

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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Introduction

Recommended methods for monitoring compliance with RoHS limits for PBDEs can be divided into two main approaches: screening and high-accuracy chemical analysis. Screening is usually performed via solid sampling techniques that can only quantify elemental Br as a proxy for the total BFR content. 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 polymers. These traditional techniques can have a number of analytical drawbacks aside from being time consuming and expensive. For these reasons a method that combines the convenience of a solid sampling technique with compound specific quantification is highly desirable. Direct Insertion Probe (DIP) is a solid sampling inlet system that introduces the analytes directly into the ion source of a mass spectrometer (in this case a Thermo Scientific™ DFS™ Magnetic Sector High Resolution Mass Spectrometer) by thermal desorption. Having a strong matrix effect, this technique is used for qualitative evaluation, because it is often impractical or impossible to produce reasonably representative solid reference materials at different concentrations in order to build a calibration curve. In this study, we use ad-hoc prepared Acrylonitrile Butadiene Styrene (ABS) solid reference materials (RMs) containing different concentrations of BDE209 to develop a 5-point calibration curve that showed linearity ($R^2 > 0.999$) over a concentration range of 0.1 - 2% w/w BDE209. Relative standard deviation between triplicate determinations of BDE209 ranged from 0.32% to 0.42%. The limit of detection (LOD) obtained for BDE209 was 0.112 mg/kg, 4 orders of magnitude lower than the EU's maximum allowed concentration (MAC) in plastic. To our knowledge, this is the first method for compound specific quantification of BDE209 that does not require any sample preparation, reducing the analysis time from roughly 14 hours to 12 minutes with comparable quality of results.

MATERIALS AND METHODS

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%.

The Thermo Scientific™ DFS™ magnetic sector high resolution mass spectrometer (HRMS) was used for DIP-HRMS analysis. The probe (Fig.1) temperature program is software controlled. The Thermo Scientific™ ISQ™ QD Single Quadrupole GC-MS System was used for the comparison of mass spectra obtained with the most common GC-MS technique (and relative sample preparation).

RESULTS

Octa-BDE and deca-BDE were measured and their ratio evaluated to test the reproducibility of the fragmentation. 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 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 – defined as the intensity of the signal given by the target mass on a blank measurement – was below 1/3 of the instrument detection limits. This result was foreseeable, considering that each sample, and the crucible containing it, was removed from the

probe before inserting a new sealed crucible containing a different sample, therefore no physical residues of the previous sample could be left on the one following (unlike a traditional GC analysis, where polymeric residues might build up in the injector liner and in the column and create a memory effect).

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).

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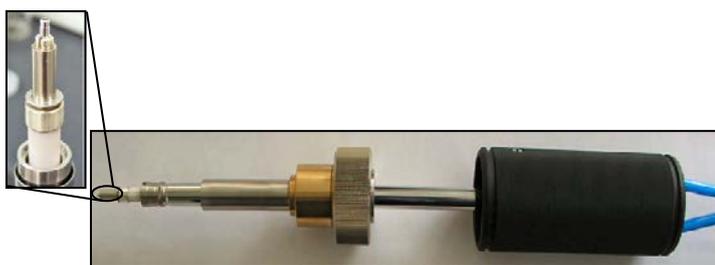


Fig. 1 Water cooled DI Probe (Temp. range: 25 C°– 400 C°); Tip with Crucible

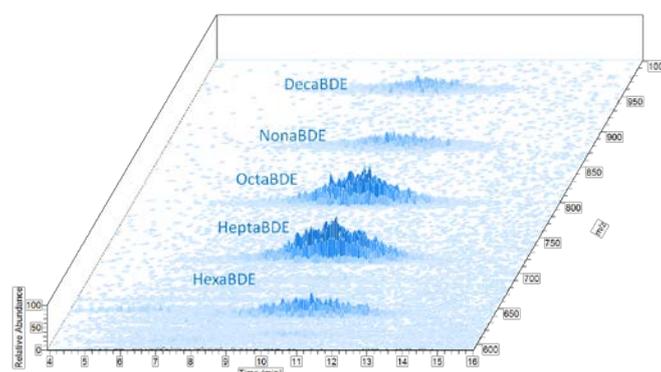


Fig. 2 Thermal degradation and fragmentation pattern of BDE209 respectively in the DIP and in the ion source