

A New GC–ICP–MS Method for Compound Specific Determination of Brominated Flame Retardants

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Overview

Purpose: Develop a simultaneous, accurate and precise method for compound specific brominated flame retardant (BFR) quantification for PBDE congeners 28 to 209 without debromination.

Methods: A Thermo Scientific™ Trace™ 1310 Gas Chromatograph (GC) was interfaced with a Thermo Scientific™ iCAP™ Q ICP-MS to analyze PBDE technical mixes and WEEE material.

Results: BFR technical mixes and polymeric solid reference material extracts were successfully characterized and their detailed relative compositions compared to those reported in the literature.

Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs), which are commonly found in electrical and electronic equipment (EEE) and household textiles for flame retardancy purposes. Due to the ubiquitous use and poor recycling practices, these substances are now found in consumer goods that do not require flame retardancy, such as kitchen utensils, children's toys and food contact materials.

The three most important commercial BFR mixtures, c-pentaBDE, c-octaBDE and c-decaBDE, cover the vast majority of the market: the c-decaBDE mixture was the most produced accounting for 83.3% of the global market demand. In plastic materials commonly associated with EEE and recycled materials, these BFRs are not covalently bonded to the polymer chains. As a result, they may leach into the environment and due to their toxicity and tendency to bio-accumulate, pose a significant risk to the natural environment and human health. Furthermore, the toxicity of the BFR varies based on the number of Br atoms. Therefore, it is important to differentiate between BFRs with different levels of bromination. Consequently, the RoHS Directive 2011/65/EU, effective since 2013, dictates that PBBs and PBDEs (classes covering the most largely used additive BFRs, including deca-BDE) concentrations should be a maximum of 0.1 weight % in homogeneous material.

Simultaneously measuring the concentration of flame retardants containing different numbers of Br atoms rapidly and at high sensitivity and precision has hitherto been problematic. This is because higher brominated compounds (nona- and deca-BDE) are more labile and tend to debrominate into less brominated congeners (usually by losing two Br atoms at a time). To accommodate this, two GC columns are often used to cover the entire spectrum of possible PBDEs, a longer one (15 to 30 m) to achieve separation between the many lower brominated BDEs and a shorter one (6 m) to detect higher brominated compounds without decomposing them [Stapleton, 2006.]. This is time consuming and complex. Therefore a method based on ICP-MS detection was developed with a goal to accurately and rapidly quantify BFRs in plastic materials and subsequently consumer products.

Methods

Samples and sample preparation

Technical mixes, penta-BDE (Bromkal 70-5DE; penta DE-71), octa-BDE (Bromkal 79-8DE) and deca-BDE (Saytex 102E) (Cambridge Isotope Laboratories), were used to determine if the method presented here maintained the relative ratio of compounds across the chromatogram (Fig. 1a and 1b). A solid standard (ERM EC591, Institute for Reference Materials and Measurements) of polypropylene matrix was used to account for the matrix effect of real sample material (i.e. polymeric matrix in the inlet system), which was cold-solvent quiescently extracted and analyzed.

GC-ICP-MS

A Thermo Scientific Trace 1310 GC was interfaced to a Thermo Scientific iCAP Q ICP-MS. Sample introduction was via a Thermo Scientific™ TriPlus™ autosampler. Simultaneous analysis of PBDEs from congener 28 to congener 209 was undertaken during the same chromatographic run.

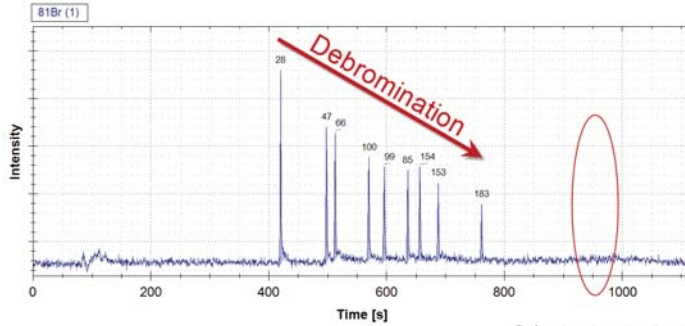
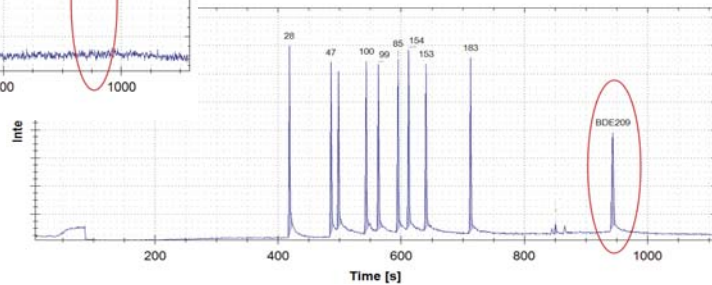


FIGURE 1a. On the left: a chromatogram of a standard mixture containing congeners BDE28 to BDE209. A standard chromatographic method causes a descending trend in intensity towards higher degrees of bromination, with the most labile congener BDE209 not visible

FIGURE 1b. On the right: a chromatogram of the same standard mixture: the relative intensities of each congener are respected and the BDE209 congener is visible as a sharp peak based on an improved chromatographic method.



Results

Calibration

Calibration curves (Fig. 2a and 2b) for each congener of the standard mix were developed by diluting the standard with nonane to create six calibration levels (2.5 ng/mL to 100 ng/mL). The correlation coefficient for each congener was $R^2 > 0.99$. A calibration curve was obtained using the ERM EC591 Solid Reference Material extracts in order to evaluate the matrix effect on the linearity of the data: the linearity was optimal for each measured congener ($R^2 > 0.99$; Fig. 2b).

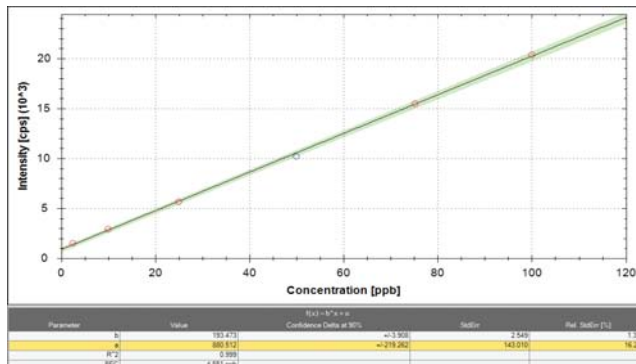


FIGURE 2a. Calibration curve for PBDEs standard mixture

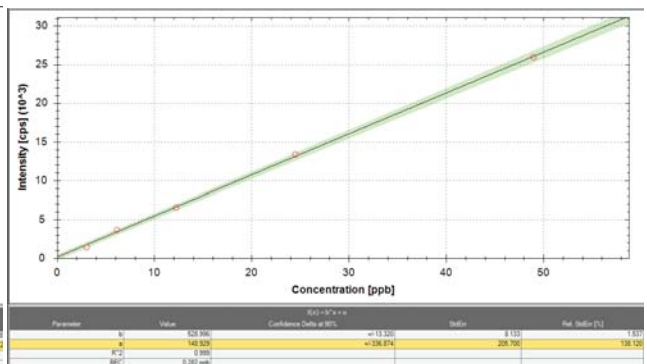


FIGURE 2b. Calibration curve for PBDEs in a ERM EC591 solid reference material extract

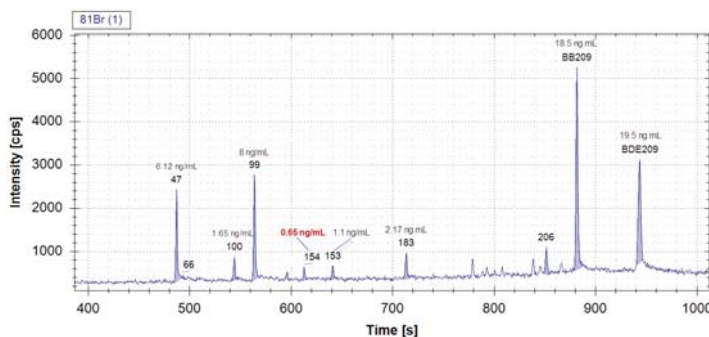


FIGURE 3. Chromatogram of the solid RM ERM EC591 with an improved chromatographic method that eliminates debromination

Table 1: GC-ICP-MS instrument parameters for PBDE analysis	
GC Column	DBSMS capillary column 0.25 mm I, 0.1 µm film thickness, 15m length (J&W Scientific, Agilent)
Injection mode and liner	PTV Splitless with SilicoSteel
Injection temperature	100°C
Injection volume	1 µl
Carrier flow (He)	3 to 4.5 ml/min
Make up gas flow (Ar)	950 ml/min
Interface temperature	270°C
Initial temperature	100°C
Initial time	2 min
Ramp rate	15°C min ⁻¹ ; 8°C min ⁻¹ ; 25°C min ⁻¹
Final temperature	280°C
Final time	4 min
Forward power	1400 W
Isotopes and dwell times	⁷⁹ Br is 100 ms; ⁸¹ Br is 80 ms
Transient acq. time	1200 secs

Conclusion

- The calculated LOD for this technique is 1.8 pg of analyte on-column (comparable to GC/LR-ECNI-MS [Eljarrat et al, 2002]). At least a ten-fold improvement is to be expected when coupling the GC to a sector field ICP-MS instrument. However, congeners peaks were measurable down to a 0.65 pg of on-column analyte. (Fig 3)
- By virtually eliminating the decomposition of higher brominated compounds into the lower brominated ones, quantification of the complete range of congeners was possible.
- Thanks to the programmed flow, chromatographic run times are reduced and by employing just one GC column, the number of analysis per sample is halved (Table 1).

References

- Eljarrat et al, 2002 . J Mass Spectrom 37: 76-84
 Stapleton, 2006. Anal Bioanal Chem 386: 807-817

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