Method Optimization for Rapid Analysis of Brominated Flame Retardants in Polymers: with DART-Orbitrap HRAM

Antonella Guzzonato[1, 2], Olaf Scheibner[2], Tabiwang N. Arrey[2], Thomas Moehring[2], Stuart Harrad[1]
[1]School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK
[2]Thermo Fisher Scientific (GmbH) Bremen, Hanna-Kunath-Str 11, 28199 Bremen

Poster Note 64757

OVERVIEW

Purpose: The aim of this study was to explore the capabilities of- and to develop a method for screening compound specific BFRs in polymers without any sample preparation.

Method: Direct Analysis in Real Time (DART) coupled to Q Exactive Focus mass spectrometer.

Results: Compound specific analysis of BFRs is achieved under ambient conditions with no chromatographic separation. Linear proportionality is observed between signal intensities and reference concentration of the Standard Reference Material (SRM).

INTRODUCTION

Brominated Flame Retardants (BFRs), are organic compounds, some of which carry a risk to human health and accumulate in the environment. Their toxicity varies with the degree of bromination; therefore it is important to perform compound specific quantification analyses.
Many legislative bodies have created the necessity for customs and importer compliance for Electric and Electronic Equipment (EEE) and the BFR content of Waste Electric and Electronic Equipment (WEEE/EEE) goods to be checked [2].
For these reasons a method that is not only suitable for high throughput sampling, with little or no sample preparation but also unequivocally identifies and quantifies BFRs is highly desirable.
A suitable candidate for this purpose is a sampling technique able to perform ambient desorption ionization coupled with a high resolution (the Orbitrap achieves a 70,000 FWHM at *m/z* 200 resolving power) mass spectrometer that allows accurate mass determination to "make up" for the absence of information that is instead given in the most commonly used chromatographic separations.
The DART source has similar working principles to Atmospheric pressure chemical ionization (APCI), a cold plasma (metastable He/N2) reacts with oxygen and water molecules in air, creating reactive multimolecular ions which are directed towards the solid sample surface to ionize the analytes evaporated from the sample (Figure 1). The ions produced in this manner are transported by a heated capillary, through the Stack-ring ion guide lens (S-lens) and to the mass analyzer.

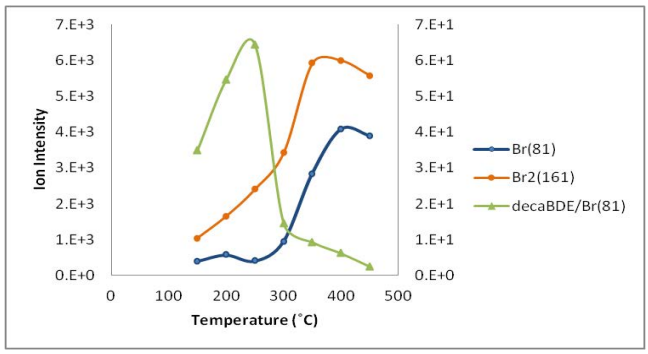
MATERIALS AND METHODS

For optimization purposes, solid reference materials (SRM) made of Acrylonitrile Butadiene Styrene (ABS) were produced by homogenizing different concentrations of decabromodiphenyl ether BDE-209 in the polymeric matrix. In total, nine SRM were created covering a BDE-209 concentration range of 0.1% to 15%.
Samples were ionized using a DART ion source Time (DART , IonSense Inc., Massachusetts)[1] and analyzed on a Thermo Scientific™ Q Exactive™ Focus mass spectrometer.
The DART was operated in the negative ion mode at 350˚C with Nitrogen as the carrier gas. The gap between the inlet and the DART apparatus was 1 cm. Samples were introduced manually by holding the plastic sample between the cold plasma jet and the detector inlet.
After a preliminary test, it was observed that using helium as a collision gas (cold plasma) causes stronger fragmentation, because of high first ionization potential (24.6eV) limiting the possibility of seeing the parent ions of the higher brominated PBDEs. For this reason nitrogen (with a first ionization potential of 14.5eV) was used, providing a "softer" fragmentation.
The MS was operated in negative ion mode, the full scan mass range was set to 70-1050 during the preliminary phases of the method optimization, and then set to 700-1050 to improve selectivity, sensitivity and signal-to-noise (S/N). Spectra were recorded with a resolution setting of 70000 at m/z 200. Source parameters such as the collision gas, the S-lens voltage, the gas temperature and capillary temperature on the Q Exactive Focus mass spectrometer were optimized for these samples.
Fragmentation patterns were simulated using the Mass Frontier 7.0 software and used to identify daughters ions. Evaluation of Total Ion Current and mass spectra was performed using Qual browers in Thermo Scientific™ Xcalibur™ 2.2 SP1.48. Descriptive statistics evaluation was done using Microsoft Excel 2007.

Result

Source temperature Profile
Since the vapor pressure of the molecule forming the sample can differ considerably, depending on the polymer type and on the inorganic fillers and additive inside the polymer, it is important to build a temperature profile for each matrix (polymer) analyzed in order to account for matrix effects. An easy way to do this is by placing the sample in front of the DART source and ramp the gas temperature for about 15 seconds for every step on difference positions from 150˚C, in steps of 50 degrees, up to 450˚C . These experiments were performed using an *ad-hoc* plastic reference material made of ABS homogenized with 8% wt. of decaBDE. It's possible that in one material the ion abundance of the observed analyte maxes out at a different temperature than another material even though it is the same chemical, this is because different components in the plastic might act to create a matrix effect when co desorbed with the chemical of interest. For this reason the same procedure should be repeated with different reference material to matrix match the sample. The total ion current (TIC) and the relative intensity of Br isotopes (Figure 1) are used as a measure of-respectively-the total intensity of the signal and the degree of fragmentation.

Figure 1. Atomic and molecular Br signal intensity with varying gas temperature.

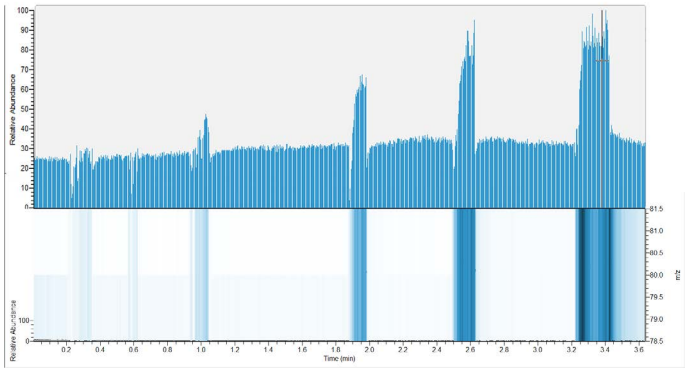


Decomposition of decaBDE follows a quasi-exponential behavior with temperature increase, reaching a plateau after 350˚C. The green trace represents the ratio between decaBDE and atomic Br, showing that the Br (atomic and molecular) are coming from the decomposition of the parent ion.

As the gas temperature increases not only the level of fragmentation (Figure 2) but also the intensity of the parent ion (decaBDE) increases (Figure 3). After evaluation, the most suitable gas temperature for this matrix proved to be 350˚C.
Decomposition of decaBDE occurs at very similar temperature to its boiling point, which causes it to thermally degrade during analysis. For this study the temperature profile is built for decaBDE inside Acrylonitrile Butadiene Styrene (ABS) matrix to find the best compromise between the amount of analyte released by the heat applied on the surface of the ABS polymer and possible decomposition to other compounds (which results in a drop of signal intensity of the BDE-209 in favor of lower brominated compounds). To do so, data were acquired at different source (DART) temperatures and the resulting spectra evaluated. BDE-209 signals and atomic Br were identified by observing the isotope pattern of Br and their ratio evaluated as a rough measure of the degree of decomposition (when the temperature is too high, the BDE-209 signal decreases and the free Br signal increases). Our results show that at source temperatures below 200˚C, BDE-209 is not observed (because not enough analyte is evaporated), while above 350˚C, thermal decomposition of the compound of interest is experienced. The optimum was found to be at 350˚C.

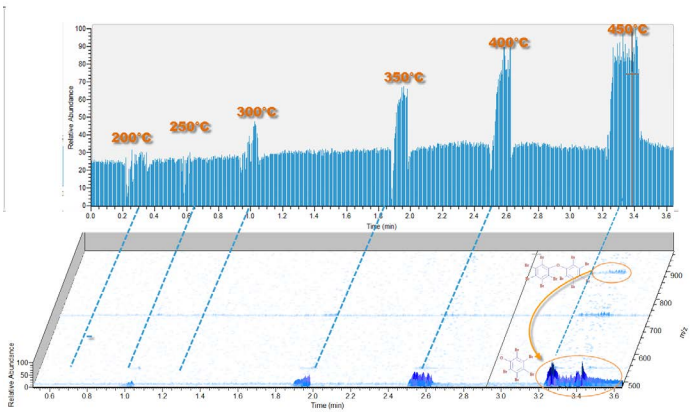
Thermo SCIENTIFIC

Figure 2. Fragmentation degree vs. total signal intensity.



Upper window showing the TIC signal acquired during the temperature profile experiment. Lower window shows (with matching time axis) an ion map of the two Br isotopes: it is possible to see an increase in relative abundance corresponding to the increase in the source temperature.

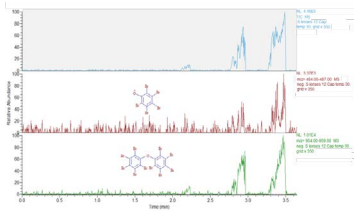
Figure 3. Fragmentation pattern vs. gas temperature



Ion map of the temperature profile experiment. Fragmentation of the parent ion (m/z 959.1676) into pentabromo phenolate , characterized by producing the fragmentation pattern for APCI and calculating the de-protonated accurate mass of the daughter ion (m/z/ 486.58306)

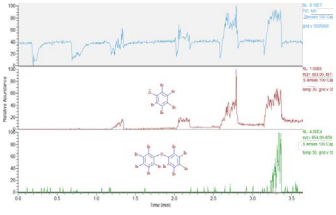
The capillary temperature does not only influences the fragmentation degree, but also the kinetic energy of the ions passing through it, therefore capillary temperature and S-lens value for this inlet system tend to be interdependent.
Starting with the assumption that a lower capillary temperature is the best choice to be able to see higher brominated BDEs, the S-lens value was tuned to obtain maximum ion transmission. Looking at the transmission efficiency for different S-lens values it is shown (Figure 4) that for lower S-lens values (Figure 4a), the transmission for the higher masses (parent decaBDE) appears to be better than for the most intense fragmentation ion (pentabromophenolate). Setting the S-lens at a higher value (Figure 4b) the transmission of the fragmentation ion is better than the parent ion. The reason for this might depend on the low capillary temperature. With these settings it was possible to identify decaBDE as a parent ion unambiguously with the use of isotopic pattern recognition and accurate mass determination (Figure 5).

Figure 4a. S-lens 12



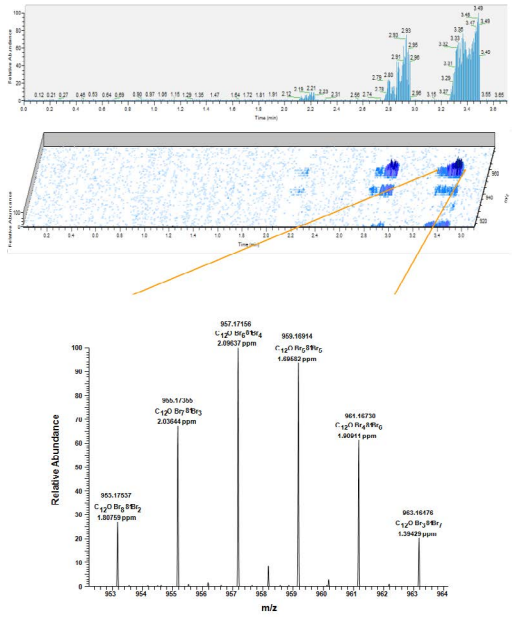
Keeping the capillary temperature the same and varying only the S-lens value to 12, the transmission for the higher masses (parent decaBDE) appears to be better than for the most intense fragmentation ion (pentabromophenolate). The background is also lower than for higher S-lens settings.

Figure 4b. S-lens 100



Setting the S-lens at a value of 100 the transmission of the fragmentation ion is better than the parent ion.

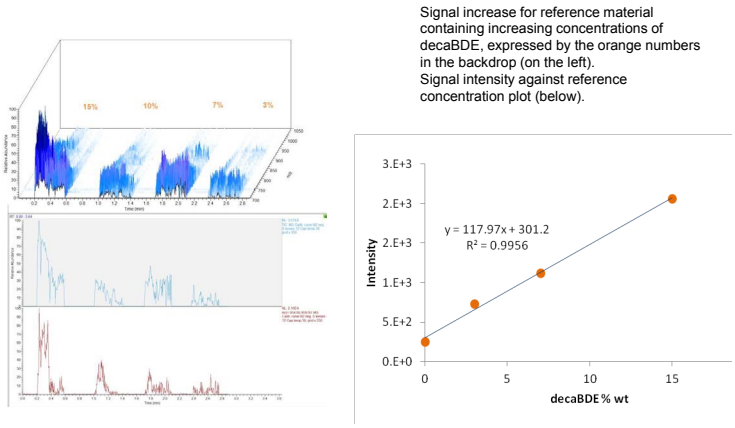
Figure 5. Accurate mass determination



From the top: TIC of temperature profile for the SRM built with the final instrument conditions. Ion map showing simultaneous ion signals for each temperature step. Mass spectrum recorded for decaBDE, on the labeld the del value between the recorded accurate mass and the theoretical mass is expressed. The very low difference observed in this study is crucial for the accurate mass determination to be effective.

An attempt to a calibration curve was made and, although a visible proportionality between reference concentration in the solid standards and signal intensity for decaBDE (m/z 959.1676) ion was visible (Figure 6), there is still room to improve linearity (R^2=0.995) and increase the sensitivity towards the lower concentrations.

Figure 6. Signal proportionality for increasing decaBDE concentrations



CONCLUSIONS

The analyte could not be seen in SRM containing BDE-209 concentrations lower than 1% other than in its [-2Br] fragment.
Performing a Selective Ion Monitoring study in the future will most certainly improve the quality of the calibration and the sensitivity of the technique.
Achieving this degree of linearity and accuracy without any sample preparation and performing the analysis under ambient conditions, can be considered a very good starting point for the exploration of this application.
In addition, as well as BDE-209, the method is capable of determining hexa-BDE, penta-BDE, and octa-BDE, preliminary results for these determinations were obtained analyzing an inter-laboratory sample as reference material and will be presented in a future study.

REFERENCES

1. Cody RB, Laramee JA, Durst HD. Anal. Chem. 2005; **77**; 2297.
2. Guidance on best available techniques and best environmental practices for the recycling and disposal of articles containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606857 (ELUTE).