

## Untargeted screening of novel brominated flame retardants in indoor dust using a Q-Exactive high-resolution accurate mass spectrometer

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### Introduction

Due to the legislative ban of specific brominated flame retardants (BFRs), several new brominated flame retardant (NBFRs) have been developed by industry. To explore their presence in different environmental compartments and ultimately understand their environmental fate, analytical methods have to be developed for targeted analysis [1]. Classically these compounds are determined by GC-based instrumental methods. In recent years LC-based methods coupled to low resolution mass spectrometers have been developed [2]. The advance of high resolution instrumentation facilitates accurate measurements and identification of unknowns, degradation and transformation products. Further the bromine isotopic pattern aids in identifying relevant substances, as well as the use of mass defect plots, a technique starting to be more commonly used in environmental science [3].

### Materials and methods

*Sampling.* Dust samples were collected according to an established protocol [4] in offices, laboratories and instrument assembly rooms. In summary, in carpeted rooms, 1 m<sup>2</sup> of carpet was vacuumed for 2 min and in rooms with bare floors, 4 m<sup>2</sup> was vacuumed for 4 min. Samples were collected using nylon sample socks (25 µm pore size) that were mounted in the furniture attachment tube of the vacuum cleaner.

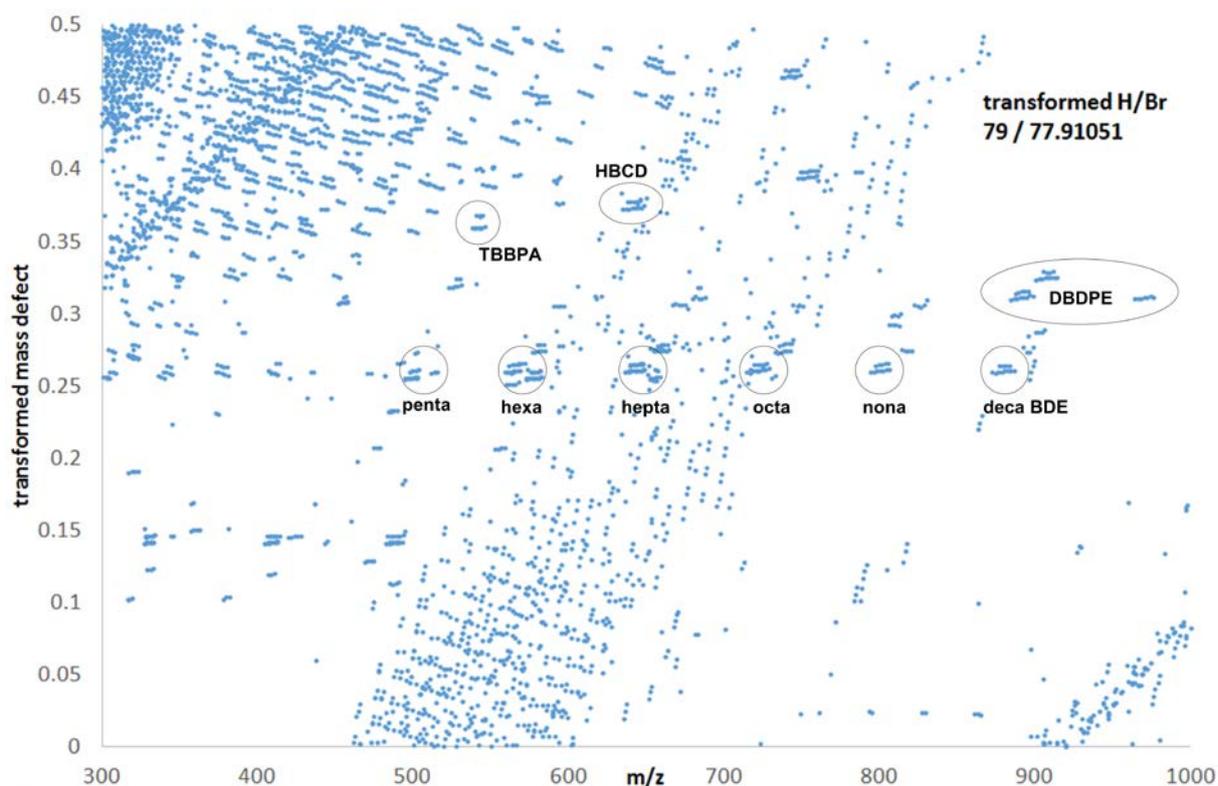
*Extraction and clean-up.* 0.5 g of dust was weighed, spiked with mass-labeled internal standards and mixed with diatomaceous earth as dispersant. Extraction was conducted using a Thermo Scientific™ Dionex™ ASE™350 accelerated solvent extractor. Use of different solvent mixtures (hexane, dichloromethane and acetone) was investigated. Further in-cell cleanup using layers of silica and Florisil™ in the ASE cell was performed to reduce possible matrix interferences. Samples were evaporated to dryness using a Thermo Scientific Rocket™ Evaporator system and then reconstituted in 2 mL methanol:toluene (1:1).

*UPLC-HRMS measurement.* Final extracts were separated using a Thermo Scientific Accucore™ RP-MS 100x2.1mm, 2.6µm column on a Thermo Scientific Accela™ HPLC system (Accela™ 1250 Pump and Open autosampler). A 15 min. gradient elution program with water (mobile phase A) and methanol (mobile phase B) at a flow rate of 400 µl/min. Samples were analyzed on a Q Exactive™ mass spectrometer with an APCI source in negative ionization mode at a resolution of 70,000.

*Data interpretation.* Raw data files were processed using both Thermo Scientific Xcalibur™ and Thermo Scientific Compound Discoverer™ version 2.0 software. The Compound Discoverer workflow includes the detection of unknowns compounds, elemental composition predictions, hides background from blanks, performs a ChemSpider library search and scores the compounds based on selected bromine isotope patterns. In addition and as a comparison mass defect plots were created using Microsoft® Excel to visualize the presence of brominated compounds.

## Results and discussion

Full scan experiments were conducted to screen for the presence of brominated compounds. From the obtained data a mass defect plot was constructed to estimate the number of brominated compounds within the dust samples. Halogenated compounds have a unique negative mass defect, which readily distinguishes them from other molecules in a complex mass spectrum. Furthermore, homologous series of compounds can be easily visualized. One mass scale applicable to environmental analytical chemistry is defined by the substitution of a hydrogen atom by a chlorine atom (H/Br) [3]. The conversion used here is based on the multiplication of each peak of a chosen mass spectrum by 78/77.91051 and plotting the nominal mass vs. the transformed mass defect. The resulting mass defect plot is shown in Figure 1.



**Figure 1. Mass defect plot of extracted dust sample transformed with H/Br scale 79/77.91051 scale**

The mass defect plot was then compared to the results obtained from the suspect screening using Compound Discoverer. Both confirmed the presence of brominated flame retardants in the sample, legacy BFRs (Penta up to DecaBDE, TBBP-A, HBCDs), as well as NBFRs (EH-TBB, BEH-TBP, DBDPE). For a suspect the following confirming criteria were selected: spectral similarity score (SFit>80%), accurate mass deviation < 5 ppm, as well as retention time.

The use of high-resolution accurate mass (HRAM) instrumentation facilitates identification of targeted compounds and unknowns by means of selectivity, elemental compositions and isotopic pattern scoring. Compound Discoverer™ was successfully employed as a tool for the identification of BFRs and NBFRs in dust samples. The use of relevant databases, such as ChemSpider, can significantly help in the identification of compounds.

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