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### A novel method for quantification of decabromodiphenyl ether in plastics without sample preparation using direct insertion probe-magnetic sector high resolution mass spectrometry

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## Analytical Methods

### Paper

1

2 **A novel method for quantification of Decabromodiphenyl ether in**  
3 **plastics without sample preparation using Direct Insertion Probe –**  
4 **Magnetic Sector High Resolution Mass Spectrometry.**

5 A. Guzzonato<sup>a</sup>, H. Mehlmann<sup>b</sup>, D. Krumwiede<sup>b</sup>, S. Harrad<sup>a</sup>.

6

7 We report a rapid, efficient analytical method for detecting Brominated Flame Retardants (BFRs) in plastic materials using  
8 Direct Insertion Probe with double focusing magnetic sector high resolution mass spectrometry. We acquired the total ion  
9 spectrum (30 to 1000 m/z) and observed 959 and 799 m/z ions respectively for quantification and evaluation of the  
10 fragmentation reproducibility of decabromodiphenyl ether (BDE209, MW 959 amu). *Ad-hoc* prepared Acrylonitrile  
11 Butadiene Styrene (ABS) solid reference materials (RMs) containing different concentrations of BDE209 were used to  
12 develop a 5-point calibration curve that showed linearity ( $R^2 > 0.999$ ) over a concentration range of 0.1 - 2% w/w BDE209.  
13 Relative standard deviation between triplicate determinations of BDE209 ranged from 0.32% to 0.42%. The limit of  
14 detection (LOD) obtained for BDE209 was 0.112 mg/kg, 4 orders of magnitude lower than the EU's maximum allowed  
15 concentration (MAC) in plastic. To our knowledge, this is the first method for compound specific quantification of BDE209  
16 that does not require any sample preparation, reducing the analysis time from roughly 14 hours to 12 minutes with  
17 comparable quality of results.

# Analytical Methods

## Paper

1 **Introduction** 49  
 2 Brominated flame retardants (BFRs) are a class of chemicals 50  
 3 used intentionally to impart flame retardancy in a wide range 51  
 4 of consumer goods (such as electrical and electronic 52  
 5 equipment (EEE), furniture, and textiles, etc.). They are also 53  
 6 found in many more goods and materials as an unintentional 54  
 7 result of poor recycling practices (kitchen utensils, children's 55  
 8 toys, Food Contact Materials) [1,2]. One major class of BFR are 56  
 9 the polybrominated diphenyl ethers (PBDEs). Of the several 57  
 10 types of PBDE formulation manufactured and used, the deca- 58  
 11 BDE mixture was dominant (83.3% of the global market 59  
 12 demand) [3] which to some extent, can debrominate once 60  
 13 released into the environment, resulting in a suite of less 61  
 14 brominated congeners with enhanced toxicity and ability to 62  
 15 bioaccumulate relative to the parent [3]. The RoHS recast 63  
 16 Directive 2011/65/EU effective from 2013 sets limit values for 64  
 17 polybrominated biphenyls (PBBs) and PBDEs (classes covering 65  
 18 the most largely used additive BFRs, including deca-BDE) at a 66  
 19 maximum level of 0.1 weight % in homogeneous materials. 67  
 20 European standards give guidance on how to sample, prepare, 68  
 21 extract and measure BFRs in plastics [4]. Recommended 69  
 22 methods for monitoring compliance with RoHS limits for 70  
 23 PBDEs can be divided into two main approaches: orientational 71  
 24 screening and high-accuracy chemical analysis. Screening is 72  
 25 preferred for in-situ evaluations as it is usually performed via 73  
 26 solid sampling techniques like hand-held X-ray fluorescence 74  
 27 spectroscopy (XRF) although this can only quantify Br as a 75  
 28 proxy for the total BFR content, thereby running the risk of 76  
 29 false positives. More conventional techniques are 77  
 30 recommended for high-accuracy determination of BFRs like 78  
 31 PBDEs. Specifically, RoHS requires GC-MS analysis to 79  
 32 determine the BFR content in styrenic polymers (preceded by 80  
 33 different sample preparation steps: sub-sample grinding, cryo- 81  
 34 grinding, solvent extraction, extract filtration, selective 82  
 35 precipitation for oligomer removal, and chromatographic 83  
 36 purification). These traditional techniques can have a number 84  
 37 of drawbacks aside from being time consuming and expensive. 85  
 38 Soxhlet or pressurised liquid extraction of plastics often 86  
 39 dissolves a substantial fraction of the matrix (polymer) 87  
 40 together with the target compound, rendering the ensuing 88  
 41 extract purification laborious and often leading to highly 89  
 42 variable analyte recoveries. Furthermore PBDEs are present 90  
 43 across a wide range of bromination level, from the lower 91  
 44 brominated tri-BDEs and tetra-BDEs with a low boiling point 92  
 45 the most brominated (deca-BDE) with a very high boiling point. 93  
 46 This makes it practically difficult to use the same GC-MS 94  
 47 system set-up to analyze simultaneously in a single GC run: 95  
 48

**Table 1** Composition of Reference Materials. Results obtained with Neutron Activation Analysis.

RM	BDE209 w/w %	BDE209 uncertainty ± %	Sb <sub>2</sub> O <sub>3</sub> w/w %	TiO <sub>2</sub> w/w %	CaCO <sub>3</sub> w/w %
1	0	0	3	0.7	2.4
2	0.1	0.007	5	2.4	0
3	0.5	0.035	0	0.3	3
4	1	0.07	0.4	3	1.2
5	2	0.14	2.2	1.2	1.8

ideally two different GC columns are used, causing several analytical delays (run the samples on one system set-up first, then switch columns and run them again on the second set-up), although a better solution was achieved by Ballesteros-Gómez, [5] using GCxGC to resolve coeluting interferences in the second dimension, thus eliminating the need for two different GC runs. The high boiling point and its enhanced susceptibility to degradation and debromination when exposed at the elevated temperatures of the injector, column, ion source and detector make BDE209 a challenging analyte [6-16]. To face these analytical challenges novel methods for the quantification of BFRs have been developed recently combining GC, LC or GCxGC with a soft ionization source (APCI) and a High Resolution time-of-flight mass spectrometer or for compound-specific screening using Direct Probe with HR-TOF [5]. One attempt to develop a solid sampling, compound-specific analysis was made by exploring the potential of Direct Analysis in Real Time coupled with Time Of Flight Mass Spectrometry (DART-TOF-MS), [17] but results revealed it as constituting only a qualitative method to screen for the presence of BFRs in environmental matrices. Against this backdrop, it is evident that a method that combines the convenience of a solid sampling technique with compound specific quantification is highly desirable.

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. To our knowledge, this is the first approach for compound-specific direct analysis of BFRs in polymers that does not require any sample preparation nor a GC or LC inlet. The method is validated via determination of BDE209 in

1 Acrylonitrile Butadiene Styrene (ABS) solid reference materials  
 2 (RMs), but accurate mass determination can be applied  
 3 unambiguously identify other PBDE congeners.

4 **Experimental**

5 **Overview**

6 This method involves the use of matrix matched RMs for the  
 7 compound specific quantification of BFRs in polymers. We  
 8 used ABS as our polymeric matrix as it is one of the most  
 9 common polymers used in Electrical and Electronic Equipment  
 10 (EEE) and toys. Our target BFR was BDE209 as it displays a  
 11 small temperature difference between evaporation and  
 12 thermal degradation, as a proof of concept for the DIP method  
 13 that samples the analytes via thermal desorption. Calibration  
 14 of the method was carried out using RMs at 5 different  
 15 concentrations of BDE209.

16

17 **Reference materials**

18 RMs loaded with different concentrations of deca-BDE were  
 19 produced by Fachhochschule Muenster Labor für  
 20 Instrumentelle Analytik (FMLIA). The method used to produce  
 21 and test the RMs is described in detail elsewhere [18], but in  
 22 summary, Br (in the form of deca-BDE) and Sb (in the form of  
 23 Sb<sub>2</sub>O<sub>3</sub>) were added to an ABS terpolymer melt with the aid of  
 24 an extruder. Sb<sub>2</sub>O<sub>3</sub> is generally used as a synergist FR in  
 25 combination with BFRs [19, 20]. A set of five different  
 26 reference materials was produced in the form of pellets  
 27 containing different mass fractions of both Br and Sb plus  
 28 typical fillers commonly used in ABS (see Table 1) in order to  
 29 best simulate the matrix of the samples.

30 Mass fractions of Br in the produced materials were  
 31 determined (by FMLIA) via Neutron-Activation-Analysis (NAA).  
 32 The uncertainty of NAA is about 7% (for exact values see Table  
 33 1). To assess macroscopic homogeneity a wavelength  
 34 dispersive X-ray spectrometer was used with RSD below 2% for  
 35 Br. To assess microscopic homogeneity a synchrotron radiation  
 36  $\mu$ -XRF (SR  $\mu$ -XRF) was used. The spot size of the exciting beam  
 37 was 200  $\mu$ m, the RSD for Br was 0.7%.

38

39 **Sampling**

40 No sample preparation was required. A very small amount  
 41 ( $\approx$ 0.045 mg) was scraped from the pellets of the RMs with a  
 42 scalpel, accurately weighed with a precision scale ( $\pm$ 0.0005 mg)  
 43 and inserted in the aluminium crucibles for the DIP. The  
 44 influence of the scale error on such a small sample is  $\pm$ 1.1%.

45

46 **Instrumentation**

47 The Thermo Scientific™ DFS™ Magnetic Sector High Resolution  
 48 Mass Spectrometer (HRMS) was used for DIP-HRMS analysis.  
 49 The probe temperature program is software controlled. The  
 50 Thermo Scientific™ ISQ™ QD Single Quadrupole GC-MS System  
 51 was used for the comparison of mass spectra obtained with  
 52 the most common GC-MS technique (and relative sample  
 53 preparation)[21].

The optimised conditions for BDE209 were obtained by varying one parameter at a time, performing a measurement and observing the influence of this variation on sensitivity, reproducibility and degree of fragmentation of the parent ion: faster DIP temperature ramps and higher electron energies were found to decrease the parent/daughter ratio and to increase the overall signal intensity, therefore a compromise between these two effects was found in the values reported in table 2:

<b>Ion Source temperature</b>	260 °C
<b>Source mode</b>	EI Positive
<b>DIP temperature programme</b>	40(0.5°C/min)-75-400 (2 min)
<b>Scan mode</b>	Magnetic scan
<b>Mass range</b>	30-1000 m/z
<b>Resolution FWHM</b>	20000
<b>Electron energy</b>	46 eV
<b>Emission current</b>	1 mA
<b>Acceleration voltage</b>	4800 V

To set the desired resolution of 20000 FWHM the reference gas (per fluoro kerosene (PFK), indicated in the mass spectrometric determination section) was monitored on mass 792.9499 m/z and the entrance and exit slits were closed recursively until the desired resolution was reached, these parameters were stored in the measurement conditions and the instrument response was regularly checked using the same reference gas.

## Results and discussion

### Mass spectrometric determination

As no GC column is used, the only time difference in vaporisation is dictated by the compound's vapour pressure. The RMs we used to test this method were loaded with BDE209, although due to the process they underwent to be produced (melted and extruded several times to ensure homogeneity), some thermal decomposition is likely to have produced a small amount of decomposition products inside the polymer (Fig. 1).

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) following the expression (1):

$$\Delta \frac{m}{z} = \frac{(m_{\text{obs}} - m_{\text{ref}})}{m_{\text{ref}}} \times 10^6 \quad (1)$$

Where  $m_m$  is the measured accurate mass and  $m_c$  is the exact mass. The deviation of the measured masses from the exact masses was for all isotopologues of BDE209 (averaged over 20 scans) less than 1 ppm using a dedicated pre calibrated method based on Reference material PFK which uses all the exact masses contained in the PFK mixture to perform a polynomial correction of the measured accurate masses (see Fig. 2 and Table 3).

**Table 3.** Mass Table of measured isotopes

m/z	Relative intensity	Delta (ppm)	Composition
951.1749	4.34	-0.88	C <sub>12</sub> O Br <sub>9</sub> [81]Br
953.1735	19.34	-0.16	C <sub>12</sub> O Br <sub>8</sub> [81]Br <sub>2</sub>
954.1772	2.5	0.24	C <sub>11</sub> [13]C O Br <sub>8</sub> [81]Br <sub>2</sub>
955.1718	51.57	0.16	C <sub>12</sub> O Br <sub>7</sub> [81]Br <sub>3</sub>
956.1756	6.25	-0.41	C <sub>12</sub> [13]C Br <sub>5</sub> [81]Br <sub>5</sub>
957.1696	86.22	-0.01	C <sub>12</sub> O Br <sub>6</sub> [81]Br <sub>4</sub>
958.1725	10.78	-0.46	C <sub>11</sub> [13]C O Br <sub>6</sub> [81]Br <sub>4</sub>
959.1677	100	0.16	C <sub>12</sub> O Br <sub>5</sub> [81]Br <sub>5</sub>
960.1711	12.92	0.22	C <sub>11</sub> [13]C O Br <sub>5</sub> [81]Br <sub>5</sub>
961.1658	81.39	0.38	C <sub>12</sub> O Br <sub>4</sub> [81]Br <sub>6</sub>
962.1689	10.16	0.07	C <sub>11</sub> [13]C O Br <sub>4</sub> [81]Br <sub>6</sub>
963.1634	45	0.00	C <sub>12</sub> O Br <sub>3</sub> [81]Br <sub>7</sub>
964.1666	5.79	-0.13	C <sub>11</sub> [13]C O Br <sub>3</sub> [81]Br <sub>7</sub>
965.1613	16.71	-0.05	C <sub>12</sub> O Br <sub>2</sub> [81]Br <sub>8</sub>
964.1646	1.76	-0.16	C <sub>11</sub> [13]C O Br <sub>2</sub> [81]Br <sub>8</sub>
967.1596	3.52	0.33	C <sub>12</sub> O Br [81]Br <sub>9</sub>

### Verification of the DIP-HRMS method

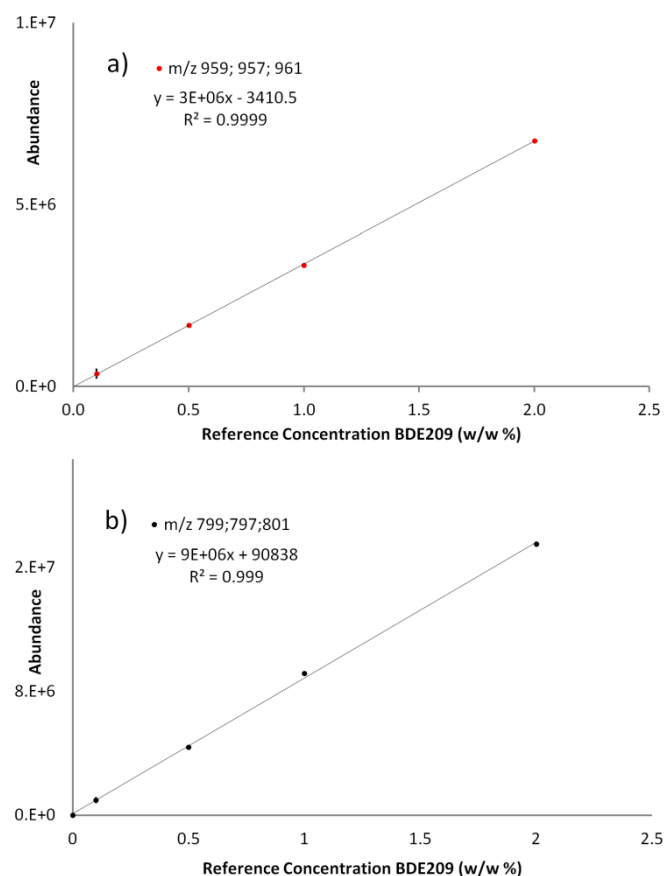
Octa-BDE and deca-BDE were measured and their ratio evaluated to test the reproducibility of the fragmentation. Although selected ion mode analysis can provide better sensitivity and transient signals that are easier to interpret, we decided to acquire in the complete mass range (m/z 30-1000) for BDE209 for three reasons: (a) when BDE209 is present in consumer goods, whether it is added voluntarily or not, its concentration is usually orders of magnitude higher than the detection limits of the DFS Magnetic Sector GC-HRMS; moreover the regulatory limits set a relatively high concentration threshold 0.1% in homogeneous material; (b) for quantitative purposes it is very important to include in the calculation every fragment (including molecular Br) deriving from the parent ions present in the samples. This approach allowed us to understand whether it was reasonable to assume that - granted a very stable fragmentation yield - the total Br would have been linearly proportional to any of the main fragments produced (octa-BDE and nona-BDE); and (c) such a wide mass range - covering the vast majority of commonly used BFRs - delivers the flexibility to identify and quantitate different compounds 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 ca. 40 scans for each "peak").

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 his octabrominated breakdown product, showing linearity over the selected range. 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 -which is octaBDE- 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. 3b). The LOD was defined as in the ICH1 Guidance (Q2,R1: Validation of Analytical Procedures) as:

$$\square\square\square = 3.3\sigma/S$$

where  $\sigma$  = the standard deviation of the response on the triplicate measurement of blank samples (RM BDE209) and  $S$  = the slope of the calibration curve. The noise - defined as the



1 Fig. 3 Calibration curves and linearity for the analysis of (a) [BDE209]<sup>+</sup>, (b) [BDE209-57  
 2 Br<sub>2</sub>]<sup>+</sup> obtained by DIP. Error bars are the SD between triplicate measurements of each 58  
 3 RM 59  
 4 60  
 5 intensity of the signal given by the target mass on a blank 61  
 6 measurement- was below 1/3 of the instrument detection 62  
 7 limits. This result was foreseeable, considering that each 63  
 8 sample, and the crucible containing it, was removed from the 64  
 9 probe before inserting a new sealed crucible containing 65  
 10 different sample, therefore no physical residues of the 66  
 11 previous sample could be left on the one following (unlike 67  
 12 traditional GC analysis, where polymeric residues might build 68  
 13 up in the injector liner and in the column and create a memory 69  
 14 effect). The calculated LOD with this method was 0.112 mg/kg 70  
 15 the LOQ was 1.120 mg/kg for BDE209, slightly lower than a 71  
 16 similar study performed with Direct Exposure Probe (DEP) [22] 72  
 17 and with the advantage of no sample preparation needed. 73  
 18 The memory effect was evaluated by calculating the RSD 74  
 19 between triplicate measurements of the most concentrated 75  
 20 RMs: the percent variation was 0.47% and no increasing trend 76  
 21 was observed. 77  
 22 Intraday stability was evaluated by performing control runs 78  
 23 RM3 at the beginning, in the middle and at the end of each day 79  
 24 of analysis. Over 3 days the intraday RSD of the signal intensity 80  
 25 for BDE209 averaged at 1.96%, while interday RSD was 0.51% 81  
 26 The method was applied to 21 real polymeric samples 82  
 27 (children's toys and food contact articles, Table 1, SI) for which 83  
 28 the BDE209 concentration was measured. BDE209 data and 84  
 29 total elemental Br measured with an X-Ray Fluorescence 85  
 30 spectrometer were plotted to evaluate if a correlation existed 86  
 31 between the two metrics. BDE209 was detected in a 87  
 32 concentration ranging from 8.8 mg/kg to 4327 mg/kg. 88  
 33 Considering that these data refer to real samples, containing a 89  
 34 suite of different BFRs, each potentially contributing to the 90  
 35 total elemental Br concentration; the correlation ( $R^2=0.86$ ) 91  
 36 between our BDE209 concentration measurements and those 92  
 37 for total Br is striking. Moreover, our measurements of BDE209 93  
 38 -which is likely to be a fraction of the total BFR content- never 94  
 39 exceeded those of total detected Br (Fig.1, SI). 95  
 40 96  
 41 **Reproducibility of the fragmentation ratios** 97  
 42 The ionisation behaviour was tested for reproducibility 98  
 43 selecting m/z 799 and m/z 959 from the time signal and 99  
 44 measuring the intensity for these masses over the selected 100  
 45 time interval. DIP offers a specific advantage with respect to 101  
 46 GC-MS analysis: as there is no column or injector between the 102  
 47 sample induction system and the ionization volume, it is 103  
 48 possible to differentiate between breakdown products (caused 104  
 49 by thermal degradation) and ionization fragments (produced  
 50 by the EI ionization process). This is easily done by comparing  
 51 the time signals for the molecular ion and for its possible  
 52 moieties as shown in Fig.1: a) and b) show the overlap, in  
 53 intensities of the time signal respectively for the  
 54 decabrominated ion and the octabrominated ion, meaning  
 55 that the latter was formed simultaneously in the source, as a  
 56 fragment of the former. Following this approach we are also

able to say that as the pentabromophenate ion (d)) was  
 detected at the same time of 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 -  
 $3.1 \pm 0.04$  (see table 4), showing it to be independent of the  
 sample concentration and suggesting very reproducible  
 fractionation behaviour. This is important as it 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. 4 shows how the ratio between m/z 799  
 and m/z 959 is almost two times higher for the traditional GC-  
 MS technique. The thermal decomposition is reduced in the  
 DIP method because the sample is introduced in a chamber  
 under vacuum (instead of under pressure as it would be in a  
 GC injector) therefore the sufficient vapor pressure is reached  
 at lower temperatures.

Table 4. Fragmentation ratio between the two main BDE209 ions.

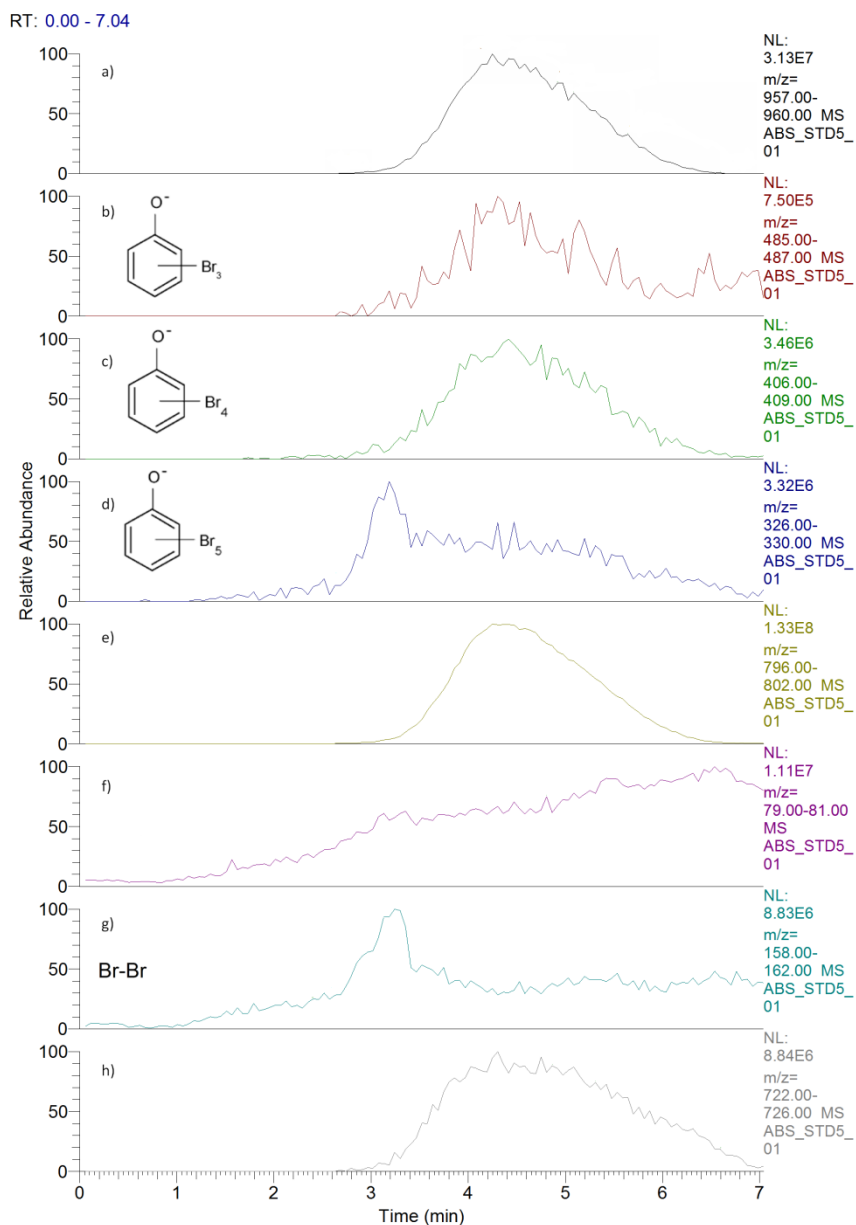
Reference BDE209 w/w %	Ratio m/z 799 and m/z959	SD
0.1	3.002	0.04
0.5	3.079	
1	3.051	
2	3.002	

## Conclusions

The method reported here represents a rapid, accurate way of  
 performing compound specific quantification of BDE209 in  
 polymers, that avoids completely the labour 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 (therefore allowing application in studies requiring  
 identification of putative source items in human exposure  
 studies) as well as future waste items. With a linear range  
 covering a concentration span of 19,000 mg/kg which for new  
 and recycled plastics represents the full range of detected  
 concentrations (a considerable improvement with respect to a  
 recent DEP study [22], where the calibration span was from 0.5  
 to 16 mg/kg) this technique can be a valid, easier, alternative  
 to existing analytical methods for monitoring RoHS compliance  
 in consumer goods. These articles belong now to a second and

- 1 third generation of recycling; and thus generally contain lower  
 2 concentrations of BFRs (compared to the concentrations of the  
 3 intentionally added BFRs in older items) as the contaminated  
 4 polymeric fractions have been mixed with new polymers  
 5 [4][23].  
 6 This is illustrated by a recent study where a Direct Injection  
 7 Probe coupled with a HR-TOF-MS was used to screen BFRs in  
 8 plastics, in which the concentration of FRs in the analyzed  
 9 samples never exceeded 1.6% in WEEE items [5].  
 10 Our method is tested here for BDE209 in ABS as a proof of  
 11 concept, but given suitable solid RMs, quantification of lower  
 12 brominated compounds in other polymers and over wider  
 13 calibration ranges will be feasible. DIP-MS optimised for PBDEs  
 14 in plastics is able to give results that are as accurate as GC-MS  
 15 [24] but are at least 50 times faster to achieve. Considering the  
 16 burgeoning need for quantification of BFRs in waste samples  
 17 [IEC 62321], we believe our method will be of significant value.
- 18
- 19 **Future developments**
- 20
- 21 This solid sampling technique has the advantage of being  
 22 completely solvent-free and hence a “greener” alternative to  
 23 techniques that involve sample preparation. It would be  
 24 desirable – in order to make it routinely available – to have a  
 25 more complete set of solid reference materials that represent  
 26 the 3 most widely used FRs (pentaBDE, octaBDE and decaBDE  
 27 commercial mixtures) in their respectively most commonly  
 28 used polymers (mainly ABS, PS, and PP/PE). The resources  
 29 required for production of such suitable reference materials  
 30 for matrix-matched calibrations with this method would be  
 31 significantly less than the multitude of sample preparations  
 32 this technique would render redundant.
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Fig. 1. Time signal obtained with DIP-HRMS (selected over the entire time signal for a) m/z 957-960; b) m/z 485-487; c) m/z 406-409; d) m/z 326-330; e) 796-802; f) m/z 79-81; g) m/z 158-162; h) m/z 722-726. It is possible to notice that the formation of the penta brominated ions (d)) corresponds to a simultaneous release of  $\text{Br}_2$  molecules (g)).



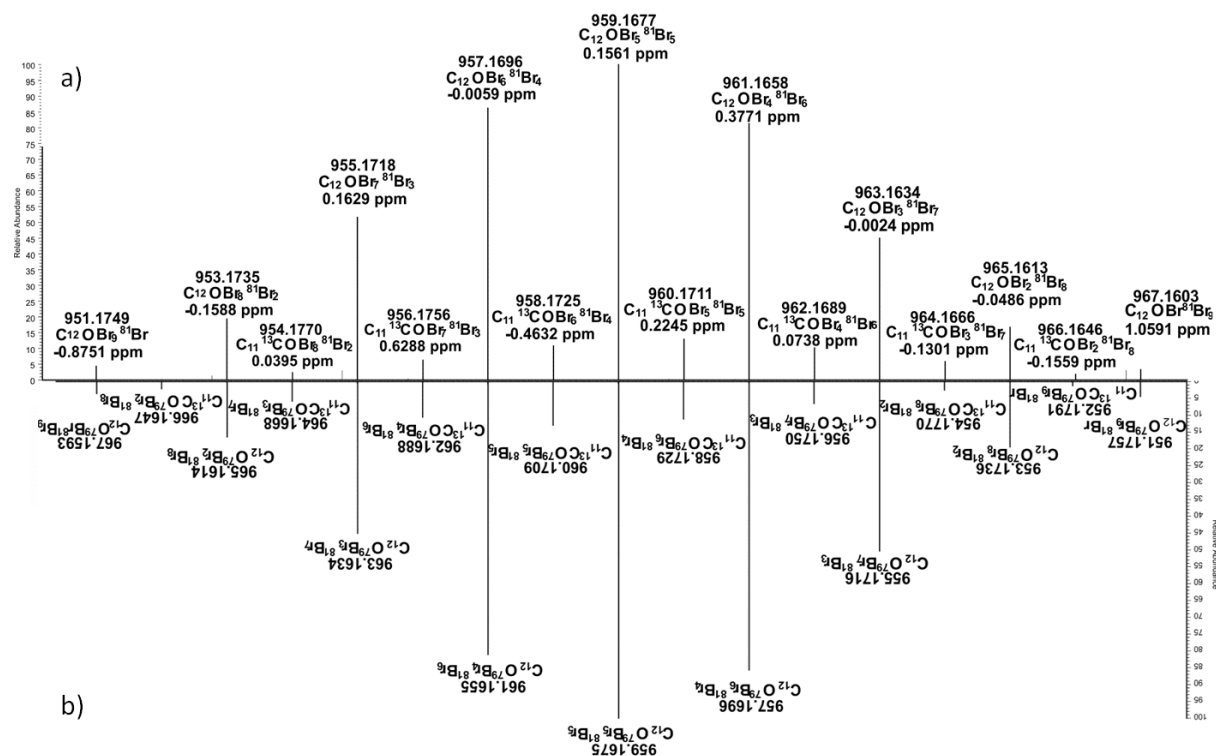


Fig. 2. Comparison of a) accurate masses measured over 20 scans for BDE209 (reported in table 3), and b) their calculated exact value.

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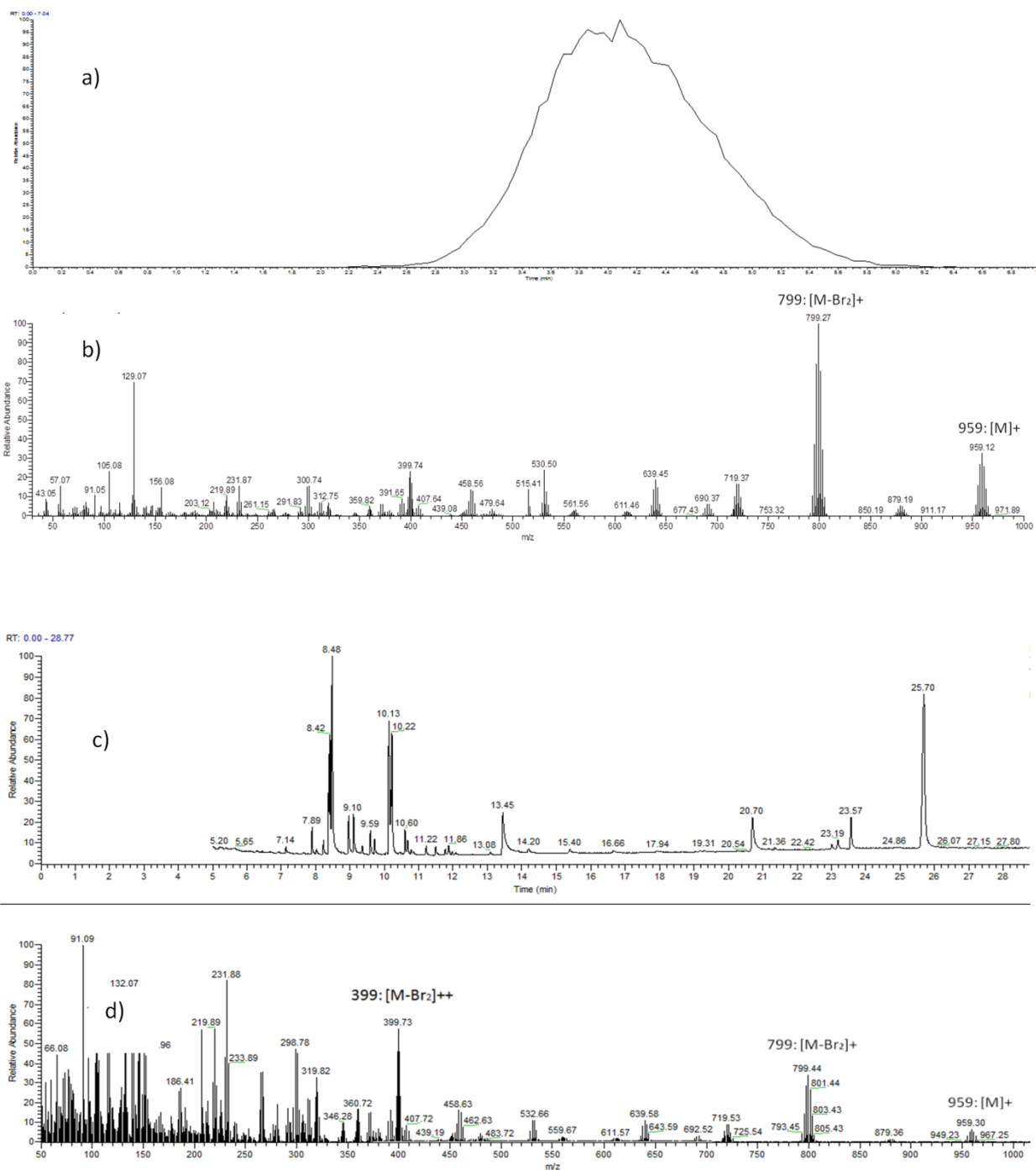


Fig. 4 TIC for the same RM (ABS with 0.5% BDE209) obtained with a) DIP-HRMS (selected over the entire time signal for m/z 799; 959), and d) GC-MS (selected over the chromatographic peak RT:25.70 corresponding to BDE209)