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Determination of decabromodiphenyl ether in backcoated textile preparation

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ABSTRACT

A simple and reproducible chromatographic method for determination of decabromodiphenyl ether (DBDPE) is presented. The mobile phase consisted of aqueous acetonitrile solution. A simple quantitative extraction method using a soxhlet extraction is proposed to extract decabromodiphenyl ether from textile backcoated sample, and, a rapid chromatographic method using spectrophotometric detection, is described for the determination of decabromodiphenyl ether. The proposed method is applied for the determination of the decabromodiphenyl ether in a backcoated textile. Complete methods validation for both the extraction and analytical methods are discussed. Linear calibration curve in a range of 0.3–300.0 mg/μL is achieved with a detection limit of 0.1 μg. The method is successfully applied to the determination of decabromodiphenyl ether in several backcoated formulations.

1. Introduction

In the last decades, flame retardants (FRs) gained enormous importance because they were widely used in everyday applications and they almost exist everywhere in our modern day life. Many of these substances are persistent and lipophilic and have been shown to bioaccumulate.

Flame retardants, which are chemicals used as additives during the manufacture process or even after the manufacture (e.g. backcoated textile), can be divided into reactive and additive flame retardants according to their use [1–4]. The reactive flame retardants are covalently bonded to the polymer and therefore less likely to leach out from its matrix, on the other hand, additive flame retardants are physically combined with the material being treated rather than chemically bonded. Therefore, they are more susceptible to migration and loss from the polymer matrix. The potential release of these compounds from the materials that contain them justifies the need of new studies to investigate the exposure risk to these materials [5].

The main purpose of the FRs is to prevent the spread of fires, or delay the time of flashover by slowing down the initial burning rate and thereby helps to increase the time of flashover. Brominated flame retardants are often the most effective flame retardant when both performance and cost are considered. In fact, they increase the flashover time through the release of free radical (Br or Cl) which react with hydrocarbon molecules to give HBr or HCl that react with the high-energy H and OH radicals to give water and the much lower energy $Br^{\bullet}$ or $Cl^{\bullet}$ radicals. The quantity of the halogenated atoms, as well as the ease of the release of the halogenated atom plays a crucial role in the effectiveness of the material as flame retardant [6–9].

Decabromodiphenyl Ether (1,1′-oxybis[2,3,4,5,6-pentabromobenzene) ($C_{12}Br_{10}O$ Mwt 959.12), (DBDPE), is a white to off-white powder shown at Fig. 1, belongs to a family of polybrominated flame retardants, and is used in polyolefins, styrenics, polyamides and thermoplastic polyester resins. Its end applications include: elastomers, wire and cable, textile coatings, electrical and electronic equipments, automotive parts, construction materials, textile back coatings and textile blends [10–14]. A great number of studies on environmental contaminants brominated flame retardants have been undertaken since the mid-1980s, however, more are still unknown about their reactivity and further studies have to be done to understand their toxicity [15–18].

DBDPE is nearly insoluble in water (20–30 mg/L), with a partial solubility in organic solvents, such as acetone, chlorobenzene, and *o*-xylene Log Octanol/Water Partition coefficient of 5.24 [14]. DBDPE is not acutely toxic to fish or marine algae [19–21], and it is not expected to show chronic toxicity for aquatic species due to its large molecular weight, negligible water solubility, low vapour pressure, and high log octanol/water partition coefficient values. It is expected that when DBDPE is entering the environment it tends to bind with the organic fraction of particulate matter. On the other hand, when DBDPE is heated to decomposition, it emits toxic fumes of bromine gas [14].

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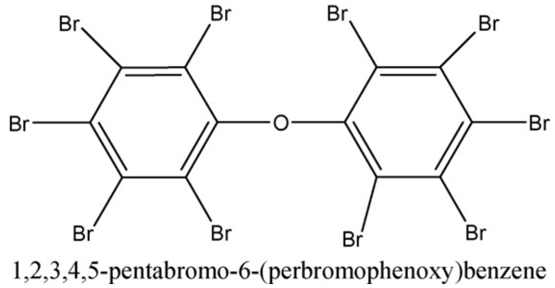

Fig. 1. Structural formula of the DBDPE.

Globally, DBDPE is the most widely used poly-brominated product. There is evidence suggesting that highly brominated flame retardants such decabromodiphenyl (DBD) are precursors of the more toxic, bio-accumulative, and persistent lower brominated flame retardants. While the degree to which this phenomenon adds to the overall risk to organisms is not known, there is sufficient evidence to warrant concern.

Up to date, the debate about the toxicity and bio-accumulative of DBDPE is still one of the hot topics for the environmental regulator. The concern related to its inclusions in the Proposed Rule Regarding Persistent Bio-accumulative Toxins (PBTs) is still an open question. Various publications have demonstrated that DBDPE can be reduced photolytically to lower brominated flame retardants, and that the rate of photolysis decreases with decreasing degree of bromination. Moreover, the described photolysis reactions typically produce a wide range of congeners, and it is extremely important to investigate whether the described processes are likely to occur in the real environment [22].

Inhalation and ingestion are possible routes of human exposure to decabromodiphenyl oxide. Exposure to DBDPE was reported to have different effects on human health. It was reported that workers exposed to it developed thyroid hyperplasia. Also it has been found to cause liver tumors in mice. Human data are insufficient. Decabromodiphenyl oxide is not mutagenic in standard bacterial mutagenesis assays and it is not genotoxic in Chinese hamster ovary cells, with or without metabolic activation [14].

In this paper, we continue our efforts to obtain reliable data on the flame retardant and exposure information by introducing a new simple, accurate and reproducible quantitative extraction technique using a soxhlet extraction and a rapid chromatographic method. Using spectrophotometric detection, which is described for other flame retardant, decabromobiphenyl, the proposed method is applied to determine the DBDPE in a backcoated textile.

2. Experimental

2.1. Chemicals

1,2,3,4,5-Pentabromo-6-(perbromophenoxy) benzene ($C_{12}Br_{12}O$) is one of great lake chemicals. Analytical grade acetonitrile and tetrahydrofuran (THF) were obtained from Merck (Darmstadt, Germany). Distilled water was used throughout.

2.2. Chromographic system

A Waters model 600 solvent delivery system was used together with an X-Terra column (100 mm × 2.1 mm internal diameter) packed with 3 μm RP18 material. Samples were injected using a Rheodyne injector with 20 μL sample loop. Detection was performed using an UV/vis diode array detector (PD 900, Waters) based on absorbance detector operating at 230 nm (0.11 AUFS). Peak evolution and quantization were made using Water millennium software. The mobile phase consisted of acetonitrile and water, with flow rate of 1.0 mL/min.

2.3. Samples

DBDPE 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, using THF solution for 6 h under boiling solvent reflux conditions. The extracted solutions were filtered using a normal filter paper (45 μm) and diluted by 1:25 in acetonitrile. Diluted samples were passed through a Nova-Pack C18 precolumn (3.9 mm × 20 mm) before injection and then injected and measured using HPLC.

2.4. Standard solution

The stock solution was prepared by dissolving accurately weighted 300.0 ± 0.5 mg of DBDPE in 100 mL of THF; the standard solutions were prepared from the above stock solution.

2.5. Validation

A validation method for the optimisation of the chromatographic method was used. The method includes: study of the repeatability of injection with at least six replicates, determination of the linear range by dilution of standard solutions, then estimation of the limit of quantification using standards, and finally, improvement of the method if necessary. The above strategy was achieved by the following steps:

1. Spike each matrix that is subject to extraction to determine the recovery of each extraction method, and compare with blanks.
2. Determine within-day reproducibility by spiking six times at three different concentrations: high, medium and low (chosen to suit the expected concentration range).
3. Determine day-to-day recovery by repeating the above steps but analyzing one high, medium and low sample each day for 6 days.

2.6. Sample treatment

Backcoated textile sample (around 2 g) containing DBDPE and a clay blank sample (contains no flame retardant) were extracted using soxhlet extraction method for a 6 h using 100 mL THF. The extracted solutions were marked up to volume using the same solvent. The extracted solutions were filtered using a filter paper and diluted (1:25) in acetonitrile before passed through a Nova-Pack C18 precolumn (3.9 mm × 20 mm) before injection.

2.7. Spiking of clay sample

Three sets of six samples of clay fabric free of FR were spiked with a known concentration of DBDPE at three-concentration levels: high, medium and low concentration, which were dissolved in THF and allowed to dry. The spiked samples were extracted using the same procedures used for the real samples and the recovery rate was calculated.

3. Results and discussion

3.1. Calibration features

The chromatographic separation of DBDPE is shown in Fig. 2. The method was applied to the determination of DBDPE from a

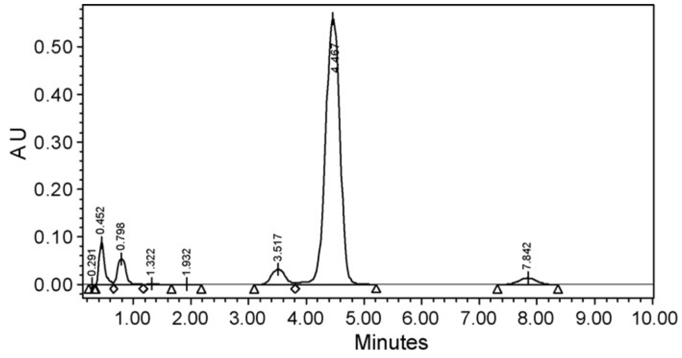

Fig. 2. Chromatogram of DBDPE, X-Terra column (100 mm × 2.1 mm internal diameter) packed with 3.5 μm RP18 material; Rheodyne injector with 20 μL sample loop; UV detection at 230 nm; flow rate of 1.0 mL/min; mobile phase of acetonitrile:water.

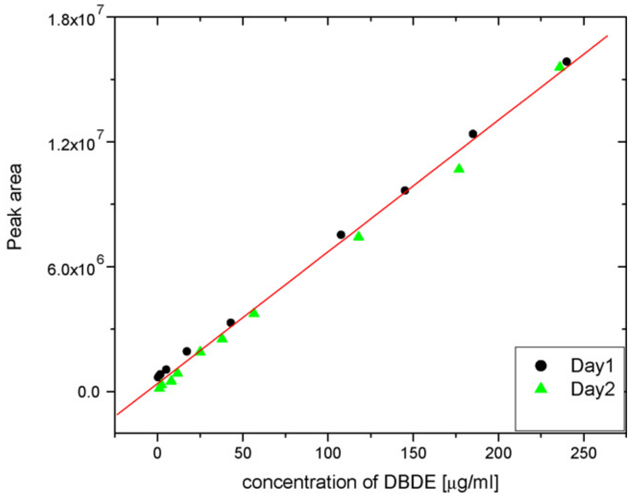

Fig. 3. Calibration curve of DBDPE, the concentration range is 0.3–300.0 μg/mL.

backcoated textile sample according to the above-described procedure. The results could be summarized as follows.

The area under the curve of HPLC chromatogram in Fig. 2 is directly related to the concentration of the DBDPE. Linearity of the method was studied through the preparation and analysis of a set of calibration standards solutions containing DBDPE (0.30–300 μg/mL). The results show that the calibration is linear and repeatable in this range. The chromatographic data produced are graphically presented in Fig. 3. The calibration curve of this compound following a linear relationship with regression parameter is represented by:

$$y = 388989 + (63265)x \quad \text{with R.S.D. equal to 0.998.}$$

Calibration experiments show that 0.1 μg/mL is the smallest concentration of DBDPE that can be detected reliably. However, this falls in the non-linear range below 0.1 μg/mL.

3.2. *Validation of extraction and sampling methods*

The results of the three sets of six samples of fabric free of FR that were spiked with a known concentration of DBDPE are summarized in Table 1. The recovery percentages of 104.6%, 96.2% and 97.7% for high, medium and low concentration levels, respectively, were achieved, which give an average recovery of 99.5 ± 4.4%.

3.3. *Soxhlet extraction of textile sample*

In order to validate the soxhlet extraction method, the reproducibility of the method was tested by analyzing different samples of DBDPE-containing fabric under identical extraction conditions (i.e., using a soxhlet extraction method) on the same day and from day-to-day. The weight lost during the extraction process on the fabric sample was also determined from recording the fabric weight before and after extraction. The results are summarized in Table 2. It was found that a complete extraction was achieved using this method and that 102% of the theoretical concentration was found. The results are summarized in Table 3. As shown, a good agreement was found with respect to the label claims for the analyzed samples, within the confidence ranges commonly accepted. The appearance of a small undesirable peak at initial time is related to

Table 1
Recovery of DBD from spiked fabric

Sample	Sample weight lost (mg)	Milligram of DBDPE added	Milligram of DBDPE recovered	%Recovery
1 H	39.1000	0.00	0.00	0.00
2 H	30.2000	28.20	29.30	103.90
3 H	26.0000	28.20	30.90	109.60
4 H	31.0000	28.20	28.10	99.60
5 H	30.6000	28.20	30.50	108.20
6 H	39.5000	28.20	28.50	101.10
Mean recovery	29.50 ± 0.20		Average %recovery	104.60
1 M	34.4000	0.00	0.00	0.00
2 M	45.6000	16.90	16.90	100.00
3 M	44.5000	16.90	14.90	88.30
4 M	49.8000	16.90	17.50	103.60
5 M	48.6000	16.90	16.40	97.00
6 M	47.3000	16.90	15.60	92.30
Mean recovery	16.30 ± 1.03		Average %recovery	96.20
1 L	42.1000	0.00	0.00	0.00
2 L	55.2000	5.60	5.58	99.60
3 L	53.4000	5.60	6.40	114.30
4 L	50.3000	5.60	5.03	89.80
5 L	52.1000	5.60	5.58	99.70
6 L	52.1000	5.60	4.76	85.00
Mean recovery	5.47 ± 0.63		Average %recovery	97.70

H: high concentration samples. M: medium concentration. L: low concentration. The samples are extracted in THF and then diluted with acetonitrile.

Table 2
Results of the soxhlet extraction of textile sample

Sample	Weight (g)	Weight lost (g)	% of wt lost	Theoretical[a] DBDPE existent in the fabric (g)	Calculated DBDPE recovered (g)	Recovery (%)
Day 1						
Clay	1.7930	0.0420	2.3000	–	–	–
S1	2.1222	0.2990	14.1000	0.191	0.186	97.3
S2	2.2209	0.2970	13.4000	0.200	0.194	97.2
S3	2.2260	0.2990	13.4000	0.200	0.189	94.5
S4	1.8426	0.2590	14.1000	0.169	0.175	103.4
S5	1.4692	0.2110	14.3000	0.132	0.149	112.7
Average %recovery 101.0 ± 7.3						
Day 2						
Clay	1.4756	0.0320	2.2000	–	–	–
S1	1.4654	0.2320	15.8000	0.132	0.139	104.9
S2	1.4943	0.2480	16.6000	0.135	0.133	98.5
S3	1.4423	0.2360	16.4000	0.130	0.131	100.4
S4	1.4645	0.2110	14.4000	0.132	0.137	103.7
S5	1.4751	0.2260	15.3000	0.133	0.145	108.9
Average %recovery 103.3 ± 4.0						

Fabric was extracted in THF. Extract solution was further diluted by acetonitrile.

[a] Theoretically, DBDPE represents 9%wt of the whole formulation.

the solvent; in fact we did not monitor any undesirable peaks due to the presence of other ingredients, which indicates that our extraction procedure is efficient and that the remaining components are being eliminated in the clean-up step (filtration step). These facts prove 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.

For the precision study samples containing 9% of DBDPE were analyzed according to the proposed procedure. The "within-day" precision or repeatability (as R.S.D.) is within 4–8.2%. The between day precision or reproducibility was averaged to 7.3% (five randomized determinations over 1 month using the same materials, apparatus and stock reagent solutions). In order to assess the absence of systematic errors, the proposed method was compared with another independent method [18] 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 those obtained by the independent method as x-values, the resulting straight line is $y = (0.2 \pm 0.1) + (0.98 \pm 0.04)x$. The corresponding Student's t tests on slope and intercept indicate, with a significance level of 5%, that there are not significant differences in the results obtained from either of the two methods, i.e., the proposed method is suitably validated. Different methods were proposed for determination of DBDE. Eljarrat et al. [23] proposed a method based on selective pressurized liquid extraction (SPLE) followed by gas chromatography-negative ion chemical ionization-mass spectrometry (GC–NCI-MS) with detection limit of 2 pg, however, that method needs a complicated extraction method. Unlike this, we consider a simple and direct method for determination of DBDE in backcoated textile with a simple mobile phase.

Table 3
Summary of the results

Parameter	
Regression parameter	$y = 388989 + (63265)x$ (R.S.D. = 0.998)
Retention time (min)	4.5 min
Calibration range	0.3–300.0 μg/mL
Limit of detection	0.1 μg/mL
Recovery range (spiked sample)	96.2–104.5%
Recovery range (sample)	101.0–103.3%

4. Conclusion

In conclusion, the proposed method for the determination of DBDPE 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 identify and analyze the DBDPE with a retention time less than 5 min. The obtained results from this research are significant.

The obtained linear range is 0.3–300.0 μg/mL with a detection limit of 0.1 μg/mL, the recovery range of the spiked sample is 96.2–104.5%, and finally the recovery range for the sample is 101.0–103.3%.

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