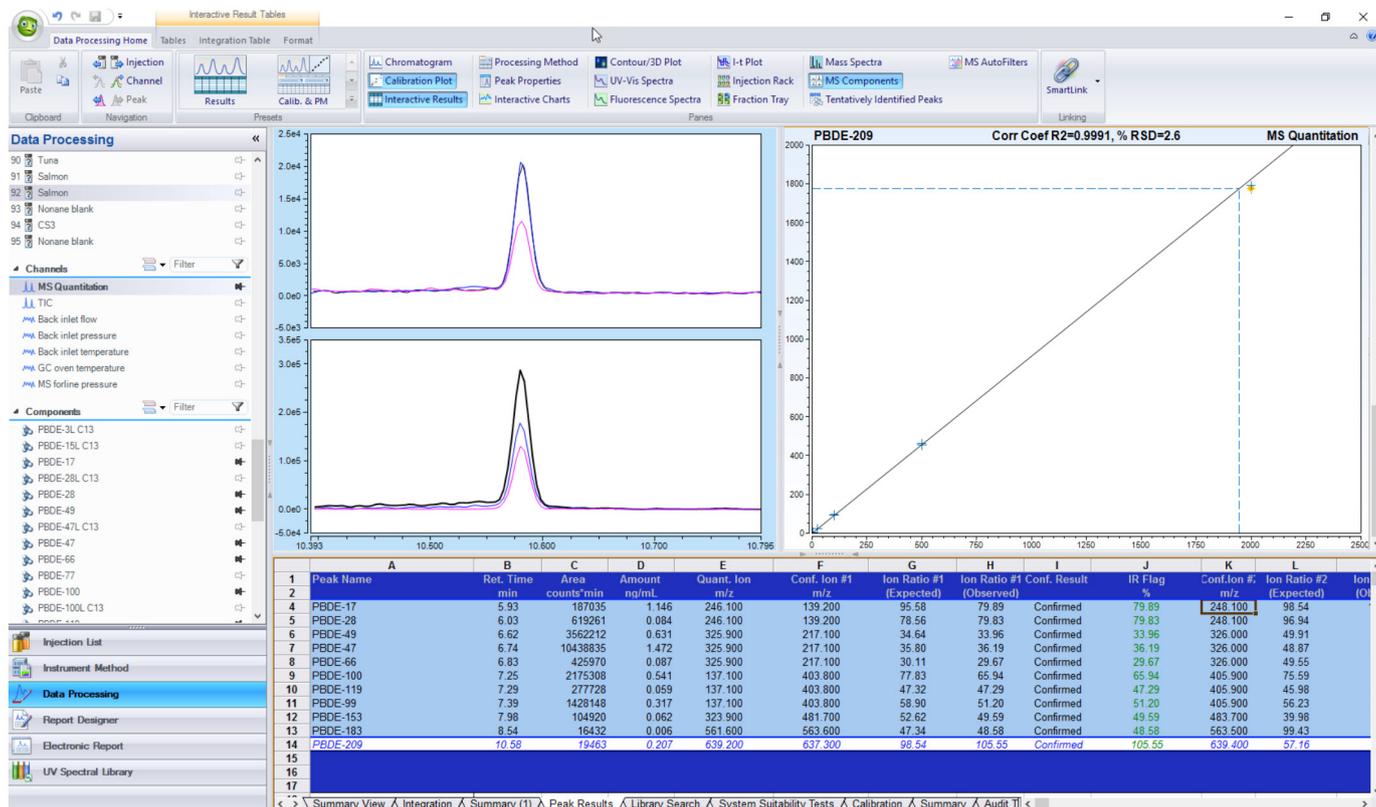| BDE isomer number	^{13}C-labeled PBDEs	Chemical Formula	Concentration (ng/mL)
3L	4-Bromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_9$BrO	100
15L	4,4'-Dibromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_8$Br$_2$O	100
28L	2,4,4'-Tribromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_7$Br$_3$O	100
47L	2,2',4,4'-Tetrabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_6$Br$_4$O	100
79L	3,3',4,5'-Tetrabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_6$Br$_4$O	100
99L	2,2',4,4',5-Pentabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_5$Br$_5$O	100
100L	2,2',4,4',6-Pentabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_5$Br$_5$O	100
126L	3,3',4,4',5-Pentabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_5$Br$_5$O	100
138L	2,2',3,4,4',5-Hexabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_4$Br$_6$O	200
153L	2,2',4,4',5,5'-Hexabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_4$Br$_6$O	200
154L	2,2',4,4',5,6'-Hexabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_4$Br$_6$O	200
183L	2,2',3,4,4',5',6-Heptabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_3$Br$_7$O	200
197L	2,2',3,3',4,4',6,6'-Octabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$H$_2$Br$_8$O	200
206L	2,2',3,3',4,4',5,5',6-Nonabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$HBr$_9$O	500
207L	2,2',3,3',4,4',5,6,6'-Nonabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$HBr$_9$O	500
209L	Decabromo[^{13}C$_{12}$]diphenyl ether	^{13}C$_{12}$Br$_{10}$O	500

Figure 1. Example of the Chromeleon CDS interactive results browser used to assess and interrogate sample data in real time

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