

# IDENTIFICATION AND QUANTIFICATION OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN ENVIRONMENTAL SAMPLES USING GAS CHROMATOGRAPHY COUPLED TO ORBITRAP MASS SPECTROMETRY

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## Introduction

Polybrominated diphenyl ethers (PBDEs) are a group of organobrominated contaminants that inhibit or suppress combustion in organics material, and due to these properties have been widely used since the 1970s as flame retardants in a wide range of commercial, and household products including textiles, building materials, electronics, furnishings, motor vehicles, and plastics.

Most PBDEs resist degradation, and bioaccumulate in environment, and food chains, and can be transported through air, and water over long distances. They have been identified, in some cases far from their place of use, in a wide range of samples including air, water, sediment, fish, birds, marine mammals, and humans.<sup>1</sup> Many PBDEs have been identified as toxic, with links to cancer, and endocrine disruption. As a consequence the use of certain PBDE (including penta, tetra and deca BDE) have been banned, and are currently present in the Stockholm Convention lists of persistent organic pollutants.<sup>2</sup>

Due to the vapour pressures, and polarity of PBDEs, gas chromatography (GC) is the standard analytical technique used, with detection using either electron capture detector (ECD), or mass spectrometry (MS). There are many analytical challenges to consider when developing a GC-MS method for the analysis of PBDEs, especially related to the active nature of high molecular mass PBDEs (e.g. BDE-209), and to the large number of compounds, resolution, and peak symmetry requirements (e.g. chromatographic separation of BDE 49 and BDE 71 can be challenging in complex environmental samples).

This work demonstrates the use of high resolution accurate mass GC-Orbitrap technology for the targeted analysis of 27 PBDE native congeners in air, ash, sediment, and sludge samples using a sensitive, fast, and robust high throughput method.

## Materials and methods

In the experiments described in this work, an approach for identification and quantification of BPDEs in environmental samples is presented. The analytical instrument used was a Thermo Scientific Exactive™ GC Orbitrap™ GC-MS mass spectrometer coupled with a Thermo Scientific™ TRACE™ 1310 GC. Sediment, sludge, air and filter dust samples (2 g), were Soxhlet extracted with n-hexane/dichloromethane (1:1), followed by Florisil purification stage (15 g), and elution with 100 mL n-hexane/DCM (80:20). The extract was then blown to dryness and reconstituted with nonane prior to GC-MS analysis. Mixed calibration standards (BDE-CSV), containing 27 native BPDE congeners were acquired from Wellington Laboratories Inc. (Ontario, Canada).

Sample introduction was performed with a Thermo Scientific™ TriPlus™ RSH autosampler, and compound separation was achieved using a Thermo Scientific™ TG-PBDE™ 15 m x 0.25 mm I.D. x 0.10 μm film capillary column. The mass spectrometer was tuned, and calibrated using FC43 to achieve mass accuracy of < 0.5 ppm. The system was operated in electron ionization mode (EI) using full scan, and 30,000 mass resolution (Full Width at Half Maxima, measured at *m/z* 200). Chromatographic data was acquired with a minimum of 12 points/peak to ensure consistent peak integration. Data were acquired, and processed using the Thermo Scientific™ TraceFinder™ software using a targeted analysis data processing workflow.

## Results and discussion:

Using the Exactive GC Orbitrap mass spectrometer operated at high resolving power a large number of PBDE congeners were detected, identified, and quantified in complex matrix environmental samples. Targeted screening experiments were developed for the PBDE congeners considered, extracted ion chromatograms for 27 PBDE congeners are shown in Figure 1a, with the excellent chromatographic separation of the critical pair (PDE-49 and BDE-71) achieved in <12 min (Figure 1b).

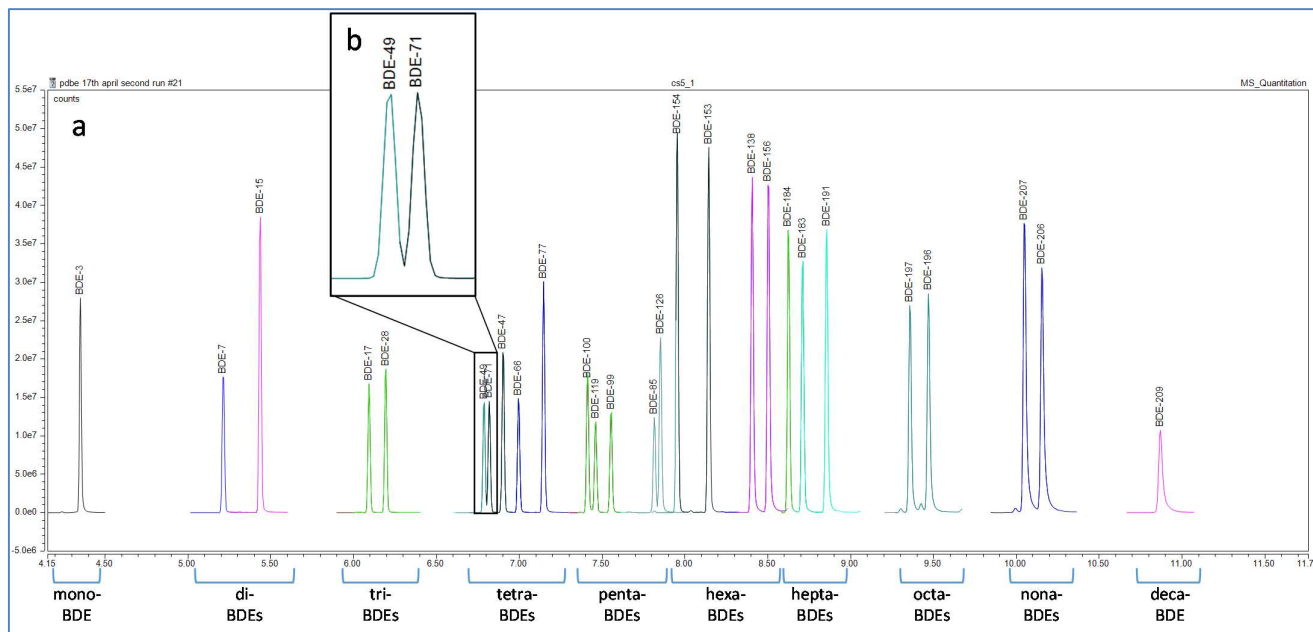


Figure 1. (a) Extracted ion chromatogram (XIC  $\pm 5$  ppm extraction window) chromatograms for 27 PBDE native congeners, (b) separation of critical pair (PDE-49 and BDE-71).

To assess the linearity, five calibration levels (1 to 400 pg on column for mono- to penta-PBDEs, 2 to 800 pg on column for hexa- to octa-PBDEs, and 5 to 2000 pg on column for nona- to deca-PBDEs) were analysed for all the congeners considered, calibration curves for PCB-209 and PCB-71 are shown in Figure 2. For all compounds excellent linearity was obtained with  $R^2$  values <0.999 and residual values %RSD <6%.

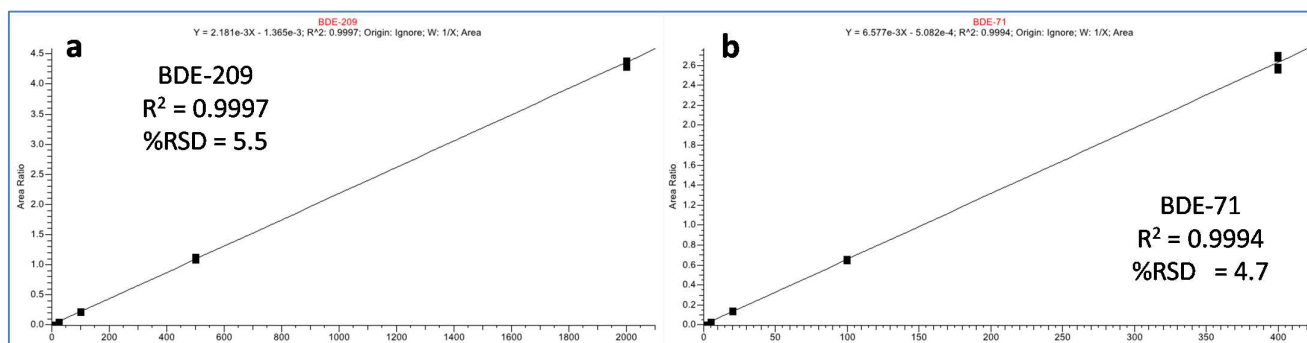


Figure 2. Calibration curves for (a) BDE-209 and (b) BDE-71

System sensitivity, defined as instrumental detection limits (IDLs) was determined experimentally for each compound by performing  $n=12$  replicate injections of the lowest serially diluted solvent standard. Calculations of IDLs were made using one-tailed student t-test at the 99% confidence interval for the corresponding degrees of freedom, and taking into account the concentration on column for each PBDE congener, and absolute peak area %RSD (Figure 3).

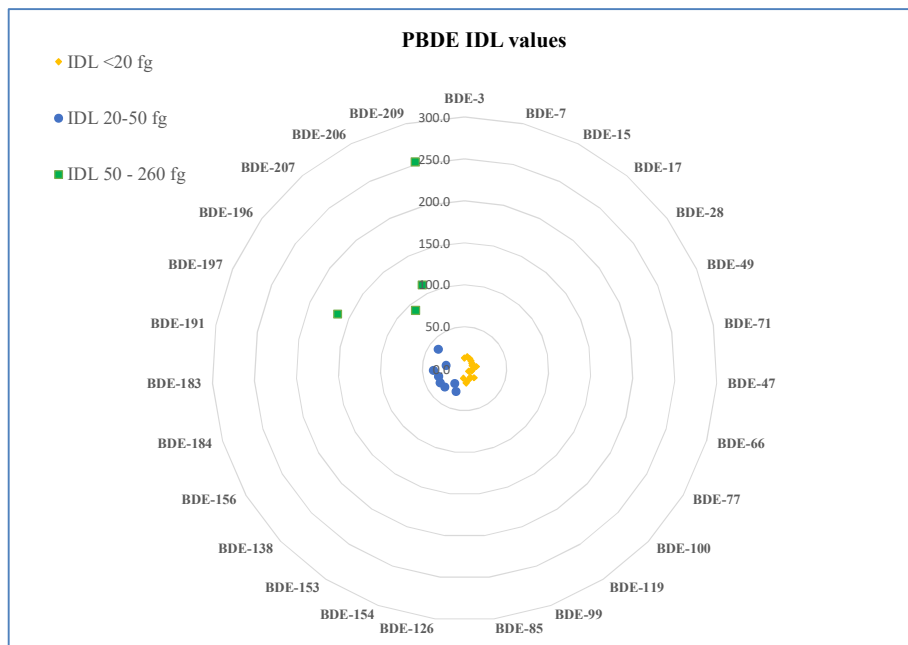


Figure 3. Calculated IDL values for 27 PBDE native congeners.

Repeatability of PBDE responses in matrix was accessed by carrying out n=12 repeat injections of a filter dust sample extract, as shown in Figure 4 for PDE-209.

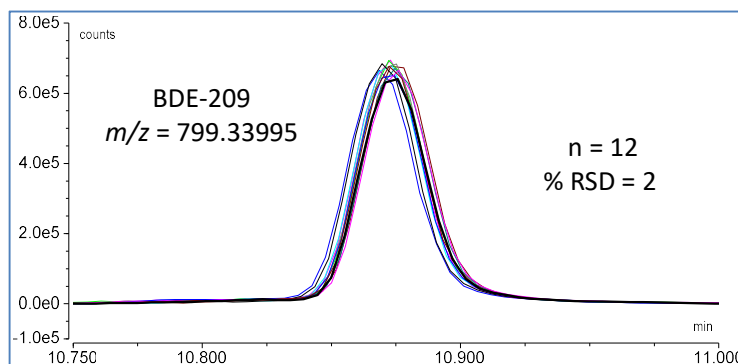


Figure 4. Replicate injections ( $n=12$ ) of a filter dust sample, overlaid XIC ( $m/z$  799.33995) chromatograms for BDE-209.

Examples of the complexity of extracted samples analysed are shown as TIC versus extracted ion chromatograms below for sludge, and filter dust samples (Figure 5 and 6 respectively). TIC and PBDE extracted ion chromatograms signal intensities (Y-axis) were normalised to simplify the visual comparison.

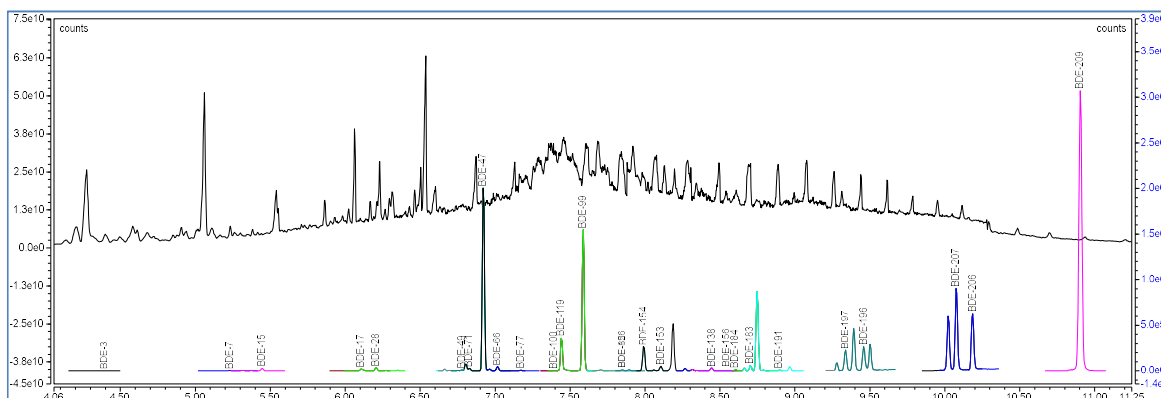


Figure 5. Sludge sample chromatograms: (upper) TIC full scan; (lower) XIC for the BPDE congeners identified in the sample.

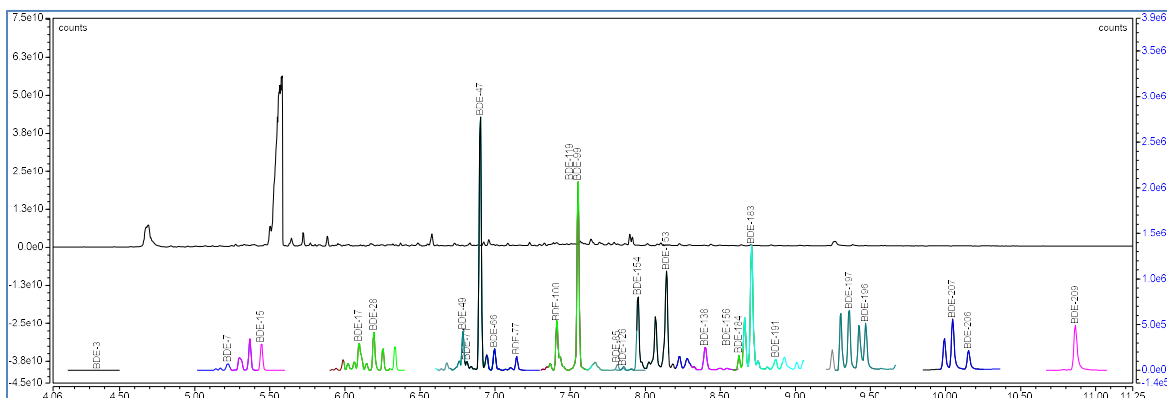


Figure 6. Filter dust sample chromatograms: (upper) TIC full scan; (lower) XIC for the BPDE congeners identified in the sample.

Maintaining mass accuracy, and spectral fidelity is critical for correct compound identification in complex environmental samples. Figure 7, illustrates the mass accuracy, and the isotopic pattern match achieved for BDE-209 with mass accuracy of < 2 ppm consistently achieved for each ion in the isotopic cluster.

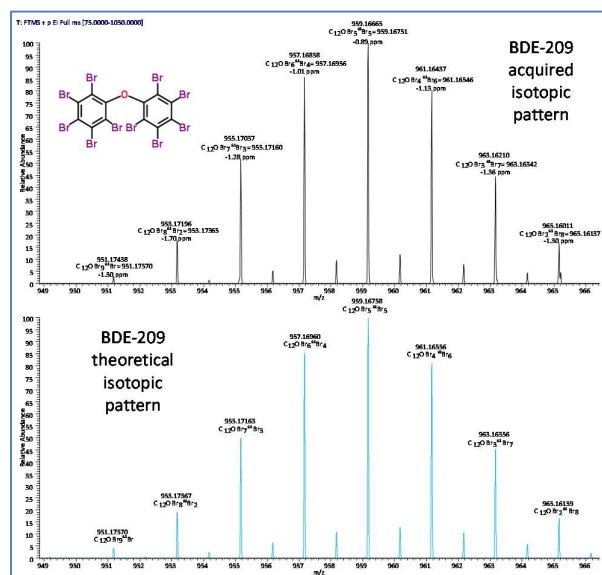


Figure 7. Mass spectrum acquired for BDE-209, acquired isotopic pattern (upper) compared against the theoretical isotopic pattern (lower).

The method described used GC-Orbitrap mass spectrometry for targeted quantification of PBDEs in complex environmental samples. Sediment, filter dust, air, and sludge samples were assessed for their PBDE content. In the sludge samples analysed, the predominant PCB congeners identified were BDE-209, 47 and 99, where as in the filter dust samples BDE-47, 119, 99, 53 and 183 were prevalent. This preliminary results offers excellent selectivity, and sensitivity for the analysis of PBDEs even in the most complex samples. Moreover, the routine high resolution offers excellent selectivity in difficult matrices, and the mass accuracy obtained allows for unambiguous identification, and elemental composition confirmation of chemical contaminants.

## References:

1. R.A.Hites. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. Environ.Sci.Technology. 38(2004) 945.
2. Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs. [Online] <http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/GuidancefortheinventoryofPBDEs/tabid/3171/Default.aspx> (accessed May 8, 2018).