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Determination of hexabromocyclododecane by flowing atmospheric pressure afterglow mass spectrometry

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ABSTRACT

The first application of a flowing atmospheric-pressure afterglow ion source for mass spectrometry (FAPA-MS) for the chemical characterization and determination of hexabromocyclododecane (HBCD) is presented.

The samples of technical HBCD and expanded polystyrene foam (EPS) containing HBCD as a flame retardant were prepared by dissolving the appropriate solids in dichloromethane. The ionization of HBCD was achieved with a prototype FAPA source. The ions were detected in the negative-ion mode.

The ions corresponding to a deprotonated HBCD species (*m/z* 640.7) as well as chlorine (*m/z* 676.8), nitrite (*m/z* 687.8) and nitric (*m/z* 703.8) adducts were observed in the spectra. The observed isotope pattern is characteristic for a compound containing six bromine atoms. This technique is an effective approach to detect HBCD, which is efficiently ionized in a liquid phase, resulting in high detection efficiency and sensitivity.

1. Introduction

Hexabromocyclododecane (HBCD) is produced in high volumes and is mainly used as a brominated flame retardant additive in expanded (EPS) and extruded (XPS) polystyrene foams used for thermal isolation in the building industry [1]. The compound is noncovalently bound to the material, and can therefore be released into the environment [2,3]. HBCD is toxic because it affects the liver and thyroid [4]; this compound persists in the environment and can bioaccumulate [5].

Because of its properties and increasing worldwide demand [6], HBCD has been recently submitted for inclusion under the UNEP Stockholm Convention on Persistent Organic Pollutants (POPs) and the UNECE Convention on Long-Range Transboundary Air Pollution on POPs [7]. In accordance with the Committee for Risk Assessment (RAC) within the European Chemicals Agency (ECHA) and Directive 67/548/EEC, HBCD is considered as hazardous and is classified as follows: R63 - Possible risk of harm to an unborn child and R64 - May cause harm to breastfed babies [1]. Moreover, in the European Union, HBCD was identified as a substance of very high concern (SVHC) and is currently being reviewed under the registration, evaluation, authorization and restriction of chemicals [8]; this regulation allows only authorized applications for HBCD after 21 August 2015. The [9] factsheet briefly describes the main regulatory status of HBCD in Europe, Japan, and North America.

The extensive use of HBCD as an additive flame retardant has led to a widespread contamination by this compound in different biotics [10–14] and abiotics [15–18], environmental compartments; therefore, monitoring of this contaminant is advisable. Numerous methods, including gas and liquid chromatography, have been developed to determine HBCD; the results have already been reported and compared [19–24]. However, these methods usually require a multistep, time-consuming procedures for sample handling, including extraction and clean-up. Therefore, the application of rapid mass spectrometric analysis with little or no sample pretreatment is essential. The use of a flowing atmospheric pressure afterglow mass spectrometry (FAPA-MS) ion source is an easy and fast approach for identifying HBCD, which makes it a desirable technique. Various atmospheric-pressure ionization sources have recently been used for direct and rapid mass spectrometric analysis with little or no sample pretreatment. The techniques referred to as ambient desorption/ionization mass spectrometry (ADI-MS) are based on atmospheric-pressure discharges to form ions, thereby directly ionizing samples under ambient conditions [25,26]. Numerous options for analyte desorption/ionization during MS have been described in the literature in recent years after introduction of desorption electrospray ionization (DESI) [27] and direct analysis in real time (DART) [28]. These techniques selectively desorb and ionize analytes, and, when combined with mass spectrometry for detection, these

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methods have provided numerous powerful alternatives to chromatographic approaches. The classification of many similar techniques is disputed [25,29,30] and [31] proposed three major categories: spray-based, laser-based, and plasma-based ionization. FAPA is the plasma-based atmospheric-pressure glow discharge ignited between a pin cathode and a plate anode [25,32–35]. Compounds are softly ionized by the reagent ions when samples are exposed to the afterglow. The source is based on helium glow discharge plasma at atmospheric pressure. One of the capillary electrodes excites the He atoms, and the reagent ions pass through the discharge cell, which results in ionization of the analyte molecules. Both positive and negative ion modes can be applied [36].

FAPA discharge is also classified as a glow-to-arc (G-A) technique and is known for its high desorption efficiency and sensitive detection [35]. FAPA discharge produces a significant amount of positive ions, including NO^+, O_2^+, N_2^+ and $(H_2O)_nH^+$. The protonated water clusters are the most abundant species. The background ions in the negative-ion mode include O_2^- as well as small amounts of OH^-, O^-, HO_2^-, O_3^-, NO_2^- and NO_3^- [35–38]. FAPA sources for MS enable for the analysis of substances with very low thermal stability due to the relatively low temperature. These methods can successfully be used for the rapid analysis of solid, liquid and gaseous samples; therefore, they can be applied to directly analyze pharmaceutical compounds, drugs and food contaminants [33,36,39–41].

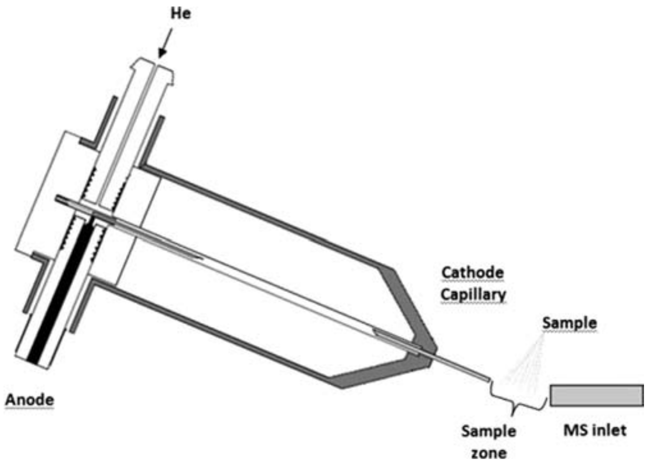

Fig. 1. Diagram of FAPA-MS. The analytes are desorbed/ionized into the gas phase and are transferred from the sample zone to the mass spectrometer inlet, where they are separated by their mass-to-charge (*m*/*z*) values and detected.

The main goal of our study was to develop a fast, effective and an inexpensive method for assessing the HBCD content in polystyrene foams as an alternative to the established gas and liquid chromatography methods. In this paper, the first application of the FAPA-MS technique for the chemical determination and characterization of HBCD is presented.

2. Materials and methods

HBCD was determined as the sum of three predominant isomers of α, β and γ using technical-grade HBCD and expanded polystyrene foam containing HBCD as a flame retardant purchased from a Polish Styrofoam factory (Termo Organika, Poland). A sample containing 10 g of expanded polystyrene foam was dissolved in dichloromethane and 7 mg/mL solution was prepared and stored in a sealed vessel at 4 °C.

For quantitative studies, i.e., estimation of sensitivity and preparation of the calibration curve, HBCD solutions have been prepared in dichloromethane and also additionally in matrix, i.e. in 1 mg/mL of polystyrene foam, which does not contain HBCD. In both cases, HBCD was prepared at the following concentrations: 4.69; 9.37; 18.75; 37.5; 75; 150; 300; 600 and 1200 μg/mL.

The desorption/ionization of HBCD was achieved with a NOVA011 (ERTEC, Poland) helium-based atmospheric-pressure FAPA source (Fig. 1). The quartz tube on the rear side is axially mounted along a Teflon dielectric that also serves as a compartment for connecting the cables that deliver a high voltage potential to the anode and houses the helium gas fitting. The FAPA source is usually placed approximately 1 cm from the MS inlet, and at an angle approximately 30° from horizontal position. The discharge tube restricts the flow of the plasma stream and helium afterglow. The plasma cavity is integrally connected to a classic TV flyback operating in current mode as the high-voltage generator. The discharge power is adjustable between 3–30 W. The open-circuit voltage (20 kV) ensures that the helium discharge self-ignites; this discharge is continuously delivered at 1.0 L/min. The end of a hollow cathode tube (2 mm O.D., 1.5 mm I.D, and 11 mm outside length) is fitted to the stainless steel body of the cavity equipped with few 8 mm diameter holes for observing the discharge.

The technical HBCD and expanded polystyrene foam solutions were manually sprayed (application volume 10 μL) in a reproducible manner, using simple perfume atomizer, over the sample zone of the FAPA-MS, and ions were detected in the negative-ion mode using a Bruker Esquire 3000 quadrupole ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany). The sample zone was located in 1 cm space between the FAPA ion source and the MS

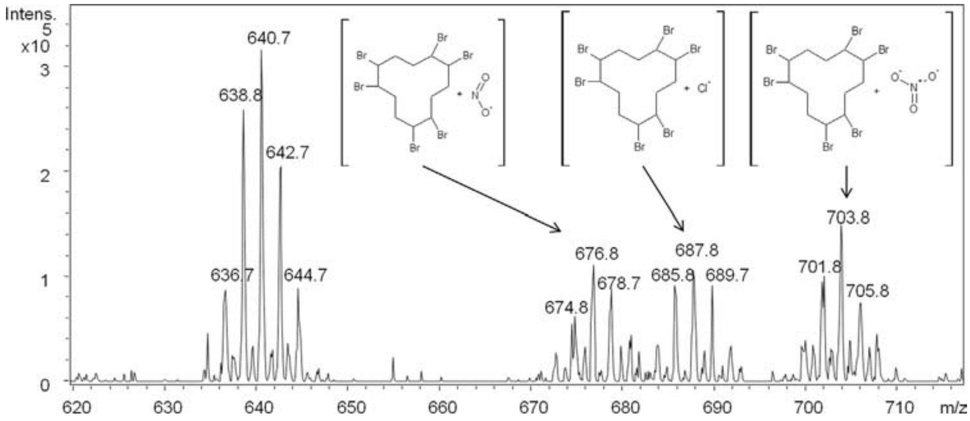

Fig. 2. Spectrum of 10 mg/mL solution of HBCD. An isotope pattern indicating six bromine atoms is observed. The ion at *m*/*z* 640.7 attributed to a deprotonated HBCD molecule generates the most intense signal. The obtained HBCD and Cl^- adducts (*m*/*z* 676.8), NO_2^- (*m*/*z* 687.8) as well as the NO_3^- species (*m*/*z* 703.8) generate signals of somewhat lower intensities.

inlet. Standard ESI source settings were used, except the capillary voltage. A much lower potential (1 kV) compared to the ESI standard setting (4.5 kV) was used. The isolation width and fragmentation amplitude were 5 *m/z* and 0.4 V, respectively. A large isolation width was used to include the complete isotope pattern of the deprotonated HBCD molecule for the product ion spectra.

3. Results

We have shown that FAPA can directly desorb/ionize HBCD in a liquid phase while maintaining high sensitivity. The spectrum obtained during the analysis of the technical sample (10 mg/mL) is shown in Fig. 2.

The observed isotope pattern is a characteristic for a compound containing six bromine atoms. The most intense peak is observed at *m/z* 640.7 and corresponds to the deprotonated HBCD molecule. This ion was selected as a precursor ion. The ion at *m/z* 676.8 is attributed to a chlorine adduct formed from dichloromethane. Furthermore, ions at *m/z* 687.8 and 703.6 are observed. On the basis of the information presented by Shelley [38], these ions correspond to NO_2^- and NO_3^- HBCD adducts, respectively.

From each solution prepared for quantitative studies, 10 µL injections were repeated three times with an atomizer and the calculated peak heights were averaged with an RSD not exceeding 25% for each concentration. Good linearity in the experimental range up to 600 µg/mL was observed with the following linear equations: for HBCD dissolved in dichloromethane $y = 5.81 \bullet 10^6 x + 243293$,

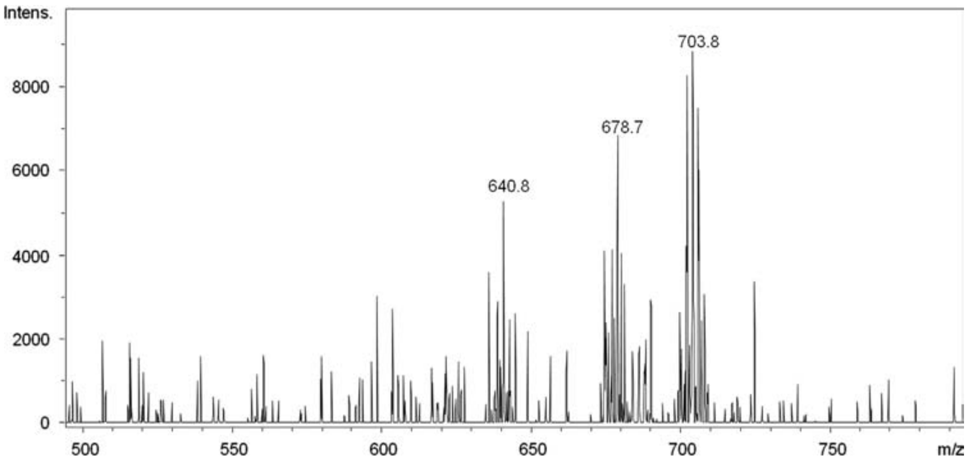

Fig. 3. Mass spectrum of 1 mg/mL polystyerene foam matrix dichloromethane solution spiked with HBCD, obtained for the lowest detected concentration of HBCD (LOD – 10 µg/mL).

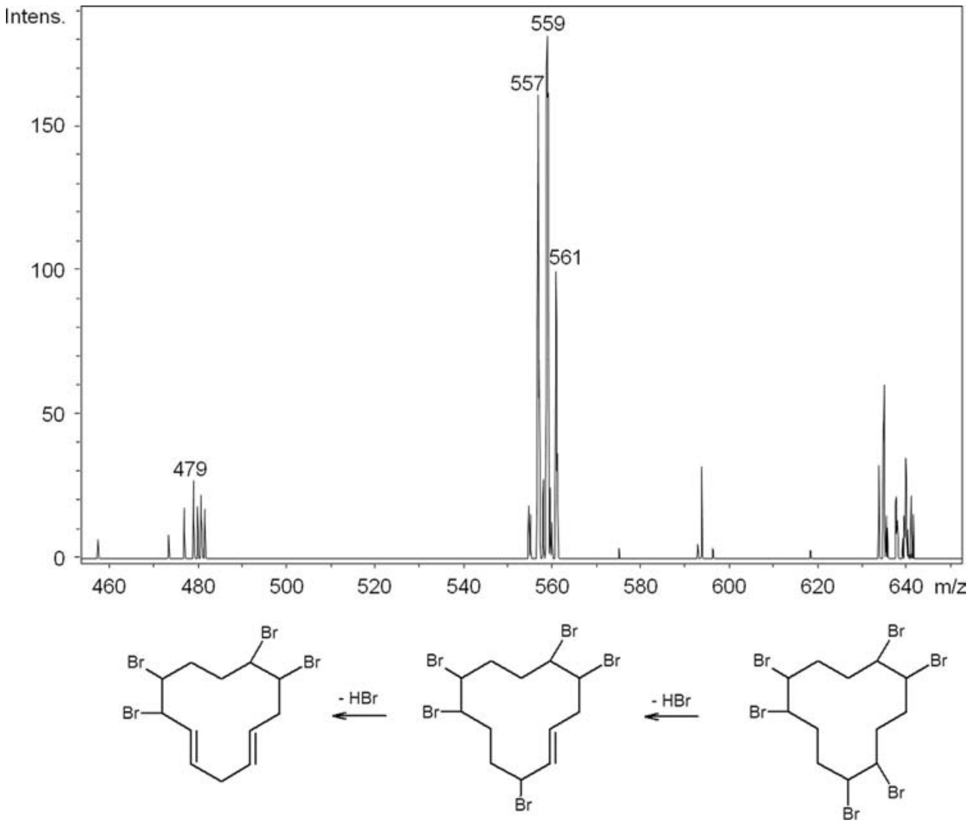

Fig. 4. Product-ion MS/MS spectrum of the HBCD precursor and a scheme showing the subsequent debromination of HBCD.

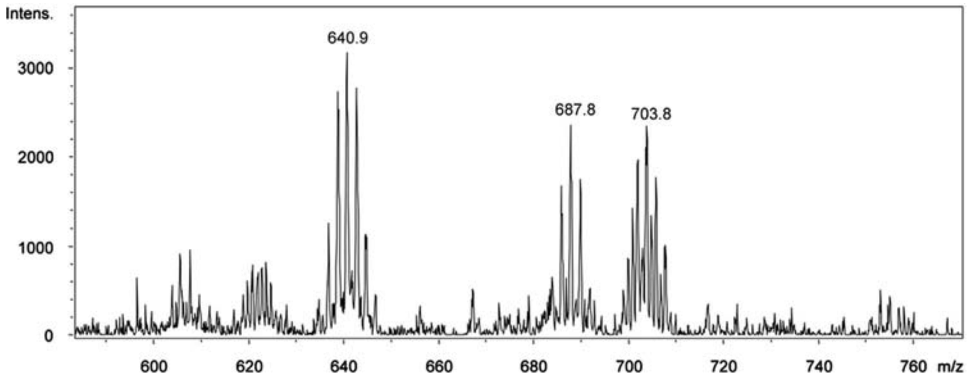

Fig. 5. Mass spectrum of HBCD present in the matrix solution (EPS, 7 mg/mL). The ion assigned to deprotonated HBCD produces the most intense signal. The intensities of peaks of the obtained HBCD adducts with NO_2^- (*m/z* 687.8) and NO_3^- (*m/z* 703.8) are of somewhat lower abundance.

$R^2 = 0.984$; and for HBCD dissolved in matrix, $y = 5.69 \cdot 10^6 x + 67583$, $R^2 = 0.997$. Based on the experiments, the LOD for HBCD was estimated at 10 μg/mL for both cases, as the presence of matrix reduced the signal intensity only by approximatly 10%. For LOD measurements the MS mode was used. The mass spectrum representing 1 mg/mL polystyrene foam (HBCD-free) matrix spiked with the lowest concentration of HBCD (LOD) is shown in Fig. 3.

The product-ion spectrum of the HBCD precursor ion is shown in Fig. 4. Fragmentation yields several types of ions generated under experimental conditions. The ions at *m/z* 479.0 and 559.0 correspond to the deprotonated compound and debrominated adduct, respectively. Because of the high symmetry of the compound, the generated product ions in the MS/MS spectrum could not identify the location of the debromination; however, the fragment ions in the MS/MS spectrum unambiguously identified the analyte.

FAPA-MS analysis of samples prepared by dissolving EPS in dichloromethane produced similar results. The isotopic pattern is a characteristic for a compound containing six bromine atoms; the most intense signals are assigned to the deprotonated adduct (*m/z* 640.9). The NO_2^- (*m/z* 687.8) and NO_3^- adducts (*m/z* 703.8) were also observed as relatively abundant peaks. The ion assigned to the chlorine adduct was not observed. The spectrum obtained for the EPS sample (7 mg/mL) is shown in Fig. 5.

4. Conclusions

Rapid analysis by FAPA-MS was used for chemical characterization of HBCD. This technique was an effective and fast approach for detecting the total HBCD in technical products and EPS foam while requiring little sample preparation (dissolution in dichloromethane). Chromatographic analysis usually requires an appropriate multistep and time-consuming procedure for sample preparation, including extraction and clean-up. Therefore, FAPA is a desirable approach with a shortened preparation time and a simplified analytical procedure. Liquid-phase HBCD is efficiently ionized, which results in high detection efficiency and sensitivity. The FAPA source has very versatile applications; however, further work is necessary due to our insufficient knowledge regarding the adducts formed during such analyses.

Although the qualitative detection of HBCD via FAPA-MS is relatively straightforward, quantitative results are much more difficult to attain, which presents a fundamental challenge. However, this method may be sufficient for monitoring the withdrawal of HBCD from use and its replacement with alternatives present in polystyrene foams. This simple and powerful FAPA-MS technique could be used to determine the HBCD content in polystyrene foams as a routine method.

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