ANALYSIS OF DECABROMODIPHENYL ETHER IN TEXTILES TREATED BY FLAME RETARDANTS (FRs)

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Abstract

Brominated flame retardants(BFRs) have been widely used as additive or reactive chemical in polymers and textiles. An analytical methods for polybrominated diphenyl ethers (PBDEs) in textile samples using gas chromatography/mass spectrometry (GC/MS) and thermal desorption (TD)-GC/MS were described. Decabromodiphenyl ether (deca-BDE) in textiles was extracted using ultrasonification method with n-hexane/ methylene chloride (1:1, v/v) for GC/MS analysis. For purification, the absorbent of silica was applied to retain the impurities. Analysis of deca-BDE with TD-GC/MS, which is not required for extraction and cleanup.

In the monitoring of deca-BDE in textiles, TD-GC/MS using the pyrolysis system is effective. However, the determination of low concentration of deca-BDE in textiles by GC/MS analysis is appropriate

1. Introduction

Flame retardants (FRs) are incorporated into potentially flammable materials, such as plastics, rubbers and textiles, to slow down and/or inhibit the initial phase of a developing fire. Thus, FRs perform an important service in our modern society by reducing the number of fires and limiting the consequences of fires that do develop. Common applications of FR chemicals include the plastic housings of electronic appliances and in printed circuit boards as well as in upholstery and construction materials[1, 2] .

New fire retarding compounds were developed, including inorganic compounds as well as organohalogen chemicals, organophosphate esters and less common nitrogen containing compounds [3, 4].

Most present-day halogenated flame retardants are used in the area of electronics in the manufacturing of circuit boards, casings for home and office electronics, including mobile phone equipment. A smaller proportion of world production of flame retardants goes to the textile and paper industries.

Coated textile materials are common applications for protection against flame and are based on the synergy between antimony and bromine, usually deca-BDE.

Over the last 10-15 years, there have been indications of increased environmental and human levels of these compounds, although the levels are still lower than those for PCBs and DDT.

The PBDEs have been reported as pollutants in various types of environmental samples, like fish[5-7] , sewage sludge[8] and milk [9], but few data in textiles have been published.

In this study, we concentrated our effort on dissolving and developing analytical methods for brominated flame retardants[1, 2].

Materials and Methods

Reagents

Methylene chloride and hexane, residue analysis grade, were purchased from J. T. Baker (Phillipsburg, NJ, USA). Silica gel (100~200 mesh, Sigma Chemical Co.) and anhydrous sodium sulfate reagent grade (Aldrich) were rinsed and then activated.

Samples and Analytical condition

1) Analysis of deca-BDE in textiles

Samples were four kinds of interior materials in car which was used from ten years ago and three kinds of interior foam in car and three kinds of curtains were treated flame retardants recently. Samples were extracted using ultrasonification (SH-3600) method with 25ml of n-hexane/ methylene chloride (1:1, v/v). Interfering materials in the extract were removed on 5g of silica gel column and the elution containing deca-BDE with 100

ml of n-hexane was collected.

2) Comparison of analytical methods

Sample materials were three kinds of curtains which were treated flame retardants.

Comparison of analytical methods for deca-BDE determination in textiles was performed with GC/MS and TD-GC/MS.

Apparantus

1) GC/MS measurements

GC–MS analysis was performed with an Agilent 6890 Plus (Palo Alto, CA, USA) gas chromatograph equipped with an automatic split–splitless injector, and an inert mass spectrometric detector (MSD) Agilent 5973N, which is equipped with an inert ion source. A capillary GC column 30m· 0.25 ㎜, coated with a DB-5 MS stationary phase (film thickness 0.25 ㎛) was used. Samples were injected in splitless mode at an injector temperature of 290℃ and at an initial column temperature of 100℃ after 1 min, the temperature was ramped at 20℃/min to 300℃. The latter temperature was held for 70 min.

2) Thermal desorption (TD)-GC/MS measurements

For a rapid determination of deca-BDE in textiles by TD-GC/MS measurement, a temperature-programmable micro-furnace pyrolyzer ((Frontier Lab, PY-2020iD) was directly coupled with a quadrupole MS (Agilent 5975i). Approximate 100ug of samples was placed in a sample cup and subjected to the pyrolyzer maintained at 350℃. A capillary GC column 30 m · 0.25 ㎜, coated with a DB-5 MS stationary phase (film thickness 0.25 ㎛) was used. Samples were injected in splitless mode at an injector temperature of 300℃ and at an initial column temperature of 100℃ After 3 min, the temperature was ramped at 20℃/min to 300℃. The latter temperature was held for 60 min.

Results and Discussion

In analysis of deca-BDE in textiles (four kinds of interior materials in car, three kinds of interior foam in car and three kinds of curtains) by GC/MS, deca-BDE were not detected .

In comparison of analytical methods, sample analysis performed using GC/MS(a) and TD-GC/MS(b), is shown in Table 1.

The impurities were not shown in total ion chromatogram using GC/MS due to remove them during the cleanup procedure of sample (B', C' and D' three kinds of curtains) treatment.

For validation of ceca-BDE analysis by py-GC/MS method, 2uL of deca-BDE(1000ppm) was spiked in the textile.

In the case of TD-GC/MS using the pyrolysis system, which is not required for extraction and cleanup, several impurities from textiles were detected in total ion chromatogram; however, different retention times in GC could be separated with deca-BDE.

Conclusion

For the monitoring of deca-BDE in textiles, TD-GC/MS using the pyrolysis system which can be confirmed in the presence of deca-BDE in textiles is effective. This method have the advantage of rapid, simplicity, economy and small amount of sample, while conventional GC/MS method is needed a lot of time and high amount of solvent. However, the determination of low concentration of deca-BDE in textiles by GC/MS analysis is appropriate.

Acknowledgements

This work was supported by outstanding researchers program of Korea Research Foundation (2006-KRF-531-C00083).

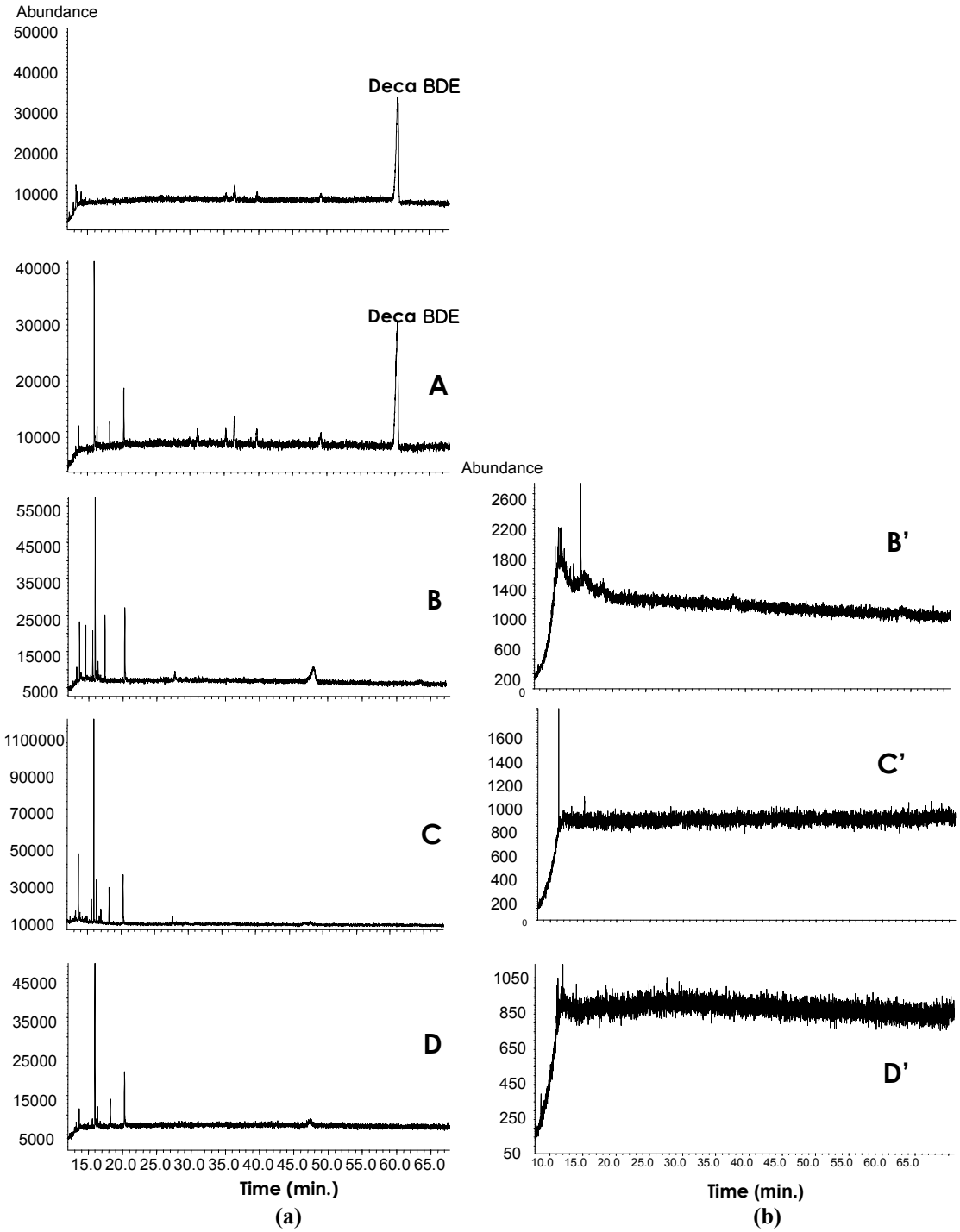

Fig. 1 Chromatogram of deca-BDE in textiles.
(a) TD-GC/MS (b) GC/MS
A: textile spiked deca-BDE STD. B, C, D: three kinds of curtains
B', C', D': three kinds of curtains

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