# DETERMINATION OF FLAME RETARDANT HEXABROMOCYCLODODECANE DIASTEREOMERS IN TEXTILES

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## Introduction

Hexabromocyclododecanes (HBCDs) are the principal brominated flame retardant (BFR) in polystyrene foams used mainly for thermal insulation in the building industry, but are also used in upholstery textiles including furniture, draperies and wall coverings.[1] Since widening pollution and potential environmental impacts of HBCDs are of particular concern, Japanese Government classified this compound as a Type I Monitoring Chemical Substance in the Law Concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, *etc*., whereas in Europe and the U.S. it is not subject to regulatory restriction at present. Recently, wide ranges of HBCD concentrations were found in house dust samples,[2,3] indicating that its significant sources are very possibly present indoors. As textile has high-specific surface area among various upholsteries we use, HBCDs added to textile may have high potential to be emitted into the indoor environment and contribute as sources of indoor air and dust pollution. Although there are studies focused on residual levels and profiles of HBCDs in biota[4–7] and environmental media,[8,9] quantitative analysis of HBCDs in consumer products has not been conducted so far.

The technical mixtures of HBCDs consist mainly of three diastereomers, α-, β-, and γ-HBCDs with a composition of 10–13%, 1–12%, and 75–89%, respectively.[10] The physico-chemical properties are different among these three isomers and, hence, the environmental fate and accumulation features in organisms may also be different. Since the thermal rearrangement of HBCD diastereomers and the decomposition of HBCDs occur at the temperature above 160˚C and 240˚C, respectively, gas chromatography-mass spectrometry is not considered the optimal technique for the analysis of HBCD diastereomers.[11] Presently, liquid chromatography coupled tandem mass spectrometry (LC-MS-MS) is frequently used for HBCD analysis, because, in addition to its ability to chromatographically resolve the HBCD diastereomers, no thermal degradation or analyte composition transmutation occurs during analysis. However, we still need further studies to evaluate a possibility of thermal isomerization during sample extraction since some methods require quite high temperature.

Based on such a background, the aims of this study are to establish a concise and rapid procedure to analyze HBCD diastereomers in textile, and to understand the actual situation of HBCD contents and its isomer profiles in commercially available textiles in Japan.

## Materials and Methods

Ten different kinds of textiles mainly for curtains on the market were used in this study. They were found to contain bromine in percentage range by a handheld X-ray fluorescence (XRF) analyzer (Innov-X Systems). To evaluate extraction efficiency, reproducibility, and the possibility of isomerization of HBCD diastereomers, three different methods of extraction including Soxhlet, ultrasonic, and soaking extractions with toluene and dichloromethane (DCM) were applied to three of the ten textile samples (textile 1–3) in triplicate (Figure 1). During the ultrasonic extraction, ice was put in the water bath to prevent temperature increase. Each extract was diluted with

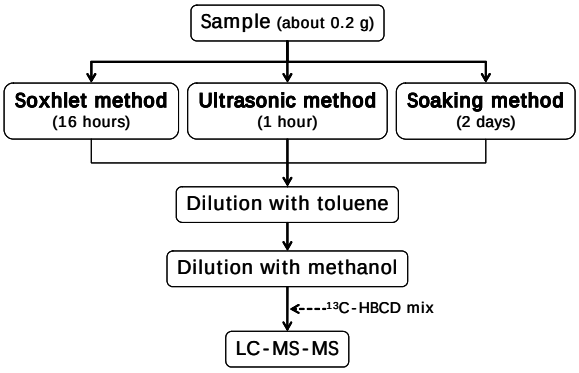


Figure 1. Flow chart of the analytical method evaluated for measuring HBCDs in textile samples.

toluene and methanol, and then spiked with $^{13}$C-labelled α-, β-, and γ-HBCDs as internal standards. Identification and quantification of HBCD diastereomers were performed using LC-MS-MS (Alliance 2695/Quattro Ultima, Waters) in the multiple reaction monitoring mode based on *m*/*z* 640.6→ *m*/*z* 79 and *m*/*z* 652.6→ *m*/*z* 79 for the native and $^{13}$C-labelled diastereomers, respectively. Besides, elution of HBCDs from the textile was confirmed by analyzing bromine intensity on cross-section of the fiber using a scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX). The remaining textile samples (*n* = 7, textile 4–10) were then analyzed using the method established in this study.

**Results and Discussion**

*Evaluation of extraction procedure*

Total HBCD concentrations obtained from different extraction methods tested in this study are summarized in Figure 2. Coefficients of variance of detected concentrations by all the procedures were almost within 10%, suggesting that HBCDs were distributed homogeneously in textiles, not locally heterogeneous. From SEM-EDX analysis, we have also confirmed the uniform distribution of bromine on cross-section of the fiber from the textile before any extraction processes. The highest HBCD levels were detected using Soxhlet and soaking extraction with DCM for all the three textiles examined. Intriguingly, for both ultrasonic and soaking methods, extracted amounts of HBCDs with toluene were approximately 1% of those with DCM. On the other hand, in the case of Soxhlet extraction HBCD levels were similar when using toluene and DCM. These results may indicate that extraction efficiency of HBCDs was enhanced by high temperature during Soxhlet extraction with toluene as boiling point of this solvent is 110.6˚C. As for soaking method with DCM, the concentration of HBCDs did not show apparent increases even when the soaking time was extended. As no bromine peak was observed in the fabric soaked in DCM for two days by SEM-EDX analysis, it was ascertained that the technical HBCD mixtures added to textile can be almost completely and promptly extracted by DCM.

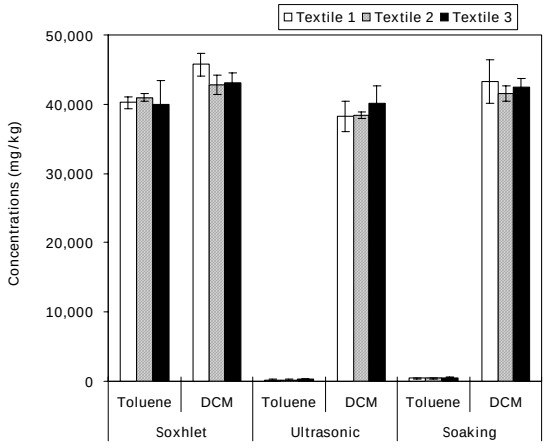


Figure 2. Total HBCD concentrations in textile 1–3 obtained using different extraction methods.

When comparing the diastereomer profiles of HBCD in the different methods tested, the proportion of α-diastereomer to total HBCDs tended to increase when toluene was used as extraction solvent (Figure 3). The HBCD profiles were nearly identical when DCM was used. Although Soxhlet extraction method using toluene was considered one of the forcible ways to extract HBCDs from textiles as shown in Figure 2, there was a slight increase in the % contribution of α-HBCD to total HBCDs accompanied by a decrease in that of γ-HBCD during Soxhlet extraction using toluene compared to DCM (Figure 3). The influence of photolysis, if any, was minimized by using amber glassware throughout the procedures under the ultraviolet protection light. Therefore, this result suggests that γ-HBCD starts isomerization at the temperature at the boiling point of toluene (110.6˚C) to some extent. Therefore, it needs careful attention when samples were extracted by a Soxhlet extractor using toluene.

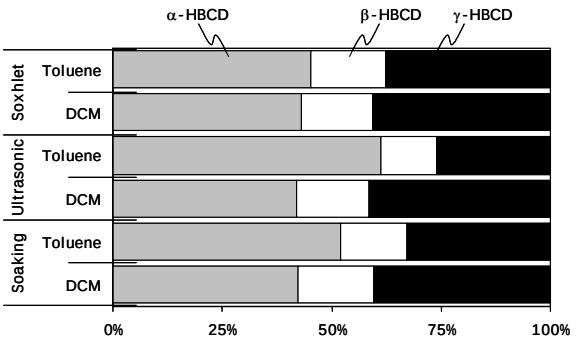


Figure 3. Diastereomer compositions of HBCDs in textile 1 obtained using different extraction methods.

Among the procedures compared in this study, all the three extraction methods with DCM can be regarded as appropriate ways to analyze HBCDs in textile samples. However, Soxhlet extractor requires large variety of glassware, and cross-contamination from

high concentration samples should be checked routinely since the apparatuses are not disposable. As for ultrasonic extraction, the temperature of water bath is easy to raise in a while during the procedure; therefore we need to put ice frequently to prevent the effect of increased temperature. Considering all the various factors together, the method of soaking extraction with DCM was the most facile procedure to analyze HBCD diastereomers in textiles. This method does not require any special techniques and can be conducted by just putting textile samples in DCM and leaving them in the dark at room temperature for a couple of days.

*Levels and profiles of HBCD diastereomers in textiles*

Except a single textile sample (textile 10), HBCDs were detected in all the samples analyzed with concentrations ranging from 22,000 to 55,000 mg/kg (i.e., 2.2–5.5%). Although bromine content in textile 10 analyzed by a handheld XRF was 88,000 mg/kg, which was the highest level among the ten samples used in this study, HBCDs were not detected in this sample. This result indicates that this product might be flame-retarded by BFRs other than HBCDs. Further analysis of other BFRs such as polybrominated diphenyl ethers, decabromodiphenyl ethane, and bromophenols is required. In Japan, flammable items including draperies and carpets used in the high-rise buildings, underground malls, and the public facilities such as theaters, hospitals, and hotels are obligated to use flame-retarded products. Therefore, the concentrations of flame retardants including HBCDs in the indoor environment of the above-mentioned places are expected to be much higher than those at homes. Risk assessments for the exposure to BFRs in those public facilities compared to homes should be one of the important issues to be tackled.

As shown in Figure 4, although γ-HBCD always forms the majority (>75%) with a small amount of the others in the technical mixtures of HBCD, the % proportions of α-, β-, and γ-diastereomers to total HBCDs in the textile samples analyzed in this study were 25–46%, 12–17%, and 38–62%, respectively. This apparently higher proportion of α-diastereomer in textile products compared to the technical mixtures may indicate that γ-HBCD can isomerize to α-diastereomer by heating processes to incorporate the commercial formulation into treated materials, or α-diastereomer preferentially absorb onto textile materials during manufacturing of flame-retarded consumer products. Furthermore, textiles with higher total HBCD concentrations tended to show larger contribution of α-diastereomer (Figure 4), implying that types of the technical HBCD mixtures incorporated and/or the temperature during heating processes will differ depending on the products.

The fact that the flame-retarded textile products in our surroundings already have contained substantial amount of α-HBCD compared to the technical mixtures is essential for understanding HBCD accumulation features in the indoor environment and also in biota including humans. So far, the studies focused on HBCD diastereomers accumulated in higher trophic animals reported the predominance of α-diastereomer.[4-7, 12] This phenomenon has been ascribed to isomer-specific biomagnification of α-HBCD in the upper trophic level and also low bioavailability of γ-diastereomer. However, from the results of this study, it can be said that it is not always appropriate to compare HBCD diastereomer profiles in the environment directly with those in the commercial mixtures. Recently, Abdallah et al[3] also found the marked shift from the predominance of γ-HBCD in the technical mixtures towards α-diastereomer in house dust from UK, Canada, and U.S. Their findings raised the possibility that the observed predominance of α-diastereomer in humans[12] may not be attributable solely to *in vivo* metabolism[5] or dietary exposure. As the diastereomer profiles in some dust samples were similar to those found in the textiles of the present study, their results indicate that fibers from the flame-retarded textile might be an important component of dust. Further studies are required to evaluate emission behaviors of HBCDs from textiles into the indoor environment and to estimate their contribution to air and dust pollution.

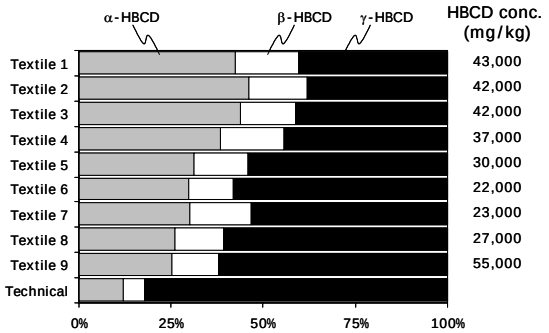


Figure 4. Diastereomer compositions of HBCDs in the commercially available textiles in Japan (textile 1–9) compared to the technical mixtures. Total HBCD concentrations detected in the textiles are also shown.

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