



Identification of the Dominant Molecular Ion Adducts Present in the LC-MS spectrum of β -HBCD

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Introduction

Hexabromocyclododecanes have found use as additives in flame retardants for the inhibition of fires in polystyrene foams, textiles, and a variety of other materials.^{1,2,3} Unfortunately, since these compounds are not chemically bound to the matrix to which they are applied, it is possible for leaching into the environment to occur.¹

An increase in the production of HBCDs and their use in the building industry has led to a corresponding increase in the detection of these compounds in the environment.^{4,5} For this reason, many research groups have developed techniques to analyze environmental samples for HBCDs.^{6,7,8,9,10,11} Since quantitative analysis of the HBCD isomers by GC-MS has been shown to be non-isomer specific, LC-MS/MS has emerged as a suitable analytical alternative. Although it is possible to separate the α -, β -, and γ -HBCD diastereomers (see Figure 1) by LC-MS using a C-18 column, a number of molecular ion adducts may be observed. Important among them is the [M+36]⁺ ion which is particularly dominant at low concentrations. The relative strength of this adduct has been shown to be affected by the concentration of buffer (NH₄OAc) in the mobile phase.⁸

The objective of this work was to reveal the identity of the [M+36]⁺ and [M+80]⁺ molecular ion adducts of β -HBCD. Our findings may be particularly important in the refinement of analytical methods for HBCDs since these adducts are often produced under the conditions commonly used for the analysis of these compounds by LC-MS.

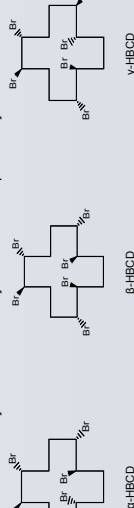


Figure 1: Structures of the α -, β -, and γ -HBCD diastereomers.

Experimental

Analysis of β -HBCD was carried out through infusion of 50ppm solutions into a Micromass Quattro micro API mass spectrometer under negative electrospray conditions. The source operating conditions were optimized for the formation of the [M+36]⁺ adduct and the conditions are listed in Table 1. In order to determine the identity of the [M+36]⁺ adduct, 100 μ L aliquots of a 50ppm β -HBCD standard in toluene were brought to final volume with an organic diluent and spiked with a series of acids (see Table 2 for preparation of the 5ppm solutions). 5ppm and 0.25ppm control solutions were prepared by diluting 100 μ L and 5 μ L of a 50ppm β -HBCD standard in toluene respectively with water and an organic diluent (see Table 2).

Table 1: Optimized tune parameters for the [M+36]⁺ HBCD adduct^a

Capillary (kV)	3.00
Cone (V)	40.00
Source Temperature (°C)	100
Desolvation Temperature (°C)	100
Desolvation gas flow (L/hr)	200
Syringe pump flow (μ L/min)	15.0

^a Cone gas flow = off

Table 2: Preparation of the modified β -HBCD solutions.

Solution	Additive	Volume of Additive ^b	Volume of Diluent ^c	Final Volume	Final Conc.
Control 1	Water	150 μ L	845 μ L	1 mL	0.25 ppm
Control 2	Water	135 μ L	765 μ L	1 mL	5 ppm
1	HCl	135 μ L	765 μ L	1 mL	5 ppm
2	NaOH	135 μ L	765 μ L	1 mL	5 ppm
3	HF	135 μ L	765 μ L	1 mL	5 ppm
4	HF	135 μ L	765 μ L	1 mL	5 ppm

^b Concentration of dilute acids is ~0.7 mmol/L

^c Diluent = 80:20 MeOH:ACN with 10mM NH₄OAc

Results and Discussions

It was found that the addition of dilute HCl to the β -HBCD solution resulted in an increase in the ion response of the [M+36]⁺ adduct (see Figure 3) in comparison to that observed for the control (see Figure 2). This result suggested that an HCl adduct was being formed, but in order to verify these preliminary findings β -HBCD was treated with HBr and HF. It was believed that these acids should form corresponding adducts through similar hydrogen bonding or electrostatic interactions.

It should be noted that very dilute acid solutions were used in order to observe an increase in the signal of the adducts and a corresponding decrease in the analyte cluster signal. It was not our intention to convert all of the analyte to its adduct.

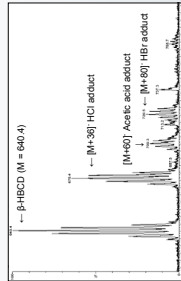


Figure 2: Spectrum of 5ppm β -HBCD

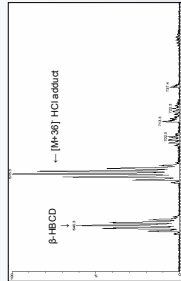


Figure 3: Spectrum of β -HBCD with HCl

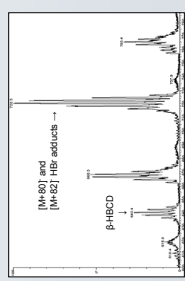


Figure 5: Spectrum of β -HBCD with HBr

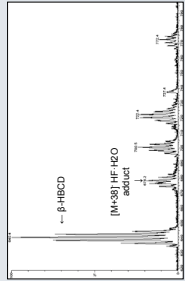


Figure 6: Spectrum of β -HBCD with HF

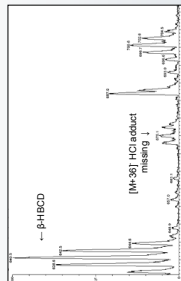


Figure 4: Spectrum of β -HBCD with NaOH

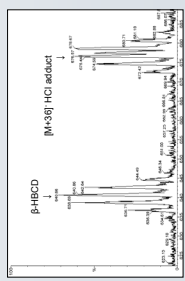


Figure 7: Spectrum of 0.25ppm β -HBCD

Results and Discussions continued...

Further evidence of the formation of such adducts was obtained upon the addition of dilute HBr to the β -HBCD standard. Analysis of the spectrum associated with this solution indicated the formation of [M+80]⁺ and [M+82]⁺ adducts (see Figure 5) in a ratio of approximately 1:1. Furthermore, addition of HF resulted in the formation of an [M+36]⁺ adduct, which corresponds to an HF-H₂O adduct (see Figure 6). Also, as expected, the addition of dilute NaOH resulted in the elimination of the [M+36]⁺, [M+80]⁺, and [M+82]⁺ signals (see Figure 4). There are other less prominent adducts present in the spectra of β -HBCD, but their identities are unknown at this time.

A comparison of β -HBCD controls at different concentrations (see Figure 2 and Figure 7) shows an increase in the relative intensity of the HCl adduct [M+36]⁺ at 0.25ppm. The increased prevalence of the adduct at lower concentrations could translate into an increase in the error associated with quantification of these compounds at low levels.

Conclusions

The formation of adducts with HBCD is of great importance since the composition of environmental matrices may have an effect on the strength of the molecular ion signal depending on the extraction procedure. If quantitative analysis is carried out using SIR or MRM transitions, it is possible to underestimate the amount of HBCD present in the sample if an unknown percentage has been converted to any one of the adducts shown. Although the source of the HCl has yet to be determined, a possible origin is an impurity in the ammonium acetate buffer.

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