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Routine and robust quantification of PBDEs in food by GC-MS/MS

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Keywords

Food analysis, polybrominated diphenyl ethers (PBDEs), electronics, textiles, trace analysis, gas chromatography, triple quadrupole mass spectrometry, selected reaction monitoring, routine, robust, TSQ 9000, advanced electron ionization (AEI), Chromeleon

Goal

The aim of this study was to demonstrate the robust performance of the Thermo Scientific™ TSQ™ 9000 triple quadrupole GC-MS/MS system with the advanced electron ionization (AEI) source for the routine quantification of polybrominated diphenyl ethers (PBDEs) in complex food matrices.

Introduction

PBDEs constitute an important class of flame retardants used in materials such as textiles and plastics in the electronics industry. PBDEs can leach from these materials into the environment and enter food chains where they are persistent and bioaccumulative (vPvB).[1] For this reason 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]

There are 209 possible PBDE congeners that differ in the number and location of bromine atoms in the phenyl rings. Due to their structural similarity and identical masses, gas chromatography mass spectrometry is the analytical technique of choice for PBDE congeners separation and quantification. Higher mass PBDEs (such as deca, nona, and octabromo BDEs) are prone to breaking down in both the GC injector and analytical column, which can affect the limits of detection as well as the peak shape to potentially challenge the required resolution and sensitivity. Robust analytical detection and quantification of PBDEs in complex food matrices requires instruments and chromatography consumables that deliver exceptional performance. This translates into achieving long-term stability in terms of peak area and relative response factors so that multiple batches of samples can be analyzed with minimal maintenance.

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The aim of the experiments described in this technical note was to test the suitability of the TSQ 9000 AEI system for routine quantification of PBDEs in food. This was done using the Thermo Scientific™ TraceGOLD™ TG-PBDE column and ultra-inert (UI) Thermo Scientific™ LinerGOLD™ 6 baffle PTV liner. The suitability for routine food safety analysis of PBDEs was assessed by monitoring a solvent standard QC relative response factor (RRF) drift and deviation from the calibration average. This was achieved through the repeated injection of a QC standard at intervals throughout a sequence of 320 injections of samples, standards, and blanks. The concentration(s) of PBDEs in the QC standard corresponded to 10–50 pg on column, equivalent to 13–63 ng/kg in food samples. The system robustness was evaluated by assessing the peak area stability of over 105 injections of a complex fish extract containing incurred residues. Importantly, all analyses were performed using a single PTV liner and no column maintenance.

Experimental

Calibration standards containing 27 native PBDE congeners at five concentration levels and 16 (^{13}C-labeled) PBDE internal standards were acquired from Wellington Laboratories, Inc. (Ontario, Canada). For the assessment of RRF stability, a mid-calibration concentration standard was defined as the quality control (QC) standard and injected directly. The details of the standard preparation can be found in the supporting 2018 PBDE application note.[3] Sample preparation is described in a scientific paper by A. Fernandes et al.[4]

A TSQ 9000 triple quadrupole GC-MS/MS instrument equipped with an AEI source was coupled with a Thermo Scientific™ TRACE™ 1310 GC with Instant-Connect PTV injector.

Liquid injection (2 µL) of the sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH autosampler and a LinerGOLD 6 baffle PTV liner 2.0 mm × 2.75 mm × 120 mm (P/N 453T2845-UI).

Chromatographic separation was achieved by using a TraceGOLD TG-PBDE 15 m × 0.25 mm I.D. × 0.10 µm (P/N 26061-0350) film capillary column. Additional details of instrument parameters and consumables used can be found on the Thermo Scientific™ AppsLab™ Library of Analytical Applications.

Data were acquired using timed-SRM, processed, and reported using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software, version 7.2. Chromeleon CDS allows instrument control, method development, quantitative/qualitative analysis, and customizable reporting all within one platform.[5]

Results and discussion

Robustness was assessed based on absolute peak area response for PBDEs present in the n=105 sequential injections of a fish extract containing incurred residues. The suitability of the system for routine PBDE analysis was then assessed by evaluating the stability of the RRFs over a 320-injection sequence for a mid-calibration solvent-based PBDE standard.[3]

Robust sample analysis in routine GC-MS/MS

To assess system robustness, a fish extract containing incurred PBDE residues was injected 105 times, and the absolute peak area response was plotted for all PBDEs detected (Figure 1). The absolute amount on column varied from 11 fg to 9 pg, and each analyte detected had the ion ratio within tolerance of ±30% based on the average ion ratio calculated from the calibration. The results demonstrate consistent system response with peak area % RSD <10% for 105 consecutive injections. Notably, no inlet, column, MS maintenance, or MS tuning were performed over the injection sequence.

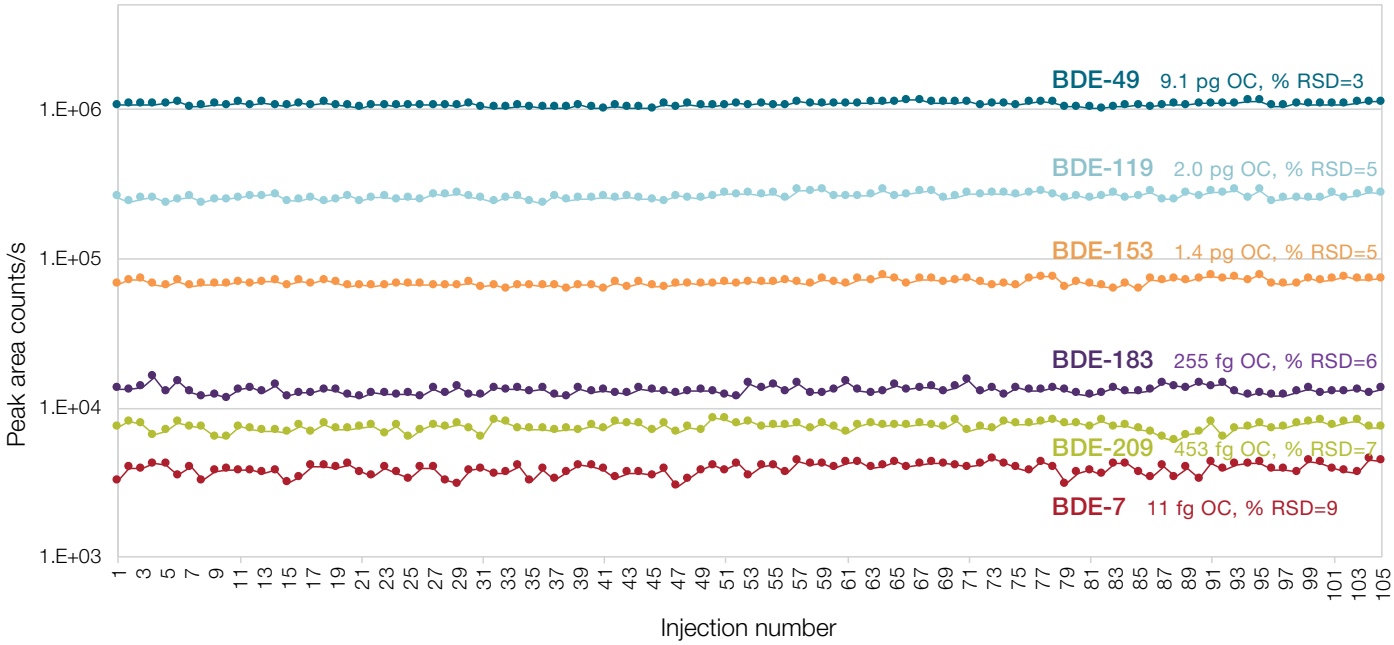

Figure 1. The absolute peak area (without internal standard adjustment) for di through deca BDEs; BDE-7, BDE-49, BDE-119, BDE-153, BDE-183, and BDE-209 detected in the 105 injections of a fish extract containing incurred residues. The following is shown: (i) total on column (OC) BDE amount in fg or pg, (ii) peak area % RSD for n=105 matrix injections.

Relative response factor stability in QC solvent standards

To test the suitability of the AEI source for routine GC-MS/MS analysis, a mid-calibration level QC solvent standard was injected every 20 matrix injections and the average RRF % RSD was monitored for each PBDE congener (Figure 2). The RRF % RSD calculated over a 320-injection sequence that took 3.5 days to complete (which included over 250 matrix injections) were <10% for all of the 27 targeted PBDEs. Stable RRFs are important because drift and variability can result in inaccurate quantification and QC failures leading to repeat analyses. This demonstrates the excellent system stability over a near full working week with no liner replacement, column trimming, MS maintenance, or system tuning.

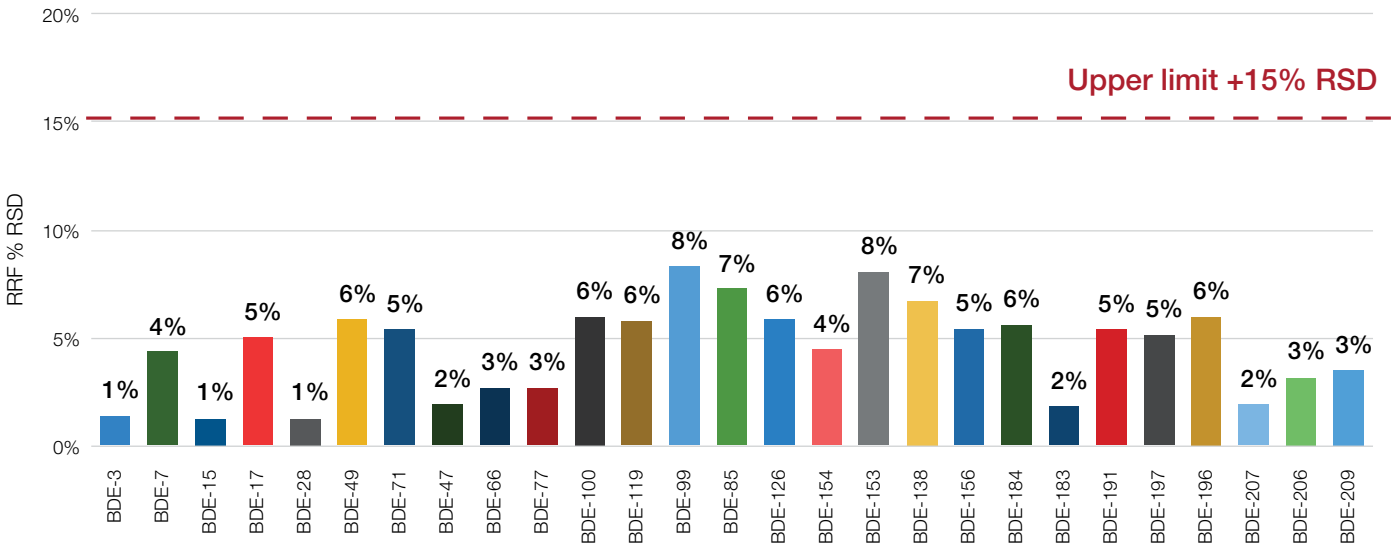

Figure 2. Stability of RRF (% RSD) for 18 QC injections calculated over a 320-injection sequence containing blanks, standards, and over 250 matrix injections

In the results for all PBDEs, the RRF values calculated for the QC standards across the batch of 320 injections were all within the RRF tolerance window of ±15%, compared to the mean calculated from the calibration. Similarly, QC RRF outliers can result in samples within bracketed QCs requiring reanalysis, which increases the cost per sample. In the calculated BDE-209 example (Figure 3), the RRF % RSD for n=18 QC injections was 3% and was within the lower and upper bound limits ±15% derived from the average RRF of the calibration.

Conclusion

The purpose of these experiments was to assess the robustness and suitability of the TSQ 9000 GC-MS/MS system while demonstrating the following:

- The system robustness as demonstrated by peak area repeatability calculated as % RSD from n=105 consecutive injections of a fish extract containing incurred residues showed excellent system stability with peak areas % RSDs for detected PBDEs being <10%.
- Excellent system stability over a 320 injection sequence containing over 250 matrix injections was demonstrated for all 27 native PBDEs in a mid-calibration level injected QC standard with the RRF % RSDs all being <10%.
- For all injected QC standards (n=18) over the 320 injection sequence the RRFs were all within ±15% of the measured value across the calibration curve with no liner change, column trimming, or MS maintenance and tuning.

Taken together, the results of the experiments described in this work demonstrate robust analytical performance of the TSQ 9000 GC-MS/MS system, which makes it an ideal tool for routine laboratory work such as analysis of trace level food contaminants.

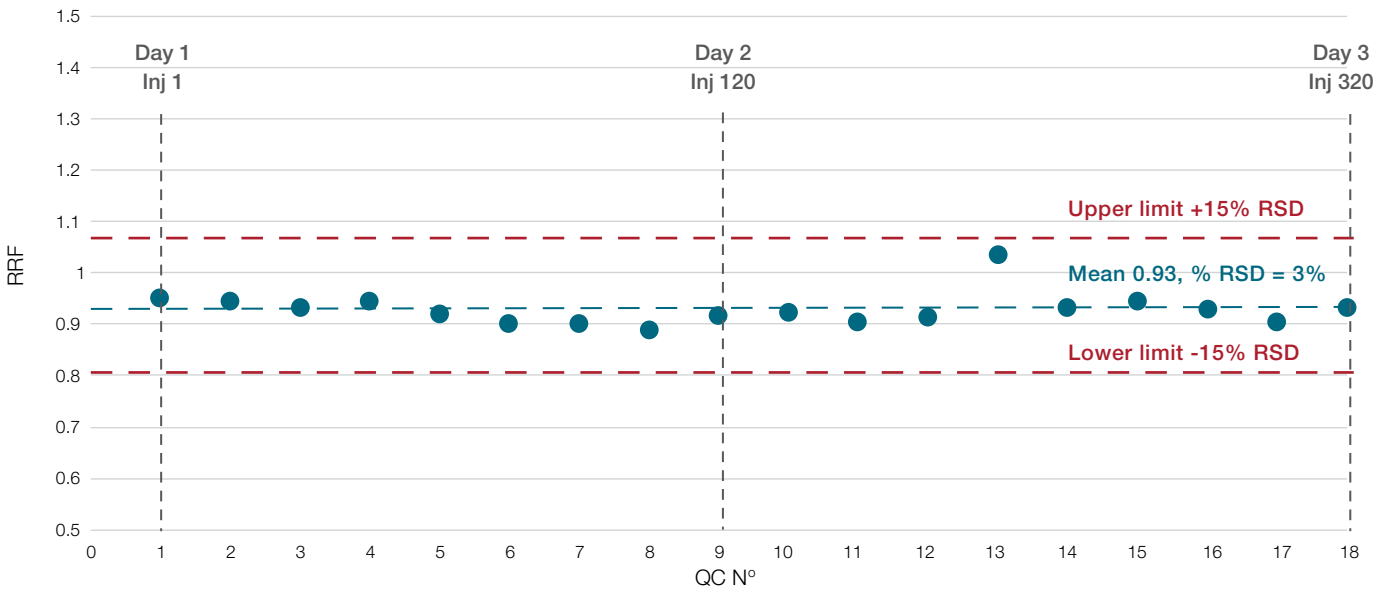

Figure 3. Chart showing the individual RRF values calculated for mid-level standard QCs for BDE-209 (10–50 pg OC, 13–63 ng/kg in food sample) ran throughout the 320-injection sequence. The ±15% tolerance RRF upper and lower limits are annotated using the red dotted lines and the mean RRF for the QCs is displayed using the teal dotted line.

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