thermoscientific

Quantification Of Decabromodiphenyl Ether In Microplastics Using Direct Insert Probe Coupled With Magnetic Sector High Resolution Mass Spectrometer In Full Scan Mode

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INTRODUCTION

In 2019 the World Health Organization (WHO) called for further investigations and assessment for microplastics in the environment and their potential impacts on human health.
Plastic debris is found in the environment in a very wide range of sizes. In the early 1970s the first finding of tiny beads and fragments of plastic, especially polystyrene, in the ocean were reported. The term “microplastics” was introduced in the mid-2000s. Today, it is used extensively to describe plastic particles with an upper size limit of 5 mm.

It is known that microparticles can be ingested by marine organisms, and further studies are needed to assess on the extent to which microplastics represent a hazard to marine life – and may provide a pathway for transport of POPs such as BFRs through the food web. However, as BFRs are known to enter human’s body by hand-mouth contact, it is very likely that they can also enter by food containing microplastic which is contaminated with POPs. To-date no methods have been established to determine POPs in microplastics like there are for monitoring compliance with RoHS limits of PBDEs. These recommended methods can be divided into two main approaches: orientative screening and high-accuracy chemical analysis. Screening is preferred for in situ evaluations as it is usually performed via solid sampling techniques like hand-held X-ray Fluorescence spectroscopy (XRF) although this can only quantify Br as a proxy for the total BFR content, thereby running the risk of false positives. More conventional techniques are recommended for high-accuracy determination of BFRs like PBDEs. Specifically, RoHS requires GC-MS analysis to determine the BFR content in styrenic polymers (preceded by different sample preparation steps: sub-sample grinding, cryogrinding, solvent extraction, extract filtration, selective precipitation for oligomer removal, and chromatographic purification).
These traditional techniques have several drawbacks aside from being time consuming and expensive. Soxhlet or pressurized liquid extraction of plastics often dissolves a substantial fraction of the matrix (polymer) together with the target compound, rendering the ensuing extract purification laborious and often leading to highly variable analyte recoveries. Especially for very small individual particles in microplastics such a sample preparation is not suitable. In addition, by using a GC method, the high boiling point and its enhanced susceptibility to degradation and debromination when exposed at the elevated temperatures of the injector and column make BDE209 a challenging analyte.
We present here a simple, sensitive and rapid method using Direct Insertion Probe (DIP) in combination with magnetic sector high resolution mass spectrometry (HRMS). This method characterizes target compounds without a chromatographic separation needed, solely via accurate mass determination combined with a traditional library search. It does not require any sample preparation nor a GC or LC inlet. The method is validated via determination of BDE209 in Acrylonitrile Butadiene Styrene (ABS) solid reference materials (RMs), but accurate mass determination can also be applied to unambiguously identify other PBDE congeners.

MATERIALS AND METHODS

Samples and Sample Preparation

Br (in the form of deca-BDE) and Sb (in the form of Sb_2O_3) were added to an ABS terpolymer melt with the aid of an extruder. Sb_2O_3 is generally used as a synergist FR in combination with BFRs. A set of five different reference materials was produced by Fachhochshule Muenster Labor fur Instrumentelle Analytik in the form of pellets containing different mass fractions of both Br and Sb plus typical fillers commonly used in ABS in order to best simulate the matrix of the samples. Mass fractions of Br in the produced materials were certified via Neutron-Activation-Analysis (NAA). The uncertainty of NAA is about 7% . To assess macroscopic homogeneity a wavelength dispersive X-ray spectrometer was used with RSD below 2% for Br. To assess microscopic homogeneity a synchrotron radiation m-XRF (SRm-XRF) was used. The spot size of the exciting beam was 200 mm, the RSD for Br was 0.7%.
No sample preparation was required. A very small amount (≈0.045 mg) was scraped from the pellets of the RMs with a scalpel, accurately weighed with a precision scale (0.0005 mg) and inserted in the aluminum crucibles for the DIP. The influence of the scale error on such a small sample is 1.1%.

Instrumentation

The Thermo Scientific™ DFS™ Magnetic Sector High Resolution Mass Spectrometer (Fig.1) in EI mode equipped with a Direct Insert Probe was used with a resolution of 20 000 FWHM.
DIP temperature ramps and electron energy was optimized on BDE209 for best sensitivity, reproducibility and degree of fragmentation of the parent ion. Perfluoro kerosene (PFK) was used for checking the tuning and calibration of the instrument.

Figure 1:Thermo Scientific DFS Magnetic Sector GC-HRMS.

Data Analysis

Thermo Scientific™ Mass Frontier™ Software was used to simulate all the potential BDE209 fragments and hence identify target ions, for this method we chose the molecular ion of decaBDE (m/z 959) and its main breakdown product (m/z 799) octaBDE. Isotopic patterns and exact masses corresponding to these two ions were simulated using the Thermo Scientific™ Xcalibur™ Software. The exact masses were used to calculate the mass measurement error (ppm). The deviation of the measured masses from the exact masses was for all isotopologues of BDE209 (averaged over 20 scans) less than 1 ppm. (see Fig. 2).

RESULTS

Verification of the DIP-HRMS method

As the concentrations of BDE209 containing plastics is typically orders of magnitude higher than the detection limits of the DFS magnetic sector GC-HRMS all experiments were carried out in full scan mode (m/z 30–1000) which allows to cover all possible fragments including molecular Br simultaneously.
The calibration curve was determined by analyzing each of the five solid RMs (0%, 0.1%, 0.5%, 1%, 2% w/w of BDE209) in triplicate. Intensities were considered selecting the 3 most intense m/z values from the isotopic pattern and averaging the intensities of the time signals corresponding to those 3 masses. Scans from the tails of the transient signal were excluded when their relative intensity was less than 5% of the most intense scan (this corresponds to approx. 40 scans). The signal intensity of BDE209 (average intensity between m/z 959, 957, 961) was plotted against the reference value of the RMs. In the same way, the signal intensity of the -2Br fragment (average intensity between m/z 799, 797, 801) was plotted against the reference value. The correlation factor R_2 was >0.999 for both BDE209 and its octabrominated breakdown product. The calibration curve for BDE209 was obtained by averaging the signal intensity of the three most abundant isotopologues of BDE209, m/z 959, 957, 961 for each calibration level (Fig. 3a). The calibration curve for the main fragmentation product of BDE209 was obtained by averaging the signal intensity of the three most abundant isotopologues of octaBDE, m/z 799, 797, 801 for each calibration level (Fig. 3).
The LOD was defined as in the ICH1 Guidance
(Q2, R1: validation of analytical procedures) as 3 times the standard deviation of the response on the triplicate measurement of blank samples (RM BDE209) divided by the slope of the calibration curve. The noise was below 1/3 of the instrument detection limits.
The calculated LOD with this method was 0.112 mg· kg^{-1}, the LOQ was 1.120 mg· kg^{-1} for BDE209, slightly lower than a similar study performed with Direct Exposure Probe (DEP),[3] and with the advantage of no sample preparation needed. The memory effect was evaluated by calculating the RSD% between triplicate measurements of the most concentrated RMs: the percent variation was 0.47% and no increasing trend was observed. Intraday stability was evaluated by performing control runs of RM3 at the beginning, in the middle and at the end of each day of analysis. Over 3 days the intraday RSD of the signal intensity for BDE209 averaged at 1.96%, while inter-day RSD was 0.51%.

The method was applied to 21 real polymeric samples (children's toys and food contact articles, for which the BDE209 concentration was measured. BDE209 data and total elemental Br measured with an X-ray fluorescence spectrometer were plotted to evaluate if a correlation existed between the two metrics. BDE209 was detected in a concentration ranging from 8.8 mg · kg^{-1} to 4327 mg · kg^{-1} . Considering that these data refer to real samples, containing a suite of different BFRs, each potentially contributing to the total elemental Br concentration; the correlation (R2 = 0.86) between our BDE209 concentration measurements and those for total Br is striking. Moreover, our measurements of BDE209 – which is likely to be a fraction of the total BFR content – never exceeded those of total detected Br.

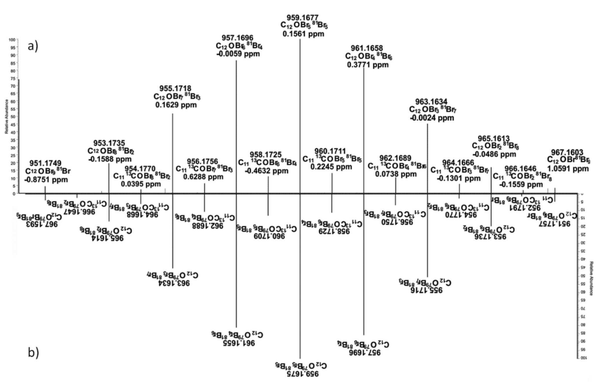

Figure 2. Comparison of (a) accurate masses measured over 20 scans for BDE209 and (b) their calculated exact value.

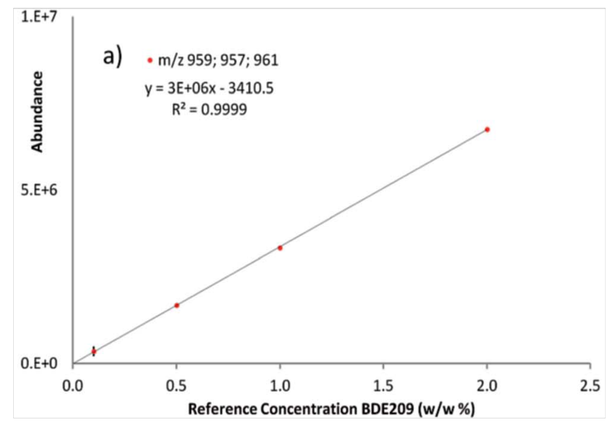

Figure 3. Calibration curves and linearity for the analysis of (a) [BDE209]+, (b) [BDE209-Br_2]+ obtained by DIP.

Reproducibility of the fragmentation ratios

The ionization behavior was tested for reproducibility by selecting m/z 799 and m/z 959 from the time signal and measuring the intensity for these masses over the selected time interval. DIP offers a specific advantage with respect to GC-MS analysis: as there is no column or injector between the sample introduction system and the ionization volume, it is possible to differentiate between breakdown products (caused by thermal degradation) and ionization fragments (produced by the EI ionization process). This is easily done by comparing the time signals for the molecular ion and for its possible moieties as shown in Fig. 4 (a) and (e) show the overlap in intensities of the time signal respectively for the decabrominated ion and the octabrominated ion, meaning that the latter was formed simultaneously in the source, as a fragment of the former.

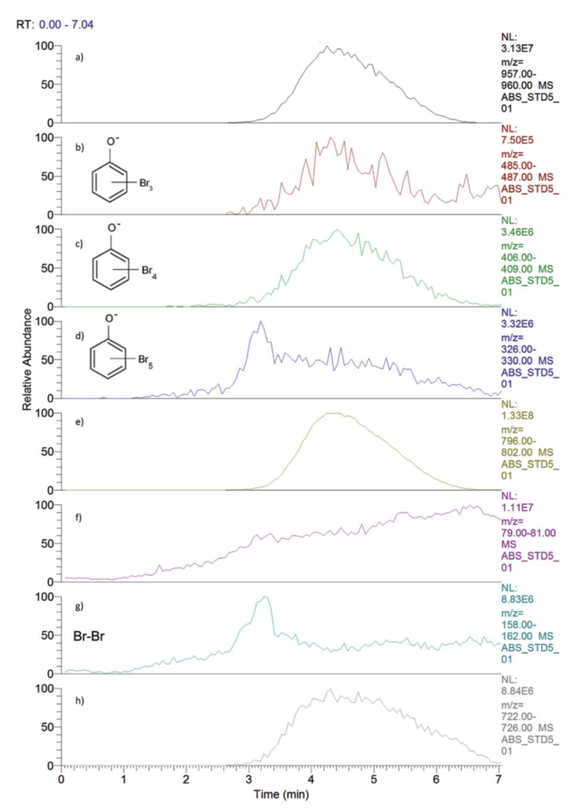

Figure 4. Time signal obtained with DIP-HRMS. penta brominated ions (d) corresponds to a simultaneous release of Br2 molecules (g).

This shows that as the pentabromophenate ion (d) was detected at the same time as molecular bromine (g), the debromination happened in the ion source and not as a thermal process in the sample; moreover, time signals (d) and (g) are both detected before the Deca- and Octa brominated fragments meaning that their parent ion was already present in the reference material before the insertion in the source. The ratio between the molecular ion and its main fragmentation product was – for all measured concentrations – 3.1 ±0.04 , showing it to be independent of the sample concentration and suggesting very reproducible fractionation behavior. This allows subtraction of the contribution made by the BDE209-2Br fragment to the signal for m/z 799, thereby facilitating quantification of any octa-BDEs present.

A comparison between the mass spectrum of the sample RM obtained using our DIP-HRMS method and that obtained via GC-MS following traditional sample preparation methods and liquid sampling in Fig. 5 shows how the ratio between m/z 799 and m/z 959 is almost two times higher for the traditional GCMS technique.
By using the DIP method the sample is introduced at room temperature into a chamber under vacuum and then heated up. Therefore the sufficient vapor pressure is reached at lower temperatures compared to a GC method were the sample is introduced under pressure into the hot liner of the Injector.

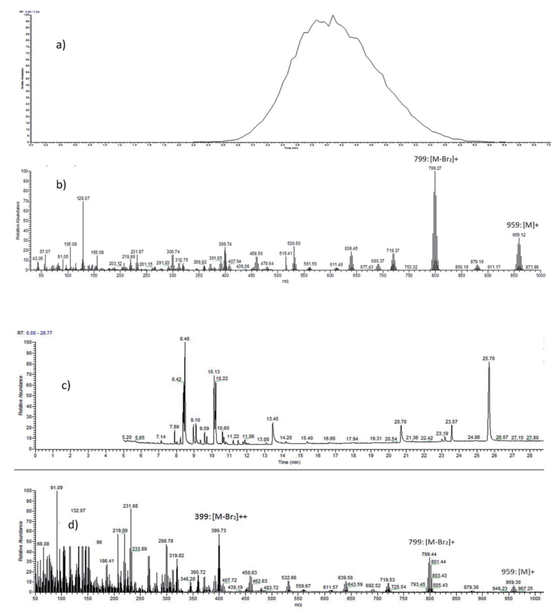

Figure 5. TIC and mass spectra for RM (ABS with 0.5% BDE209) (a-b) DIP-HRMS, (c-d) GC-MS.

CONCLUSIONS

The method reported here represents a rapid, accurate way of performing compound specific quantification of BDE209 in polymers, that avoids completely the labor intensive, time consuming preparation of the samples. Because of the conveniently small sample size required for our analysis (≈0.045 mg), this virtually non-destructive method is designed to be used on articles still in use as domestic appliances or for small particles such as microplastics. With a linear range covering a concentration span of 19000 mg· kg^{-1} which for new and recycled plastics represents the full range of detected concentrations (a considerable improvement with respect to a recent DEP study,[3] where the calibration span was from 0.5 to 16 mg· kg-1) this technique can be a valid, easier, alternative to existing analytical methods for monitoring RoHS compliance in consumer goods. Our method is tested here for BDE209 in ABS as a proof of concept, but given suitable solid RMs, quantification of lower brominated compounds in other polymers and over wider calibration ranges will be feasible. DIP-MS optimized for PBDEs in plastics can give results that are as accurate as GC-MS[4] but are at least 50 times faster to achieve. As no sample preparation is needed it can be easy applied direct to individual small plastic particles found in microplastics.

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