Asian Journal of Chemistry Vol. 19, No. 2 (2007), 921-928

Determination of Hexabromocyclododecane in Backcoated Textile Preparation

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A simple and reproducible chromatographic method for determination of one of the brominated flame retatardants (FRs), hexabromocyclododecane isomers is proposed, the mobile phase consisted of 80 % (v/v) acetonitrile aqueous solution. A simple quantitive extraction method using a soxhlet extraction is also proposed to extract hexabromocyclododecane from textile backcoated sample and a rapid chromatographic method, using spectrophotometric detection is described for the determination of hexabromocyclododecane. The proposed method is applied to determine the hexabromocyclododecane in a backcoated textile. A complete validation method for both extraction and analytical method is discussed. Linear calibration curve in range of 0.5-380 μg/mL is achieved. Detection limit are in the range 0.01 to 0.1 μg/mL.

Key Words: Flame retardants, Hexabromocyclododecane, Backcoated textile.

INTRODUCTION

Every year, fires kill more than 3,000 people, injure more than 20,000 and result in property damages exceeding an estimated $ 11 billion in the United States alone. Fire incidence has dropped over the past 25 years, which is partly because of the fire prevention policies requiring the presence of flame retardant chemicals in many industrial products. Flame retardants (FRs) are chemicals used in plastics, textiles, foam, electronic circuitry and other materials to prevent fires. These material could be added during the manufacturing process or even after the manufacture (*e.g.* backecoated textile)[1-3].

There are more than 175 different types of flame-retardants, which are generally divided into classes that include the halogenated organic (usually brominated or chlorinated), phosphorus-containing, nitrogen-

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containing and inorganic flame-retardants. Brominated flame retardants (BFRs) are a novel group of global environmental contaminants[1,2]. They are currently the largest market group because of their low cost and high performance efficiency. Little toxicity information is present for nearly half of the existing brominated flame retardants. Many of these are new compounds that will require basic toxicity testing, at minimum, before they are released to the marketplace. It is also important to note that not all brominated flame retardants are alike: the only thing that many have in common is that they contain a bromine atom. However, they represent a major industry, involving high-production chemicals with a wide variety of uses[3]. Recent reports have demonstrated that brominated flame retardants exist in the environment far from the locations where they are produced and/or used and that the concentrations of some of the brominated flame retardants in the environment and in humans are rapidly increasing. The widespread production and use of brominated flame retardants and strong evidence of increasing contamination of the environment and people by these chemicals, heighten the importance of identifying emerging issues and data gaps and of generating a future research agenda.

The five major brominated flame retardants are tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCD) and three commercial mixtures of polybrominated diphenyl ethers (PBDEs) or biphenyl oxides, which are known as decabromodiphenyl ether (DBDE), octabromodiphenyl ether (OBDE) and pentabromodiphenyl ether (pentaBDE). These polymers are then used in consumer products, including computers, electronics and electrical equipment, televisions, textiles, foam furniture, insulating foams, and other building materials[4]. In fact, they increase the flash-over time using the following mechanism is as follows: when exposed to high temperatures, the flame retardant molecule releases bromine as free radicals ($Br^{\bullet}$) which reacts with hydrocarbon molecules (flammable gases) to give HBr. They react with the high-energy $H^{\bullet}$ and $OH^{\bullet}$ radicals to give water and the much lower energy $Br^{\bullet}$ radical, which is then available to begin a new cycle of $H^{\bullet}$ and $OH^{\bullet}$ radical removal[5-8].

Brominated flame retardants are additives which mixed into polymers and are not chemically bound to the plastic or textiles and therefore may separate or leach from the surface of their product applications into the environment. The potential release of these compound from the materials that contain them emerge the need to a new studies to investigate the exposure risk to these material[9]. Brominated flame retardants production have increased dramatically over the past 20 years, with the largest relative increase at this time being in Asia.

Hexabromocyclododecane (HBCD) (Fig. 1) is one the most important flame retardants widely use in upholstered furniture back coating. HBCD

is a non-aromatic, brominated cyclic alkane used primarily as an additive flame retardant in thermoplastic polymers with final applications in styrene resins. HBCD is highly lipophilic, with a log K_{ow} of 5.6 and has low water solubility (0.0034 mg/L). Because of its size and halogenation, it also has a low vapour pressure (4.7×10^{-7} mm Hg). Recent studies have shown that HBCD has a strong propensity to bioaccumulate, demonstrated by a bioconcentration factor[10] of *ca.* 18,100 in fathead minnows, as well as fish-to-sediment ratios of up to 15. In fact, HBCD is not only bioaccumulative but is also persistent, with a half-life of 3 d in air and 2-25 d in water. HBCD consists of three isomers (α-, β and γ-isomers). The low-melting HBCD consists of 70-80% γ-isomer and 20-30% of α- and β-isomers. The high-melting HBCD consists of 90% or more of the γ-isomer[11]; however, small amounts of the α-diastereomer and even smaller amounts of the β-diastereomer have been found in some regions with high HBCD levels.

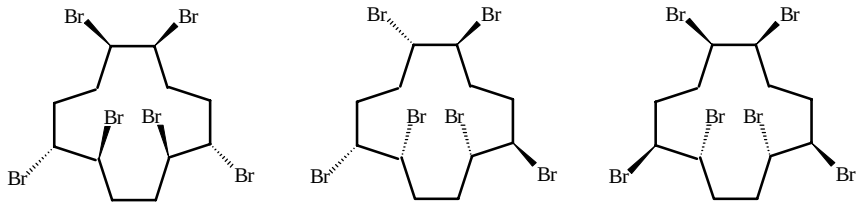

Fig. 1. Three isomers of hexabromocyclododecane

HBCD is considered to be toxic for aquatic organisms and may also cause long-term adverse effects in the aquatic environment[2,3,9].

The toxicity of HBCD has not been extensively studied and there are very few reports of effects of HBCD on people, the environmental contaminants studies of brominated flame retardants have been undertaken since the mid-1980s, however, only sparse data are available on HBCD[12-14].

The development of an easy and direct analytical method is difficult to achieve the overall aim; Obtain reliable data on the flame retardants release and exposure information for a number of common flame retardants systems incorporated into key consumer product matrices to provide reliable flame retardants release data to support formal human exposure risk assessment for oral, dermal and inhalation exposure and environmental and ecotoxicology risk assessments.

In this paper, a simple, accurate and reproducible quantitive extraction method using a soxhlet extraction and a rapid chromatographic method, using spectrophotometric detection, is described for the determination of HBCD. The proposed method is applied to determine the HBCD in a backcoated textile.

EXPERIMENTAL

1,2,5,6,9,10-Hexabromocyclodecane (1,2,5,6,9,10-HBCD), $C_{12}H_{18}Br_6$ (m.w. 641.7 g/mol) where obtain from great lack chemicals. Acetonitrile of analytical grade, were obtained from Merck. Distilled water was used throughout. Standard solutions were prepared by dissolving accurately weighed 300 ± 0.5 mg of HBCD in 100 mL of acetonitrile.

Chromographic system: A water mode 600 solvent delivery system was used together with a Water Nova-pak, C_{18} and 3.9 x 150 mm column packed with (3.9 μm particle size). Samples were injected using a Rheodyne injector with 20-μL sample loop. Detection was done with UV/vis diode array detector (Water PD 900) absorbance detector operating at 220 nm with an AUFS of 0.11. Peak evalution and quantization were made using Water millennium software. The mobile phase consisted of 80 % (v/v) acetonitrile: water and flow rate of 1.0 mL/min.

Preparation HBCD samples: Backecoated textile samples (around 2 g for each sample) contains HBCD (7.7 % wt.) and a clay blank sample (contains no flame retardants) were extracted from the fabric samples using a soxhlet extraction method. The weight of the textile was recorded before and after extraction. The samples were extracted for 6 h under boiling solvent reflux conditions in 100 mL of acetonitrile. The extracted solutions were filtered using a normal filter paper (45 μm) and diluted if necessary by 1:25, then the extracted samples passed through Water Novapak, C_{18}, 3.9 pre-column before injection and then injected and determined using HPLC. All the prepared samples were determine within day and by day-to-day.

Spiking of clay sample: Three set of six sample of fabric free of flame retardants were spiked with a known concentration of HBCD, which dissolved in acetonitrile and allowed to dry. The spiked samples were extracted using the same procedure that used for the real samples and the recovery rate was calculated. The samples were extracted in 100 mL of acetonitrile and then 1 mL of the extract was diluted to 10 mL with acetonitrile.

Validation procedure: In general, the validation strategy for the optimization of the chromatography methods will include: (a) check the repeatability of injection with at least six replicates, (b) find the linear range (or define the curvilinear response) by dilution of standard solutions and (c) estimate the limit of quantification using standards. The following steps will achieve the above strategy: (i) spike each matrix that is subject to extraction to determine the recovery of each extraction method, and compare with blanks, (ii) determine within-day reproducibility by spiking

six times at three different concentrations: high, medium and low (chosen to suit the expected concentration range), (iii) determine day-to-day recovery by repeating the above but analyzing one high, medium and low sample each day for six days.

RESULTS AND DISCUSSION

Fig. 2 shows the chromatographic separation of a α, β and γ isomers of HBCD. The method was applied to the determination of HBCD from a backcoated textile sample according to the above-described procedure. The α isomer peak appears first (at 5.9 min), β isomer (at 6.54 min) and γ isomer at 8.9 min. The percentages of the three isomers are 16.5, 12.4 and 71.2 % for α, β and γ, respectively. The HBCD total area is calculated as the summation of the area of the three-isomer peaks.

$$HBCD = \alpha + \beta + \gamma$$

The area percentage of α, β and γ obtained is in good agreement with the result obtained by independent method used by Albemarle in their method[15]. The total area under the curve is directly related to the concentration of the HBCD, as can be seen the appearance of a small undesirable peak at initial time is related to the solvent. In fact we did not monitor any undesirable peaks due to the presence of other ingredients, which indicate that our extraction procedure is efficient, and the remaining components being eliminated in the clean-up step (filtration step). These facts show the possible applicability of the proposed method for routine and quality control analysis, without possible interference problems derived from other substances, which frequently appear in the formulations.

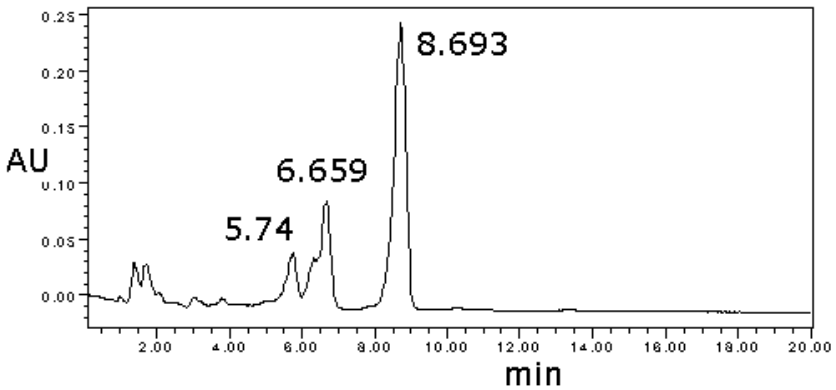

Fig. 2. Chromotograme of 1,2,5,6,9,10-hexabromocyclodecane

Linearity: The chromatographic data produced are graphically presented in Fig. 3. A calibration curve for the standard solutions contain 1,2,5,6,9,10-hexabromocyclodecane was constructed. The results show that the calibration is linear and repeatable in the range of 0.5 to 380 μg/mL and

the isomeric peaks ratios are sustained throughout. The calibration curve of this compound following a linear relationship with regression parameter is y = 2972 + 2686x with correlation coefficient (R^2) is 0.9999 and from the calibration experiments the smallest concentration of HBCD that can be detected reliably is 0.1 μg/mL if all three isomer peaks used. By using the gamma peak only, the limit of detection could be extended to 0.01 μg/mL, if required.

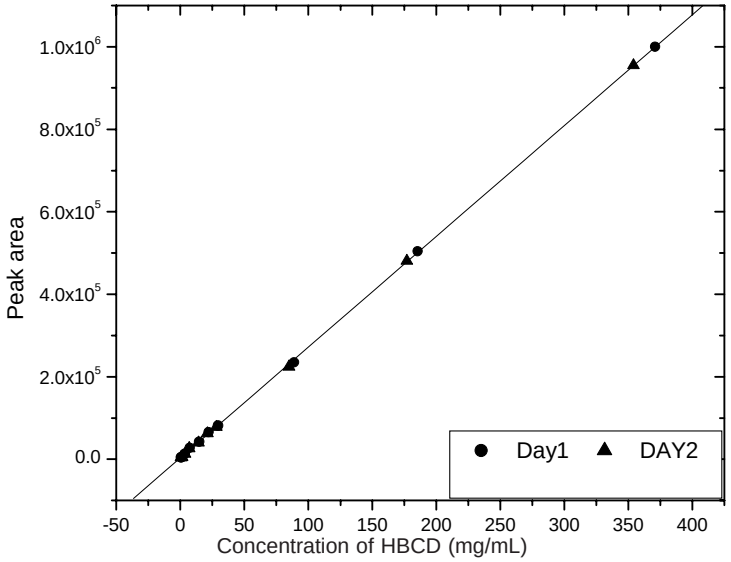

Fig. 3. Calibration curve of 1,2,5,6,9,10-hexabromocyclodecane (HBCD)

Validation of extraction and sampling methods: The results for the spiking of a set of six samples of clay fabric free of HBCD with a known concentration of flame retardant at three-concentration levels; high, medium and low concentration were summarized in Table-1. The spiked samples were extracted using the same procedure for real samples and the following results have been procured: (a) recovery percentages of 100.8, 96.9 and 111.7 % for high, medium and low concentration levels, respectively were achieved, which give an average recovery of 103.1 ± 7.1. The results for the determination of the HBCD within-day and day-to-day and the result of the reproducibility of this method are summarized in Table-2.

The study of precision, samples containing (7.7% wt.) of HBCD were analyzed according to the proposed procedure. The within-day precision or repeatability (as RSD) is within 5.4 to 6.4%. The between day precision or reproducibility was averaged to 6.9% (five randomized determinations over 1 month). In order to assess the absence of systematic errors the proposed method was compared with another independent method[15] applied to the same set of textile samples. The regression method was applied, considering the results obtained by the proposed method as y-values and

TABLE-1
RECOVERY OF HBCD FROM SPIKED FABRIC

Sample	Sample weight lost (mg)	HBCD added (mg)	HBCD recovered (mg)	% Recovery
1 H	40.2	0.00	--	--
2 H	39.6	28.4	29.2	102.8
3 H	35.0	28.4	26.8	94.4
4 H	31.0	28.4	29.9	105.3
5 H	36.7	28.4	28.4	100.0
6 H	41.3	28.4	28.8	101.5
Mean recovery			100.8 ± 3.6	
1 M	32.1	0.00	--	--
2 M	40.2	17.01	15.2	89.9
3 M	35.7	17.01	16.0	94.7
4 M	45.6	17.01	17.4	103.0
5 M	46.2	17.01	16.7	98.8
6 M	37.5	17.01	16.6	98.2
Mean recovery			96.9 ± 4.6	
1 L	35.7	0.0	0.0	0
2 L	52.2	5.7	6.1	107
3 L	45.4	5.7	6.5	114
4 L	42.3	5.7	6.5	114
5 L	39.1	5.7	6.6	116
6 L	50.1	5.7	6.1	108
Mean recovery			112 ± 4	

H = high, M = medium, L = low concentration samples.

TABLE-2
RESULT OF THE SOXHLET EXTRACTION OF TEXTILE SAMPLES

Sample number	Weight (g)	Weight lost (g)	Wt. lost (%)	Theoretical HBCD exist in the fabric (g)	Calculated HBCD recovered (g)	Recovery (%)
Day 1						
Clay	2.2220	0.0430	1.9	0.000	–	–
1	2.6243	0.3040	11.6	0.202	0.1879	93.1
2	2.6510	0.1690	6.3	0.204	0.1712	83.9
3	2.6638	0.1894	7.1	0.205	0.1768	86.2
4	2.6302	0.3068	11.7	0.203	0.1935	95.6
5	2.6294	0.2840	10.8	0.202	0.1805	89.4
Average recovery					89.64 ± 5.4	
Day 2 (The same samples in day 1, repeated)						
Clay	1.4756	0.032	2.2	-	-	-
1	2.5975	0.319	12.3	0.200	0.2038	101.90
2	2.6049	0.330	12.7	0.200	0.1954	97.72
3	2.6258	0.315	12.0	0.202	0.1786	88.50
4	2.4563	0.283	11.5	0.189	0.1926	101.90
5	2.5743	0.312	12.2	0.198	0.1814	91.70
Average recovery					96.4 ± 6.2	

those obtained by the independent method as x-values. The resulting straight line is $y = (-0.8 \pm 0.9) + (0.95 \pm 0.03)x$. The corresponding Student t tests on slope and intercept indicate that at a 5 % significance level there are no significant differences in the results obtained from either of the two methods, *i.e.* the proposed method is suitably validated.

Conclusions

The proposed method for the determination of HBCD is sensitive, rapid and practically does not require any sophisticated sample treatment, except the extraction, or and special clean-up procedure. One important advantage of the proposed method is the ability to separate the three isomers in with a retention time less than 10 min, although only one flame retardant can be analyzed.

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(*Received*: 15 May 2005; *Accepted*: 30 June 2006) AJC-5034