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Low-level consistent analysis of PBDEs in environmental and food matrices using triple quadrupole GC-MS/MS

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GOAL

The aim of this application note is to demonstrate the performance of the Thermo Scientific™ TSQ™ 9610 triple quadrupole mass spectrometer coupled to the Thermo Scientific™ TRACE™ 1610 GC for the determination of polybrominated diphenyl ethers (PBDEs) in environmental and food samples.

INTRODUCTION

PBDEs are classes of polybrominated hydrocarbons existing as mixtures of congeners with similar molecular structures but different chemical and physical properties (e.g., congeners with lower numbers of bromine atoms tend to be more volatile and to bioaccumulate more than higher brominated congeners).¹ Historically these compounds were widely used as flame retardants in a variety of products, such as plastics, furniture, upholstery, electrical equipment, electronic devices, textiles, and other household products, because of their capability to release bromine radicals that reduce both the rate of combustion and dispersion of fire when exposed at high temperatures.¹ These compounds enter the environment through emissions from manufacturing processes, volatilization from various products that contain PBDEs, recycling wastes, and leachate from waste disposal sites. They are considered ubiquitous persistent pollutants as they have been detected in the airborne particulate matter, bonded to sediments, surface water, fish, and other marine animals, and therefore represent a risk to human health. As a consequence, the use of certain toxic PBDEs with links to cancer and endocrine disruption (including penta-, tetra-, and deca-PBDE) have been prohibited, and are currently listed in the Stockholm Convention inventory of persistent organic pollutants.²

There are several challenges associated with the analysis of PBDEs in food and environmental samples. Firstly, confident low level of detection must be achieved consistently. This can be difficult due to the complexity of the matrices being analyzed. Secondly, as the PBDE congeners have similar structures and are isobaric compounds, separating these compounds chromatographically can be difficult without extended run times. Analytical laboratories must deliver results to their customers in a timely manner and instrument downtime is not acceptable. Traditionally, gas chromatography coupled to either electron capture detection (GC-ECD), mass spectrometry (GC-MS), or high-resolution accurate mass spectrometry

(GC-HRMS) is the technique of choice for analysis of PBDEs. Combining with triple quadrupole mass spectrometry (GC-MS/MS), with its high selectivity in removing interferences from the matrix that can lead to false positive erroneous results, yields sensitivity for detection of PBDEs at ultra-trace levels.

In this study, the TSQ 9610 triple quadrupole GC-MS/MS was used for the determination of PBDEs in fish oil and environmental (water and soil) samples. The Thermo Scientific™ TraceGOLD™ PDBE column was tested for chromatographic separation of the isobaric congeners; whereas selected reaction monitoring (SRM) acquisition mode ensured appropriate selectivity and sensitivity when matrix samples were analyzed. Linearity and instrument detection limits (IDLs) were assessed in the experiments for all compounds as well as an extended robustness study over n=100 injections of matrix samples to assess the reproducibility of the detection of trace levels of PDBEs.

EXPERIMENTAL

In the experiments described here, a TSQ 9610 triple quadrupole mass spectrometer equipped with a Thermo Scientific™ NeverVent™ Advanced Electron Ionization (AEI) ion source was coupled to a TRACE 1610 gas chromatograph equipped with a Thermo Scientific™ iConnect™ programmable temperature vaporizing (iConnect-PTV) injector and a Thermo Scientific™ AI/AS 1610 autosampler. The TRACE 1610 GC with its instant connect injector and detector modules allows for the reconfiguration of the instrument to adapt to different workflows in minutes. The NeverVent technology allows for ion source cleaning, filament replacement, and column exchange without breaking instrument vacuum, therefore ensuring minimum downtime to the laboratory workflow. The AI/AS 1610 GC ensures ease-of-use and cost-effectiveness for high-throughput laboratory work.

Chromatographic separation was achieved on a TraceGOLD TG-PBDE capillary column, 15 m × 0.25 mm × 0.10 μm (P/N 26061-0350). The TraceGOLD PDBE column has been developed to ensure fast analysis of PBDE with excellent separation of isobaric congeners (PBDE-49 and PBDE-71), exceeding the U.S. EPA Method 16143 resolution criteria, coupled to a thin film phase and high thermal stability (maximum temperatures up to 360 °C) for faster elution of high boiling point PBDEs (e.g., PBDE-209) with improved peak shapes.

Additional GC-MS/MS and autosampler parameters as well as a complete list of the target compounds are detailed in Table 1 and Appendix 1, respectively.

Table 1. GC-MS/MS and autosampler experimental conditions for the analysis of PBDEs

AI/AS 1610 Autosampler parameters		iConnect-PTV parameters	
Injection type	Standard	Injection temperature (°C)	65
Sample mode	Standard	Liner	PTV 6 baffle Siltek™ liner
Fill strokes	10	Inlet module and mode	PTV, splitless
Sample depth	Bottom	Injection time (min)	0.1
Injection mode	Fast	Transfer rate (°C/s)	5.0
Pre-injection delay time (s)	0	Transfer temperature (°C)	330
Post-injection delay time (s)	0	Transfer time (min)	1.50
Pre-injection wash cycles	0	Cleaning rate (°C/s)	14.5
Pre-injection solvent wash vol. (μL)	6.0	Cleaning temperature (°C)	330
Post-injection wash cycles	4	Cleaning time (time)	5.00
Pre-injection solvent wash vol. (μL)	6.0	Cleaning split flow (mL/min)	75

Table 1 continued. GC-MS/MS and autosampler experimental conditions for the analysis of PBDEs

AI/AS 1610 Autosampler parameters		iConnect-PTV parameters	
Sample wash cycles	1	Post cycle temperature	Maintain
Sample wash volume (µL)	1.0	Split flow (mL/min)	50
Injection volume (µL)	1.0	Septum purge flow (mL/min)	5, constant
		Carrier gas, flow (mL/min)	He, 1.5
TRACE 1610 GC parameters		TSQ 9610 Mass Spectrometer parameters	
Oven temperature program		Transfer line temperature (°C)	300
Temperature (°C)	100	Ion source type and temp. (°C)	NeverVent AEI, 300
Hold time (min)	2.00	Ionization type	EI
Rate (°C/min)	30	Emission current (µA)	50
Temperature 2 (°C)	330	Aquisition mode	timed-SRM
Hold time (min)	3	Q1 and Q3 resolution	Mono-hepta BDE normal (0.7 amu); Octa-deca BDE wide (1.2 amu)
GC run time (min)	12.67	Tuning parameters	AEI Smart Tune
Column TraceGOLD TG-PBDE	15 m, 0.25 mm, 1.0 µm (P/N 26061-0350)	Collision gas and pressure (psi)	Argon at 70

Data acquisition, processing, and reporting

Data was acquired, processed, and reported using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.3. Integrated instrument control ensures full automation of the analytical workflow combined with an intuitive user interface for data analysis, customizable reporting, and storage in compliance with the Federal Drug Administration Title 21 Code of Federal Regulations Part 11 (Title 21 CFR Part 11). In particular, PBDE quantitative analysis requires the use of isotope dilution, this feature is available in Chromeleon CDS from software version 7.2.9 onwards.

Standard and sample preparation**Standard preparation**

A calibration solution kit at five calibration levels (CS1 to CS5) containing native as well as ¹³C mass-labeled PBDE congeners and mass-labeled PBDE internal standards was purchased from Wellington Laboratories, Inc. (P/N BDE-CVS-G). The lowest calibration level (CS1) was furtherly diluted 1:2 and 1:4 in nonane to expand the calibration curve from 0.25 to 2,000 ng/mL. For the calculation of IDLs, standard solutions ranging from 0.03 to 1.25 ng/mL were prepared by serially diluting the 1:4 CS1 calibration standard.

Sample preparation

Water, soil, and fish oil samples were extracted and provided by Pacific Rim Laboratories Inc., Canada. A schematic of the sample preparation workflow is reported in Figure 1. Samples were dried before shipment and reconstituted with 50 µL of nonane, sonicated in the ultra-sonic bath for few minutes and vortexed before injection into the chromatographic system.

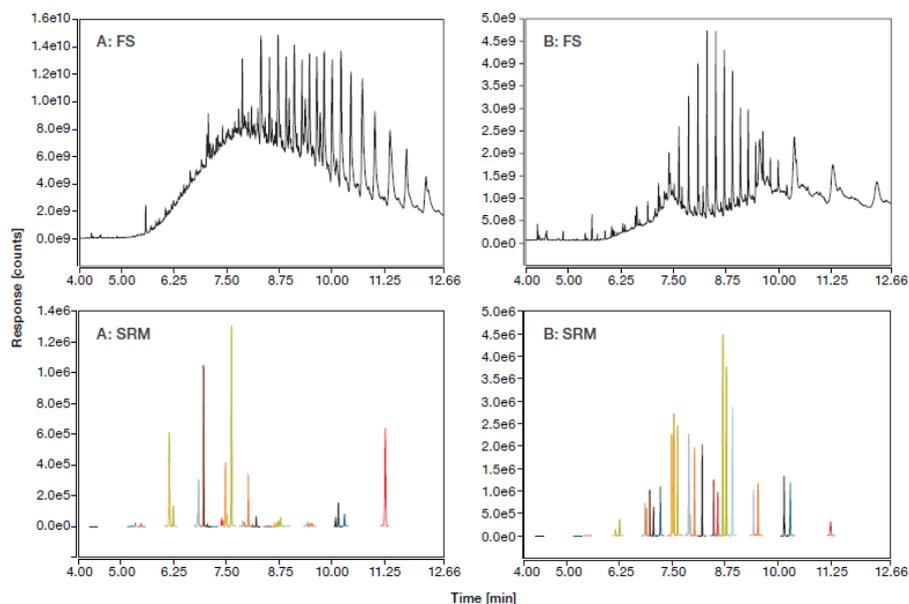


Figure 3. TIC (FS: m/z 40–1,000) and SRM acquisitions for environmental (A-left traces) and fish oil (B-right traces) sample extracts containing PBDEs showing the complexity of the matrices (FS acquisition) and the selectivity of the SRM acquisition.

Linearity, instrument detection limit (IDL), and limit of quantitation (LOQ)

The TSQ 9610 NeverVent AEI is equipped with the Thermo Scientific™ XLXR™ detector, which is an electron multiplier that offers extended detector lifetime and dynamic range. Calibration curves ranging from 0.25 to 2,000 ng/mL were prepared as detailed in the Standard preparation section. Each calibration level was injected in triplicate. Native PBDE congeners were quantified using their corresponding isotopes using isotope dilution quantitation. The target analytes showed a linear trend with coefficient of determination (R^2) > 0.990 and residual values (measured as %RSD of average response factors, AvCF %RSD) < 15%, thus confirming a wider linear range can be easily achieved as reported in Appendix 2. Full range calibration curves for PBDE-47 (0.25–400 ng/mL), PBDE-183 (0.5–800 ng/mL) and PBDE-209 (1.25–2,000 ng/mL) as well as zoomed detail (0.25–5.0 ng/mL, 0.5–10.0 ng/mL, and 1.25–25.0 ng/mL, respectively) are shown as an example in Figure 4.

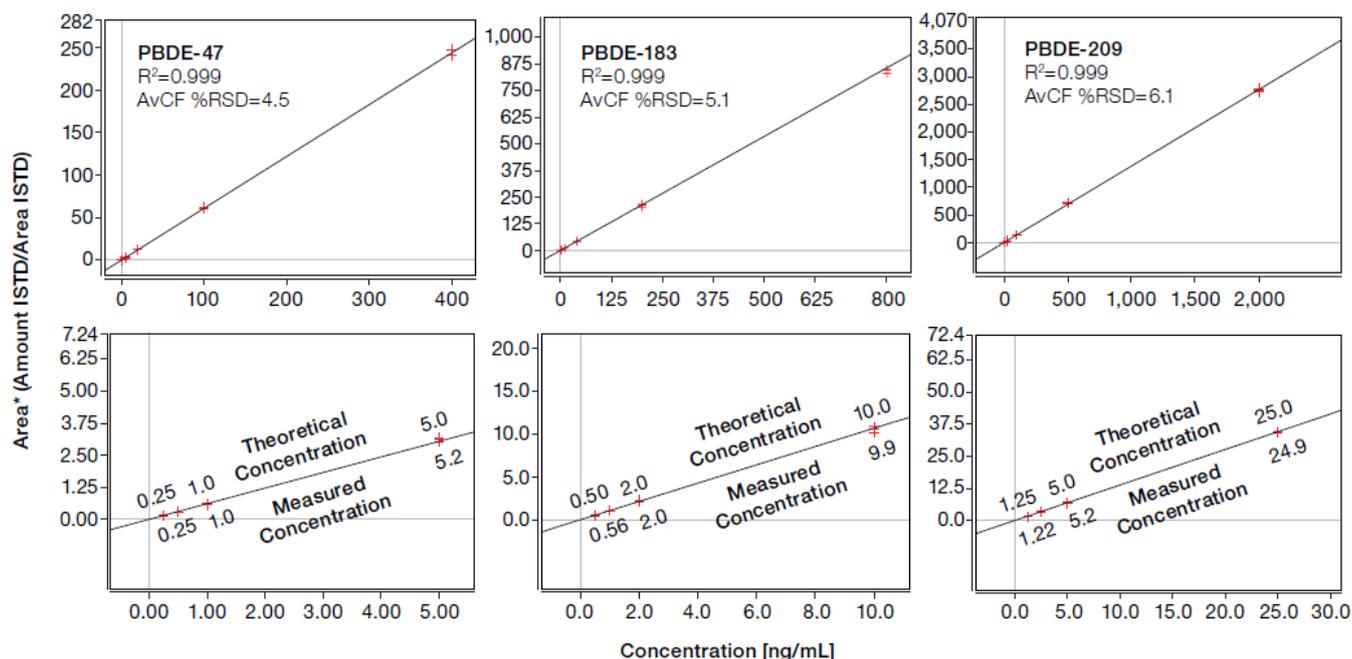


Figure 4. Example of solvent (nonane) calibration curves for PBDE-47 (full range: 0.25–400 ng/mL, zoomed detail: 0.25–5.0 ng/mL), PBDE-183 (full range: 0.5–800 ng/mL, zoomed detail: 0.5–10.0 ng/mL) and PBDE-209 (full range: 1.25–2,000 ng/mL, zoomed detail: 1.25–25.0 ng/mL). Each calibration level was injected in triplicate. Coefficient of determination (R^2) and AvCF %RSD are annotated.

The instrument detection limit was determined for all the target compounds by injecting ($n=10$) solvent standards ranging from 0.03 to 1.25 ng/mL, corresponding to 1.5 pg/L to 62.5 pg/L in water samples and 0.15 to 6.25 ng/kg in soil and fish oil samples. IDLs were calculated taking into account the one-tailed Student's t-test values for the corresponding $n-1$ degrees of freedom at 99% confidence, the concentration, and the absolute peak area %RSD (<15%) for each analyte. Calculated IDLs ranged from 5 fg to 122 fg on column (OC) corresponding to 0.25 pg/L to 6.10 pg/L for water samples and 0.025 to 0.61 ng/kg for soil and fish oil samples (Figure 5).

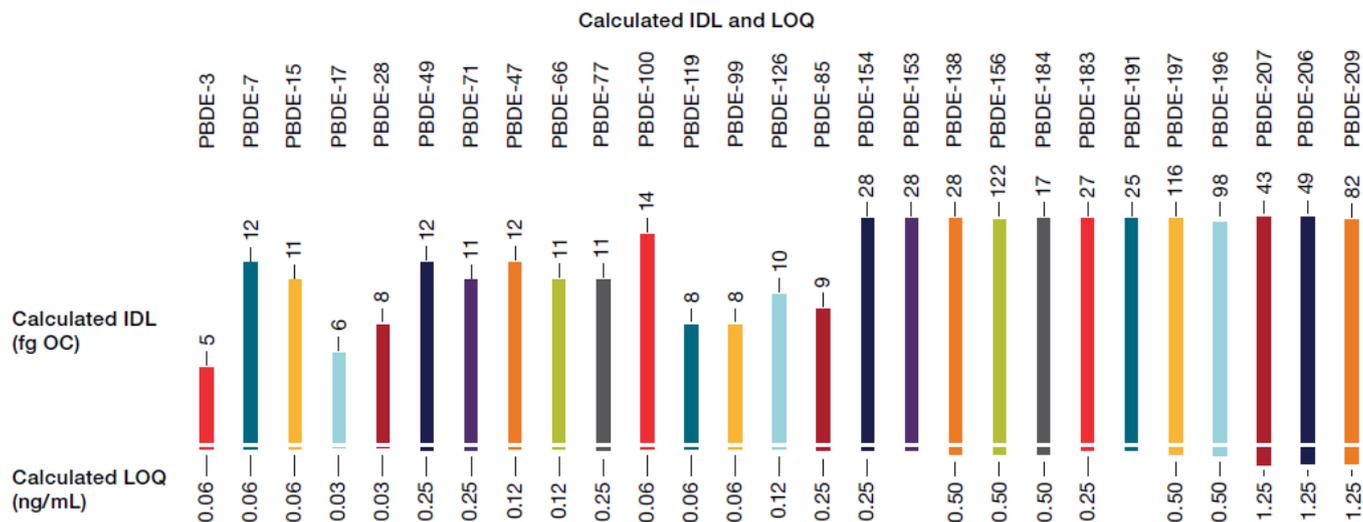


Figure 5. Calculated IDLs and LOQs for all investigated PBDEs. Calculated IDLs ranged from 5 fg to 122 fg on column (OC), corresponding to 0.25 pg/L to 6.10 pg/L for water samples and 0.025 to 0.61 ng/kg for soil and fish oil samples. Calculated LOQs ranged from 0.03 to 1.25 ng/mL, corresponding to 1.5 pg/L to 62.5 pg/L in water samples and 0.15 to 6.25 ng/kg in soil and fish oil samples.

The standard concentration for which (i) the ion ratios were within $\pm 30\%$ of the expected values calculated as an average across a calibration curve ranging from 0.25 to 2,000 ng/mL, (ii) the absolute peak area repeatability was $<15\%$ RSD, and (iii) the relative response factor (RRF) was within $\pm 30\%$ of that calculated from the average of the calibration was chosen as the LOD for individual PBDEs. The calculated LOQ, as well as ion ratios, peak area %RSD, and RRF for the investigated compounds are detailed in Appendix 3. Examples of the consistency of the RRF for some selected PBDEs are shown in Figure 6.

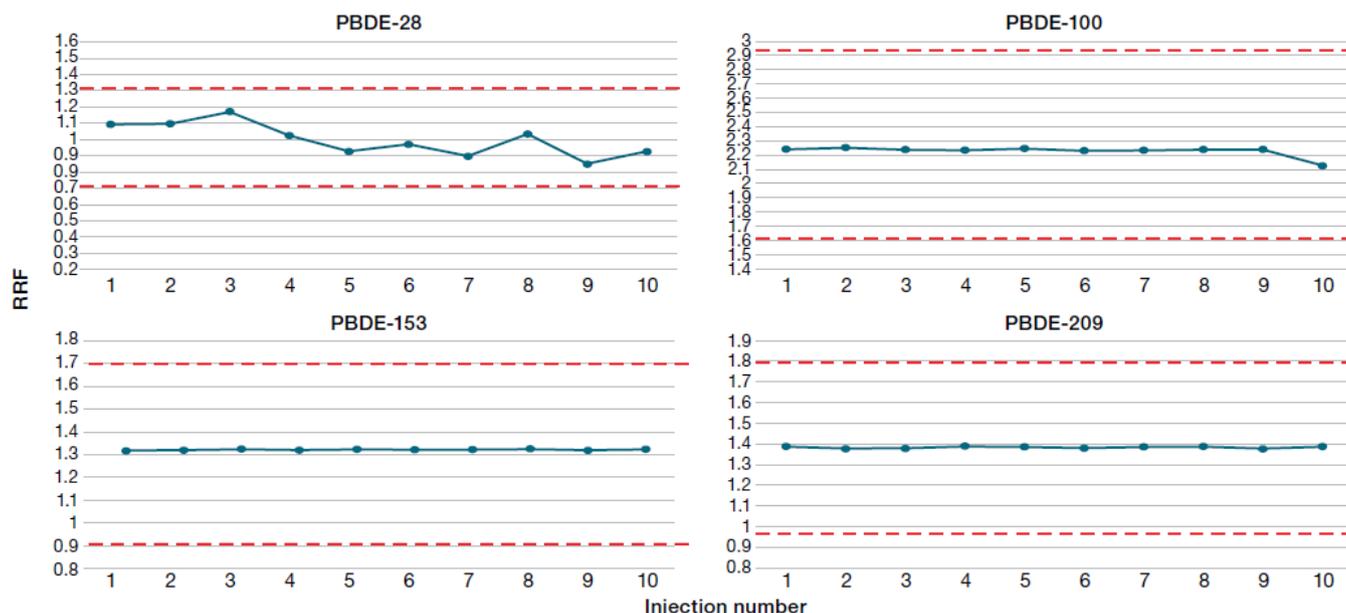


Figure 6. Examples of the consistency of the RRF for some selected PBDEs. The RRF was within $\pm 30\%$ of that calculated from the average of the calibration. The amber dotted lines represents the acceptance limits.

Robustness

Analytical testing laboratories need to process a high number of samples every day; therefore, it is critical that the instrument performs consistently. Mass calibration and resolution tuning are two of the most important aspects ensuring system performance. The Thermo Scientific™ SmartTune™ feature allows the user to check the tune status of the system with a few mouse clicks in an easy and quick fashion. Instrument robustness for everyday analysis and quantitative performance was evaluated by repeatedly injecting various environmental and fish oil extracts ($n=100$). A quality control standard in nonane (QC) at a concentration of 5.0–25.0 ng/mL was injected in duplicate every 10 samples to monitor the system stability. The SmartTune feature was used to check the instrument status at the beginning, middle, and end of the sequence. It uses the MS parameters established during the initial tuning with a clean source and intelligently assesses the performance of the system, only re-tuning when MS performance has been compromised. No inlet or MS maintenance or any re-tuning was required during the robustness evaluation. The QC showed stable response across the injections with ion ratios consistently within 30% of the calculated average from the calibration curve and QC normalized peak area %RSD $<20\%$ (Figure 7).

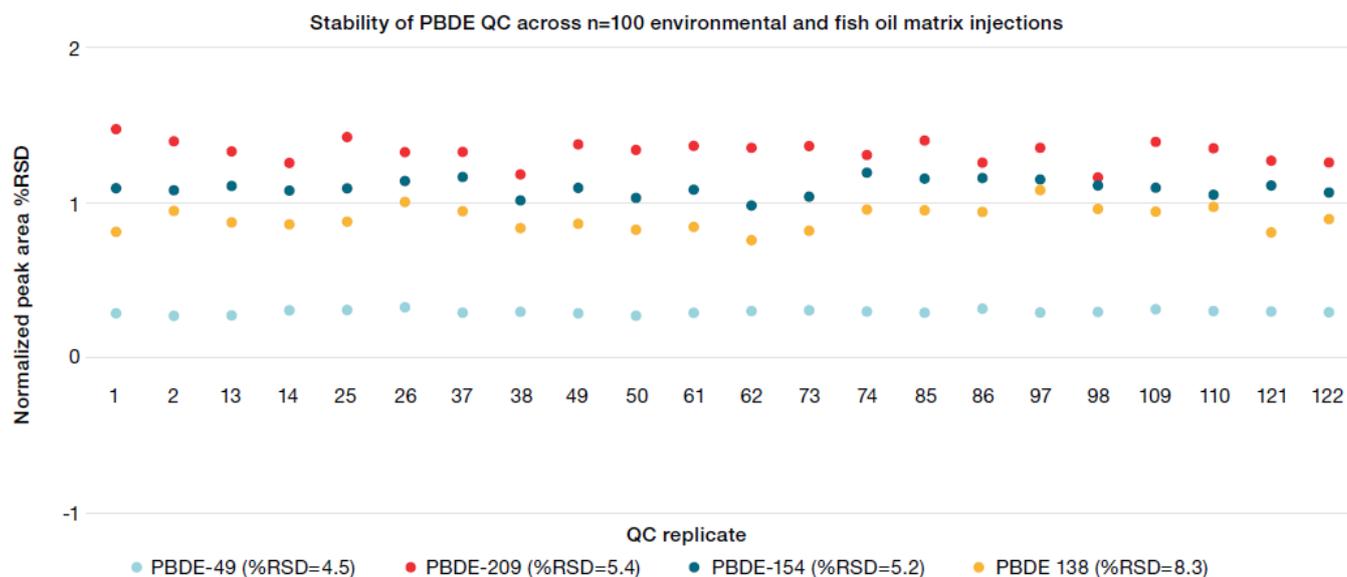


Figure 7. QC normalized peak area %RSD across a sequence of n=100 injections of various environmental and fish oil extracts.

CONCLUSION

The results obtained in these experiments demonstrate that the TSQ 9610 mass spectrometer equipped with the NeverVent AEI ion source in combination with the TRACE 1610 GC and the AI/AS 1610 liquid autosampler delivers consistent and reliable analytical performance for analysis of PBDEs in environmental and food samples.

- The high selectivity of the TraceGOLD TG-PBDE column ensured chromatographic separation of the target analytes in less than 12 minutes. Calculated resolution of the isobaric congeners PBDE-49 / PBDE-71 was 5% at the valley height, therefore exceeding the U.S EPA Method 1614 requirement of less than 40%. Furthermore, the thin film phase and high thermal stability (maximum temperatures of 360 °C) of the capillary column ensured elution of the high boiling point PBDEs (e.g., PBDE-209) with improved peak shapes.

- The XLXR detector allowed for extended linearity over a concentration range of 0.25 to 2,000 ng/mL with coefficient of determination of $R^2 > 0.99$ and AvCF %RSDs <20. Moreover, the Chromeleon CDS advanced reprocessing capability allowed for isotope dilution quantitative analysis.

- The engineered design and the improved sensitivity of the NeverVent AEI ion source allowed for low instrument detection limits ranging from 5 fg to 122 fg OC, corresponding to 0.25 pg/L to 6.10 pg/L for water samples and 0.025 to 0.61 ng/kg for soil and fish oil samples, with calculated LOQ ranging from 1.5 pg/L to 62.5 pg/L in water samples and 0.15 to 6.25 ng/kg in soil and fish oil samples. Ion ratios and RRF were within $\pm 30\%$ of the expected values calculated as an average across a calibration curve even at such low analyte concentrations.

- The enhanced robustness and reliability of the AI/AS 1610 liquid autosampler combined with the efficient transfer of the analyte through the PTV injector, the inertness of the flow path, and the stability of the NeverVent AEI ion source allowed for n=100 matrix injections without requiring any system re-tuning or maintenance of the MS or inlet.

REFERENCES

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Appendix 1. List of target analytes, retention times (RT, min), and quantifier and qualifier ions (*m/z*)

Compound	RT (min)	Quantifier ion (<i>m/z</i>)	Qualifier 1 ion (<i>m/z</i>)	Qualifier 2 ion (<i>m/z</i>)
PBDE-3	4.37	248.00/141.20	250.00/115.10	250.00/141.10
PBDE-3L C13	4.37	260.00/124.20	260.00/152.20	262.00/152.20
PBDE-7	5.26	325.90/139.20	325.90/168.20	327.90/168.20
PBDE-15	5.49	325.90/139.20	325.90/168.20	327.90/168.20
PBDE-15L C13	5.49	337.90/180.20	339.90/150.20	339.90/180.20
PBDE-17	6.16	405.80/139.20	405.80/246.10	407.80/248.10
PBDE-28	6.25	405.80/139.20	405.80/246.10	407.80/248.10
PBDE-28L C13	6.25	417.80/150.20	417.80/258.10	419.80/260.10
PBDE-49	6.85	483.70/217.10	483.70/326.00	485.70/325.90
PBDE-71	6.88	483.70/217.10	483.70/326.00	485.70/325.90
PBDE-47	6.97	483.70/217.10	483.70/326.00	485.70/325.90
PBDE-47L C13	6.97	495.70/336.00	495.70/338.00	497.70/338.00
PBDE-79L C13	7.02	495.80/228.10	497.80/230.10	497.80/338.00
PBDE-66	7.07	483.70/217.10	483.70/326.00	485.70/325.90
PBDE-77	7.21	483.70/217.10	483.70/326.00	485.70/325.90
PBDE-100	7.48	403.80/137.10	563.60/403.80	565.60/405.90
PBDE-100L C13	7.48	575.70/307.90	575.70/415.50	577.70/415.90
PBDE-119	7.54	403.80/137.10	563.60/403.80	565.60/405.90
PBDE-99	7.63	403.80/137.10	563.60/403.80	565.60/405.90
PBDE-99L C13	7.63	575.70/307.90	575.70/415.50	577.70/415.90
PBDE-85	7.89	403.80/137.10	563.60/403.80	565.60/405.90
PBDE-126	7.93	403.80/137.10	563.60/403.80	565.60/405.90
PBDE-126L C13	7.93	575.70/307.90	575.70/415.50	577.70/415.90
PBDE-154	8.03	641.50/481.70	641.50/483.70	643.50/483.70
PBDE-154L C13	8.03	653.60/493.80	653.60/495.80	655.60/495.80
PBDE-153	8.22	483.70/323.90	641.50/481.70	641.50/483.70
PBDE-153L C13	8.22	653.60/493.80	653.60/495.80	655.60/495.80
PBDE 138L C13	8.48	495.70/336.00	653.60/493.80	653.60/495.80
PBDE-138	8.48	641.50/481.70	641.50/483.70	643.50/483.70

Appendix 1 continued. List of target analytes, retention times (RT, min), and quantifier and qualifier ions (m/z)

Compound	RT (min)	Quantifier ion (m/z)	Qualifier 1 ion (m/z)	Qualifier 2 ion (m/z)
PBDE-156	8.58	641.50/481.70	641.50/483.70	643.50/483.70
PBDE-184	8.7	721.40/561.60	721.40/563.60	723.40/563.50
PBDE-183	8.78	721.40/561.60	721.40/563.60	723.40/563.50
PBDE-183L C13	8.78	733.50/573.70	733.50/575.70	735.50/575.70
PBDE-191	8.93	721.40/561.60	721.40/563.60	723.40/563.50
PBDE-197	9.43	641.50/481.70	799.30/639.40	801.30/641.50
PBDE-197L C13	9.43	811.40/651.40	813.40/653.70	813.40/655.20
PBDE-196	9.54	641.50/481.70	799.30/639.40	801.30/641.50
PBDE-207L C13	10.17	733.50/573.60	891.30/731.20	893.30/733.20
PBDE-207	10.17	879.30/719.20	879.30/721.30	881.30/721.30
PBDE-206L C13	10.3	733.50/573.60	891.30/731.20	893.30/733.20
PBDE-206	10.3	879.30/719.20	879.30/721.30	881.30/721.30
PBDE-209	11.26	797.30/637.30	797.30/639.40	799.50/639.20
PBDE-209L C13	11.26	809.40/649.80	811.40/651.30	971.20/811.30

Appendix 2. List of target analytes, calibration ranges, calculated coefficient of determination (R^2), and residual values (measured as %RSD of average response factors, AvCF %RSD)

Peak name	Retention time (min)	Calibration range (ng/mL)	Coefficient of determination (R^2)	AvCF %RSD
PBDE-3	4.37	0.25–400	0.9974	9.9
PBDE-7	5.26	0.25–400	0.9968	6.9
PBDE-15	5.49	0.25–400	0.9977	7.0
PBDE-17	6.15	0.24–384	0.9990	5.0
PBDE-28	6.25	0.25–400	0.9990	3.5
PBDE-49	6.85	0.25–400	0.9946	7.4
PBDE-71	6.88	0.25–400	0.9984	7.0
PBDE-47	6.97	0.25–400	0.9990	4.5
PBDE-66	7.07	0.25–400	0.9965	7.1
PBDE-77	7.22	0.25–400	0.9920	8.9
PBDE-100	7.48	0.25–400	0.9986	5.4
PBDE-119	7.54	0.25–400	0.9963	7.2
PBDE-99	7.63	0.25–400	0.9990	4.4
PBDE-126	7.89	0.25–400	0.9913	8.6
PBDE-85	7.93	0.25–400	0.9943	14.4
PBDE-154	8.03	0.50–800	0.9903	8.9
PBDE-153	8.22	0.50–800	0.9974	4.4

Appendix 2 continued. List of target analytes, calibration ranges, calculated coefficient of determination (R^2), and residual values (measured as %RSD of average response factors, AvCF %RSD)

Peak name	Retention time (min)	Calibration range (ng/mL)	Coefficient of determination (R^2)	AvCF %RSD
PBDE-138	8.48	0.50–800	0.9991	5.1
PBDE-156	8.58	0.50–800	0.9984	7.1
PBDE-184	8.70	0.50–800	0.9953	8.6
PBDE-183	8.78	0.50–800	0.9994	5.1
PBDE-191	8.93	0.50–800	0.9924	7.3
PBDE-197	9.43	0.50–800	0.9925	7.3
PBDE-196	9.54	0.50–800	0.9993	4.7
PBDE-207	10.17	1.25–2,000	0.9930	5.9
PBDE-206	10.30	1.25–2,000	0.9949	6.2
PBDE-209	11.26	1.25–2,000	0.9990	6.1

Appendix 3. Calculated IDLs (fg OC), LOQs (ng/mL), as well as ion ratios (IR, expected and measured), peak area %RSD, and RRF at calculated LOQ for the investigated compounds

Peak name	Quantification ion	Injected amount (pg OC)	Peak area %RSD (n=10)	Expected IR	Average measured IR	Calculated IDL (fg OC)	Calculated LOQ (ng/mL)
PBDE-3	248.00/141.20	0.06	6.1	46	44	5	0.06
PBDE-7	325.90/139.20	0.06	9.6	430	444	12	0.06
PBDE-15	325.90/139.20	0.06	13.5	120	115	11	0.06
PBDE-17	405.80/139.20	0.03	10.9	133	139	6	0.03
PBDE-28	405.80/139.20	0.03	9.0	158	156	8	0.03
PBDE-49	483.70/217.10	0.25	5.9	178	174	12	0.25
PBDE-71	483.70/217.10	0.25	7.1	182	193	11	0.25
PBDE-47	483.70/217.10	0.12	9.6	160	160	12	0.12
PBDE-66	483.70/217.10	0.12	12.4	197	184	11	0.12
PBDE-77	483.70/217.10	0.25	8.2	43	44	11	0.25
PBDE-100	403.80/137.10	0.06	13.6	116	122	14	0.06
PBDE-119	403.80/137.10	0.06	10.1	75	70	8	0.06
PBDE-99	403.80/137.10	0.06	13.1	92	91	8	0.06
PBDE-126	403.80/137.10	0.12	11.3	85	85	10	0.12
PBDE-85	403.80/137.10	0.25	6.4	183	168	9	0.25
PBDE-154	641.50/481.70	0.25	11.5	75	78	28	0.25
PBDE-153	483.70/323.90	0.25	7.0	86	86	28	0.25

Appendix 3 continued. Calculated IDLs (fg OC), LOQs (ng/mL), as well as ion ratios (IR, expected and measured), peak area %RSD, and RRF at calculated LOQ for the investigated compounds

Peak name	Quantification ion	Injected amount (pg OC)	Peak area %RSD (n=10)	Expected IR	Average measured IR	Calculated IDL (fg OC)	Calculated LOQ (ng/mL)
PBDE-138	641.50/481.70	0.50	6.2	77	75	88	0.50
PBDE-156	641.50/481.70	0.50	7.4	81	79	122	0.50
PBDE-184	721.40/561.60	0.50	6.1	50	51	17	0.50
PBDE-183	721.40/561.60	0.25	9.2	49	51	27	0.25
PBDE-191	721.40/561.60	0.25	10.8	50	53	25	0.25
PBDE-197	641.50/481.70	0.50	8.2	172	138	116	0.50
PBDE-196	641.50/481.70	0.50	7.1	139	115	98	0.50
PBDE-207	879.30/719.20	1.25	7.5	50	48	43	1.25
PBDE-206	879.30/719.20	1.25	7.3	48	46	49	1.25
PBDE-209	797.30/637.30	1.25	7.3	57	58	82	1.25

This sponsor report is the responsibility of Thermo Fisher Scientific.