DETERMINATION OF HEXABROMOCYCLODODECANE IN POLYSTYRENE FOAMS AND FOOD SAMPLES BY GC AND LC METHODS

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Introduction

Hexabromocyclododecane (HBCD) is produced in high volumes and is used mainly as an additive brominated flame retardant in expanded (EPS) and extruded (XPS) polystyrene foams that are used in the building industry for thermal isolation. HBCD is also added to textile materials and high-impact polystyrene (HIPS) applied in electrical equipment[1-3]. The compound is not covalently bound to the material, therefore it can be released into the environment. The potential sources of transport of HBCD into the environment have been discussed[4, 5].

HBCD is toxic, persistent in the environment and it has the ability to bioaccumulate. Due to these properties, the compound has been recently proposed for inclusion in the Protocol on Persistent Organic Pollutants (POPs) of the Stockholm Convention[6]. In the European Union (EU) HBCD was identified as a Substance of Very High Concern (SVHC) under Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)[7]. In accordance with the Committee for Risk Assessment (RAC) of the European Chemicals Agency (ECHA) and the Directive 67/548/EEC, HBCD is determined to be hazardous and classified as follows: R63 - Possible risk of harm to the unborn child, and R64 - May cause harm to breastfed babies[8].

Technical product of HBCD is a mixture of three predominant isomers, and depending on a producer it contains 10–13% of α-HBCD, 1-12% of β-HBCD, and 75–89% of γ-HBCD[7]. At present, separation of HBCD stereoisomers is not possible by using gas chromatography techniques because of thermal interconverting and partial breakdown of HBCD diastereomers at 160 °C. Furthermore, decomposition of this compound is starting at 240 °C[9, 10]. HBCD stereoisomers can be separated only by using reversed-phase liquid chromatography - mass spectrometry[10].

Wide use of HBCD has led to widespread contamination of this compound in a different biotic and abiotic environmental compartments and in humans[6-8]. Report of ECHA concluded that, recently none of a number of alternative flame retardants is suitable to replace HBCD in polystyrene foams[8], therefore monitoring of this contaminant in food and industry samples is highly advisable.

Materials and methods

Samples and reagents

Native isomers of α-, β- and γ-HBCD and isotopically labeled isomers of d18- γ–HBCD and ^{13}C–α-HBCD were provided by Wellington Laboratories Inc. (Canada). The purity of all standards was greater than 98%. One µg/mL stock solutions of the three individual standards, α-, β- and γ-HBCD, were prepared in methanol and were stored at 4 °C.

Calibration solution was performed at five concentration levels from 50 to 500 ng/ml for GC-MS/MS method and from 1 to 500 ng/ml for LC-MS/MS method.

Hexane, acetone and dichloromethane SupraSolv® for GC, methanol hypergrade for LC/MS, acetonitrile and water for chromatography were purchased from Merck.

Technical powder of HBCD was dissolved in dichloromethane and the five of concentrations between 10 mg/mL and 1µg/mL were prepared and stored in the sealed vessel at 4 °C.

Expanded polystyrene insulation panels provided by Termo Organica (Poland) were dissolved in dichloromethane and clean up by using silica gel (70–230 mesh ASTM, Merck). The samples were stored in the sealed vessel at 4 °C.

Farmed secies of salmon (*Salmo salar*) were extracted in Soxhlet apparatus by dichlorometane and clean up by using semipermeable membranes (ExposMeter, Sweden) and silica gel.

Methods

The determination of HBCD as the sum of three isomers of α, β and γ was performed using GC methods. Flame ionization detector (FID) and electron capture detector (ECD) were used for a screening analysis. Qualitative and quantitative analysis were performed by using isotope dilution technique in GC-MS/MS. As internal standard ^{13}C–α-HBCD was used. All the GC apparatus were equipped with DB - 5MS (J&W Scientific, 30 m; 0,32 mm; 0,25 μm) capillary column and temperature of injection was set at 250 °C. Temperature program for the GC methods were as follow:

GC-ECD Varian CP-3800	80 °C (1min) – 20 °C/min do 280 °C (1min) – 300 °C (5min)
GC-FID Varian CP-3380	50 °C (1min) – 10 °C/min do 300 °C (5min)
ID-GC-MS/MS GC2000 Series; GCQ Thermo Quest	100 °C (2 min) – 50 °C/min do 200 °C – 20 °C/min do 300 °C (15 min)

A sensitive ID-LC-MS/MS (TSQ Quantum, Thermo, USA) method was applied for the determination of three isomers of α-, β- and γ-HBCD in fish tissue. Chromatographic separation of the three isomers was achieved using Phenomenex Kinetex 2.6 u C18 100 A 50 x 2.1 mm analytical column with AQ C18 4 x 2 mm SecurityGuard cartridge (both Phenomenex, USA). Isocratic elution at laboratory temperature was used with mobile phase consisting of 30 % water and 70 % methanol.

Results and discussion

GC methods

Technical HBCD and EPS samples were analyzed by GC methods.

Chromatogram obtained from the GC-FID analysis of the technical sample at a concentration of 1 μg/mL is shown in Fig. 1. The most intense peak which corresponds to the HBCD, and lower peaks are observed. Based on the information presented by autors[9, 10] it is concluded that the lower peaks correspond with degradation products of HBCD which confirms the partial thermal decomposition of this compound in GC apparatus.

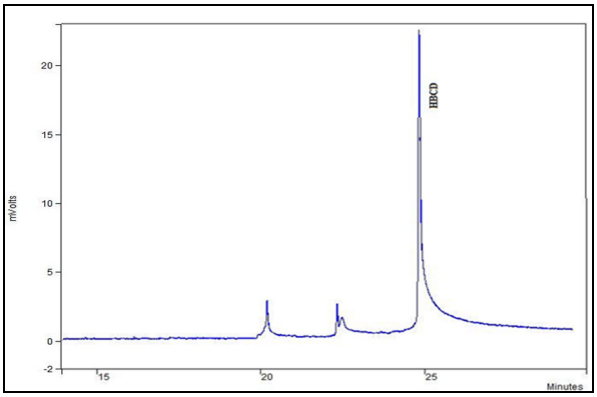

Fig. 1. Chromatogram of GC-FID analysis

Chromatogram obtained from ID-GC-MS/MS analysis of the EPS sample is shown in Fig. 2. The ion observed were as follow:

- parent ions at *m/z* 239 correspond with natural HBCD congeners and at *m/z* 251 correspond with congener-labeled 13C-α-HBCD
- product ions at *m/z* 157 correspond with natural congeners of HBCD and at *m/z* 169 correspond with 13C-α-HBCD

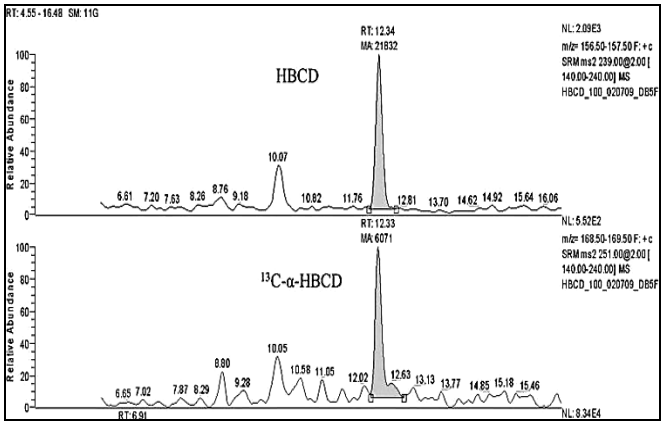

Fig. 2. Chromatogram of ID-GC-MS/MS analysis

The recoveries of HBCD lay in the range 70 – 126%. Limit of detection was 50 ng/ml Correlation factor of the linear regression line was 0.986.

LC method

The detection of the three of α-, β- and γ-HBCD isomers was carried out by means of the transition of the chlorine adduct [M-H+Cl]− of HBCD isomers to the quasi-molecular [M−H]− ion.

The recoveries of HBCD lay in the range 90 – 120 % for individual isomers. Limit of detection (LOD) was determined from chromatograms of real fish tissue samples and being 5 pg/g fresh weight for individual isomers.

Chromatogram obtained from analysis of fish tissue is shown in Fig. 3. The three α-, β-, γ-HBCD isomers and isotopically labeled d18- γ–HBCD are observed.

Correlation factors of the linear regression line were greater than 0.997 for all three isomers as shown in Fig. 4.

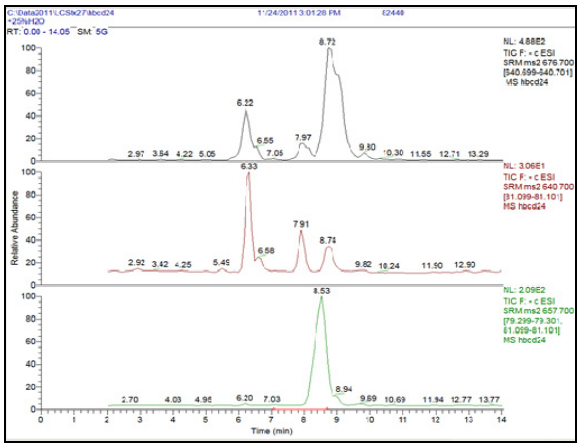

Fig. 3. Chromatogram of ID-LC-MS/MS analysis

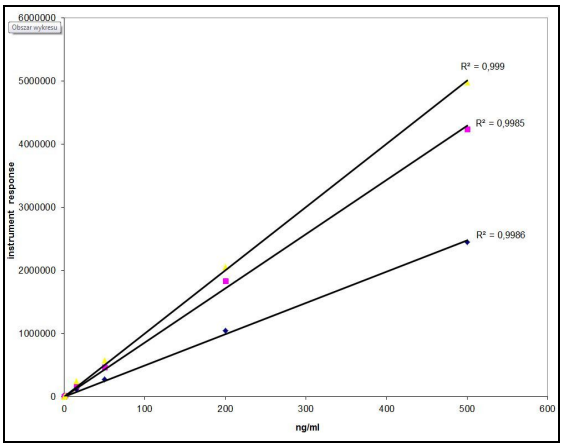

Fig. 4. Linear regression lines

A sensitive ID-LC-MS/MS method developed provides the determination of α-, β- and γ-HBCD isomers in fish tissue and could be implemented by routine laboratory practice.

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