IDENTIFICATION OF UNIQUE HEXABROMOCYCLODODECANE ADDUCTS

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Introduction

The production of technical Hexabromocyclododecane (HBCD) for use as a flame retardant in expanded polystyrene foams and upholstery textiles has made it the third most globally produced brominated flame retardant (BFR).[1-4] The additive manner in which it is incorporated into products makes it susceptible for release into the environment while its seemingly limited thermal and chemical stability predisposes it to both abiotic and biotic degradation. A number of studies have been published that identify possible HBCD metabolites and degradents[5,6]. This, taken together with the fact that all of the HBCD isomers display different physiochemical properties[7,8], results in a variation in the diastereomer profiles of technical material and biological samples[9,10]. Indeed, the analysis of HBCD and related compounds will continue to be very important considering the ubiquitous nature of this BFR in the environment.

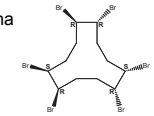
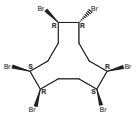
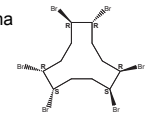
Since the structural isomers of HBCD can not be separated by high resolution gas chromatography (HRGC) due to thermal isomerization, the utilization of high pressure liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) has emerged as the preferred analytical method for the analysis of these compounds[11]. Although this method allows for an effective separation of the main isomers of the technical material, there are some analytical challenges associated with these compounds that can affect their detection limits in environmental samples, especially adduct formation[12]. It is well known that the HBCD isomers can form adducts with a number of anions that are present as trace impurities in solvents commonly used for LC-MS/MS analysis.

Objective

This work details the identification of unique hexabromocyclododecane adducts, which we have designated as “HBCD sandwiches”.

Materials and Methods

All experiments were conducted using a Quattro *micro* API mass spectrometer in full scan mode (40-1600 amu). Technical HBCD samples (Sigma Aldrich, USA) with a concentration of approximately 35 µg/mL in methanol (1.5% toluene) containing 1 of 4 additives (HCl, HBr, KI, or formic acid) were infused directly into the mass spectrometer at a flow-rate of 10 µL/min. The full scan spectra were collected using the following source conditions: capillary voltage = 3.00kV, cone voltage = 20.00V, source temperature = 110°C, desolvation temperature = 200°C, and desolvation gas flow-rate = 200L/hr.

Alpha  Beta  Gamma 

Results

Quantification accomplished by monitoring only the transitions of the HBCD molecular ion (e.g. m/z 640.5 → 79/81) may result in increased detection limits if adducts are being formed in the LCMS system. Many common LC grade solvents contain trace impurities that can result in the formation of multiple adducts during electrospray ionization. It was previously assumed that the adducts were being formed in a ratio of 1:1 (HBCD:anion). However, we have observed the formation of adducts in the ratio of 2:1 (HBCD:anion). Data were collected using a mass range that is larger than what is typically used for these compounds (40-1600 amu), and significant amounts of adducts in the range of 1300-1450 amu were observed for a sample of HBCD in methanol.

Results continued…

The subsequent addition of HCl, HBr, KI, and formic acid allowed us to confirm the identity of the observed adducts (see Figure 1). Small amounts of these novel adducts, termed HBCD sandwiches, were also observed when a sample containing a mixture of alpha, beta, and gamma HBCD was run on a C18 column. HBCD sandwiches were observed for all of the additives investigated in varying intensity. It appeared that certain sandwiches were formed preferentially over others, however this needs to be investigated further.

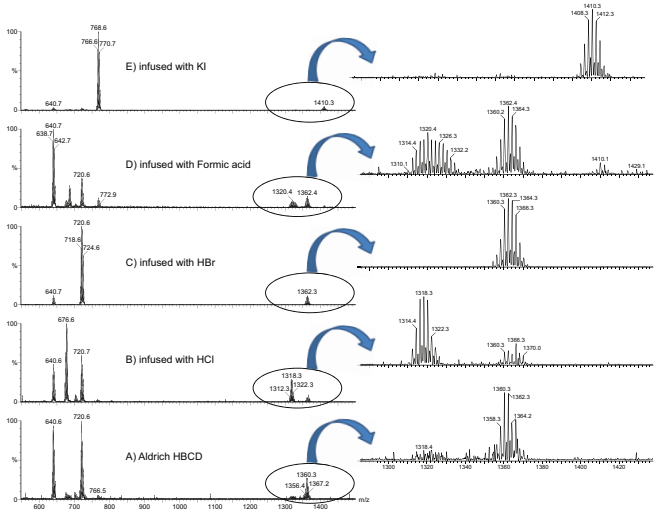


Figure 1: Spectra illustrating the presence of adducts and sandwiches for a sample of Aldrich HBCD A) without any additive, B) infused with HCl, C) infused with HBr, D) infused with formic acid, and E) infused with KI.

Conclusions

The presence of trace impurities in LC mobile phases present challenges to analysts attempting to optimize their detection limits for the HBCD isomers. The structure and configurations of these compounds predispose them to the formation of adducts and sandwiches during LCMS analysis.

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