

## Optimization of Solvent for the Determination of Polybrominated Diphenyl Ethers in High-Impact Polystyrene by GC/ECD

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Received November 17, 2011, Accepted July 16, 2012

**Key Words :** Flame retardants, High impact polystyrene, Extraction efficiency, Certified reference material (CRM), Solubility parameter

Polybrominated diphenyl ethers (PBDEs) are common flame retardants that are used in a wide variety of products such as computer casing and carpet.<sup>1</sup> These chemicals accumulate in both the environment and the human body.<sup>2</sup> Recent findings indicate that exposure to low concentrations of these chemicals may damage the nervous and reproductive systems. Recently, the European Union banned PBDE compounds through the European Directive on Waste Electrical and Electronic Equipment (WEEE) and the European Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS).<sup>3,4</sup> These laws state that products should not contain PBDEs in amounts above the limit of regulation and that products containing PBDEs should be recycled.

High impact polystyrene (HIPS) is an important material in housings and various parts of electronic devices.<sup>5</sup> In order to manage WEEE- and RoHS-related regulation of electronic waste, it is important to develop a reliable analytical method for PBDEs in plastics, including optimization of extraction.<sup>6</sup> Recently, PBDEs were extracted from solid environmental samples by soxhlet extraction, ultrasonic extraction, and accelerated solvent extraction; the typical solvents used are toluene, dichloromethane, and combinations of hexane and acetone, dichloromethane and hexane, and *n*-propanol and hexane.<sup>2</sup> To extract PBDEs from polymers, similar techniques have been used, together with organic solvents such as methanol, *n*-propanol,<sup>1</sup> toluene,<sup>7,8</sup> isopropanol,<sup>9</sup> *iso*-octane,<sup>10</sup> and a combination of hexane and acetone,<sup>11</sup> toluene and tetrahydrofuran (THF)<sup>12</sup> or toluene and *n*-propanol.<sup>7</sup> However, only Altwaiq *et al.* focused on examining the extraction efficiencies of deca-BDE from plastic matrices.<sup>7</sup> The yield of an extraction is depend on several factors, including the interactions among analytes, solvents, and matrix in the extraction system. Our current knowledge of the optimum conditions for extraction is incomplete. More study is required to select efficient solvents to extract PBDEs from important matrices such as HIPS.

To address these issues, we performed an optimization study to determine the solvent that would maximize extraction of PBDEs from HIPS resin for chromatographic

analysis. We prepared plastic samples, analyzed the sample extracts by GC/ECD, and examined the efficiency of various organic solvents for the extraction of PBDEs from the HIPS. Analytical method was verified using a certified reference material (CRM).

### Experimental Section

**Chemicals and Standard Materials.** Octa-PBDE technical mixture (octa bromo diphenyl oxide mix, FR-1208) was product of the Dead Sea Bromine Co. (Beer Sheva, Israel). PCB 153 (ChemService, West Chester, PA, USA) was used as an internal standard. PBDE standard solutions (BDE 190, 196, 197, 198, 204, 207, and 208) were purchased from AccuStandard (New Haven, CT, USA). The HIPS base material was product of the BASF Company Ltd. Korea (Polystyrol 476L, Pellet, Seoul, Republic of Korea), and calcium stearate was purchased from the Shin Won Chemical Co. Ltd. (HI-TECA, Siheung, Republic of Korea). Organic solvents (methoxy ethanol, acetone, hexane, toluene, tetrahydrofuran (THF), 1-propanol, and dichloromethane) were purchased from Burdick & Jackson (Muskegon, MI, USA).

**Instruments.** A Hewlett-Packard GC (HP-6890, Palo Alto, CA, USA) and DB-5MS (crosslinked 5% phenyl methyl silicone, 30 m × 320 μm × 0.25 μm) was used. Helium was used as a carrier gas at a flow-rate of 2 mL/min. In the on-column mode, 1 μL of sample was injected at 200 °C. An ECD detector was used at 250 °C, and for a makeup flow, nitrogen gas was used at 60 mL/min. Oven temperature was programmed as follows; The initial temperature of 90 °C was maintained for 5 min and then increased at a rate of 10 °C/min to 320 °C and maintained for 18 min. A cryogenic grinding mill (SamplePrep 6750, SPEX, Middlesex, HA7 IBQ, UK) was used to grind the plastic samples.

**Sample Preparation.** To prepare a master batch sample, 1 mm sized preground HIPS (Polystyrol 476L), calcium stearate, and the octa-PBDE technical mixture were premixed in a tumbler mixer at room temperature for 20 min and then extruded at 190 °C. The HIPS sample was prepared by extrusion of the mixture of master batch sample and additional

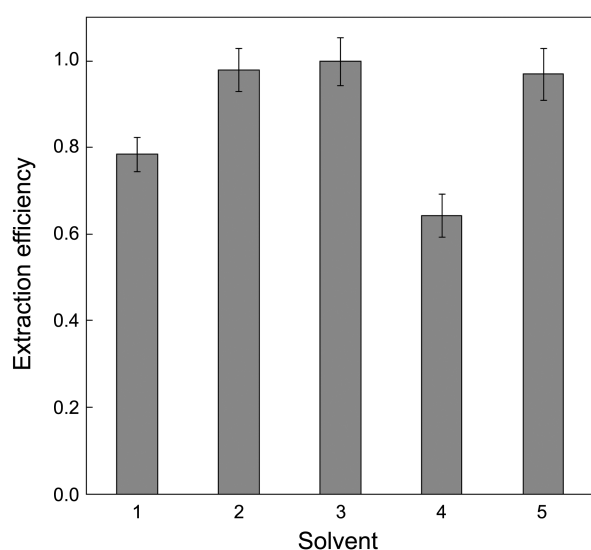
HIPS (Polystyrol 476L) at 190 °C.

**Extraction and Clean-Up.** Each sample was ground to a size of 0.1-0.3 mm under cooling with liquid nitrogen. Ground sample (0.25 g) was weighed in 50-mL centrifuge tubes (polypropylene, disposable), and PCB-153 solution was added as an internal standard. The sample was dissolved using 12 mL of an appropriate solvent by ultrasonication for 15 min and shaking for 5 min. After dissolution, 15 mL methanol was added into the sample solution to precipitate the HIPS and then passed through a disposable syringe filter. Each filtrate was collected in a new 50 mL centrifuge tube and evaporated until dry at 40 °C. The residue was then reconstituted with 20 mL toluene.

### Results and Discussion

Because a HIPS sample was dissolved (completely or partly) in all the solvents, it was extracted by dissolution with a solvent and precipitation with methanol. Figure 1 represents the efficiencies of various solvents for extracting PBDEs from HIPS. We selected these solvents because they are known as adequate solvents for PBDEs in various matrices.<sup>2,5,7-9,11</sup> The extraction efficiency of each solvent is presented as the normalized total peak area of PBDEs based on the highest total peak area (see Fig. 1). Toluene, the combination of toluene and THF (1:1), and dichloromethane yielded higher extraction efficiencies. The other solvents, such as acetone/*n*-hexane (1:1), and toluene/*n*-propanol (1:1) yielded approximately 20-25% lower extraction efficiencies than toluene, toluene/THF (1:1) and dichloromethane.

These results can be explained by the solubility parameters of the compounds. The solubility parameter was used to predict the physicochemical properties such as solubility of a material. It is the sum of the forces (van der Waals



**Figure 1.** Extraction efficiencies of various organic solvents for PBDEs in HIPS samples. 1, acetone/hexane (1:1); 2, toluene; 3, toluene/THF (1:1); 4, toluene/1-propanol (1:1); 5, dichloromethane. The extraction efficiency of each solvent is normalized based on the result of toluene/THF.

interactions, covalent bonds, hydrogen bonds and ionic bonds) that hold the material intact. The total force of the various interactions can be divided into partial solubility parameters, *i.e.*, dispersion ( $\delta_d$ ), polar ( $\delta_p$ ) and hydrogen bonding ( $\delta_h$ ). The partial solubility parameters can be calculated using the group contribution methods of Hoftizer and Van Krevelen's method and the total solubility parameter ( $\delta_t$ ), also called the three-dimensional solubility parameter, of a compound can be calculated as follows.<sup>13</sup>

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$$

In addition, the difference of the solubility parameters ( $\Delta\delta$ ) can be used to predict the mutual solubility between solute and solvent and can be calculated as follows (refers to page 219 of the reference "13").

$$\Delta\delta = [(\delta_{d,S1} - \delta_{d,S2})^2 + (\delta_{p,S1} - \delta_{p,S2})^2 + (\delta_{h,S1} - \delta_{h,S2})^2]^{0.5}$$

where S1 and S2 are corresponding to partial solubility parameter of each compounds (*i.e.* solvent-solute). In general, a solute tends to be well dissolved in a solvent when the solubility parameter components of solute and solvent have similar values (*i.e.* when  $\Delta\delta$  have small value)<sup>13</sup>

Table 1 lists the experimental solubility parameter and its components of several solvents, mixtures and polystyrene in order of increasing polarity.<sup>14</sup> We calculated the solubility

**Table 1.** Solubility parameter components of several solvents and polystyrene<sup>14</sup>

| Solvents or polymer      | $\delta_t$ | $\delta_d$ | $\delta_p$ | $\delta_h$ |
|--------------------------|------------|------------|------------|------------|
| Hexane                   | 14.9       | 14.9       | 0.0        | 0.0        |
| Acetone/Hexane (1:1)     | 16.4       | 15.2       | 5.2        | 3.5        |
| Toluene                  | 18.2       | 18.0       | 1.4        | 2.0        |
| Toluene/THF (1:1)        | 18.4       | 17.4       | 3.6        | 5.0        |
| Polystyrene              | 19.1       | 19.02      | 1.1        | 0.0        |
| THF                      | 19.5       | 16.8       | 5.7        | 8.0        |
| Acetone                  | 19.9       | 15.5       | 10.4       | 7.0        |
| Toluene/1-Propanol (1:1) | 20.0       | 17.0       | 4.1        | 9.7        |
| Dichloromethane          | 20.2       | 18.2       | 6.3        | 6.1        |
| 1-Propanol               | 24.6       | 16.0       | 6.8        | 17.4       |
| Methanol                 | 29.6       | 15.1       | 12.3       | 22.3       |
| Water                    | 48.0       | 12.2       | 22.8       | 40.4       |

Unit: MPa<sup>0.5</sup> or (J/cm<sup>3</sup>)<sup>0.5</sup>, solubility parameter  $\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$  where  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  represent dispersion force, polar and hydrogen bonding components of the solubility parameter respectively.

**Table 2.** Solubility parameter components for several selected congeners of PBDEs obtained by Hoftyer-Van Krevelen method

| PBDE Congeners | $\delta_t^a$ | $\delta_d^a$ | $\delta_p^a$ | $\delta_h^a$ | $V^b$ |
|----------------|--------------|--------------|--------------|--------------|-------|
| Hexa           | 28.3         | 27.9         | 2.02         | 3.76         | 212.6 |
| Hepta          | 29.3         | 29.0         | 1.92         | 3.66         | 223.6 |
| Octa           | 30.3         | 30.0         | 1.83         | 3.58         | 234.6 |
| Nona           | 31.2         | 30.9         | 1.75         | 3.49         | 245.6 |
| Deca           | 31.9         | 31.7         | 1.67         | 3.42         | 256.6 |
| Average        | 30.2         | 29.9         | 1.83         | 3.58         | 234.6 |

$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$ , <sup>a</sup>unit: MPa<sup>0.5</sup>, <sup>b</sup>molar volume, cm<sup>3</sup>/mol

**Table 3.** Solubility parameter differences of PBDEs/solvent and Polystyrene/solvent systems

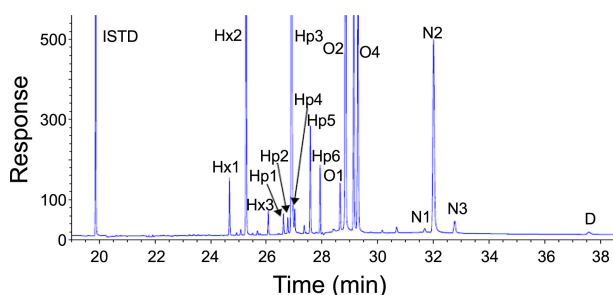
| Solvent                  | $\Delta\delta_{\text{PBDEs-solvent}}^a$ | $\Delta\delta_{\text{polystyrene-solvent}}$ |
|--------------------------|---|---|
| Acetone/Hexane (1:1)     | 15.1                                    | 6.6   |
| Toluene                  | 12.0                                    | 2.3   |
| Toluene/THF (1:1)        | 12.7                                    | 5.8   |
| Toluene/1-Propanol (1:1) | 14.5                                    | 10.4  |
| Dichloromethane          | 12.8                                    | 8.1   |

Unit:  $\text{MPa}^{0.5}$ , Solubility parameter difference  $\Delta\delta = [(\delta_{d,S1} - \delta_{d,S2})^2 + (\delta_{p,S1} - \delta_{p,S2})^2 + (\delta_{h,S1} - \delta_{h,S2})^2]^{0.5}$ . Refers to page 219 of the reference "13".  
<sup>a</sup>Average solubility parameter from hexa to deca-PBDE congeners was used to calculate " $\Delta\delta_{\text{Solvent-PBDEs}}$ ".

parameter components of PBDEs by Hoftizer and Van Krevelen's method,<sup>13</sup> by adding the contributions from all functional groups (see Table 2) because the experimental data of PBDEs is not reported in literature. Table 3 lists the solubility parameter difference for PBDEs/solvent ( $\Delta\delta_{\text{PBDEs-solvent}}$ ) and polystyrene/solvent systems ( $\Delta\delta_{\text{polystyrene-solvent}}$ ).<sup>13</sup>

Based on the solubility parameter differences, we selected the toluene/THF (1:1) mixtures as an optimum extracting solvent by relative comparison of the solubility parameter differences (see Table 3), which correspondingly shows higher extracting efficiency for PBDEs (see Fig. 1). According to the result of experiment (Fig. 1) and solubility parameter difference (Table 3), dichloromethane also can be used as an optimal extraction solvent in this study but it was not selected because it was volatile and carcinogenic. On the other hand, toluene shows the lowest solubility parameter difference with PBDEs, it also shows the lowest values with polystyrene (see Table 3) which means it can similarly dissolve polystyrene. By this reason, polystyrene can be remained in the final sample solution partly and can reduce life of the column. Therefore, it was not selected as an optimal extraction solvent.

To verify the extraction and GC/ECD method, KRIS CRM (113-03-001, high impact polystyrene) was analyzed. For this experiment, toluene/THF (1:1) was selected as the optimal extraction solvent for PBDEs in HIPS and ten CRM sample were independently prepared and analyzed by GC/ECD. As presented in Figure 2, the GC/ECD chromatogram of a sample prepared from the CRM shows the peak of each PBDEs and internal standard are separated adequately. In Table 4, the results of this experiment are presented and

**Figure 2.** GC/ECD Chromatogram of the HIPS CRM "KRIS 113-03-001" (regarding identity of each peak, refers to Table 4).**Table 4.** Measurement results and certified values of PBDEs in KRIS CRM

| Congener group | Peak code <sup>a</sup> | BDE No <sup>b</sup> | Results <sup>c</sup> mg/kg | Calibrants <sup>d</sup> | Certified value <sup>e</sup> mg/kg |
|----------------|------------------------|---------------------|----------------------------|-------------------------|------------------------------------|
| Hexa-BDE       | Hx1                    | 154                 | 10 ± 1                     | BDE-154                 | 11.4 ± 0.8                         |
|                | Hx2                    | 153                 | 79 ± 5                     | BDE-154                 | -                                  |
|                | Hx3                    | -                   | 4.0 ± 0.4                  | BDE-154                 | -                                  |
| Hepta-BDE      | Hp1                    | -                   | 4.0 ± 0.3                  | BDE-183                 | -                                  |
|                | Hp2                    | -                   | 3.0 ± 0.2                  | BDE-183                 | -                                  |
|                | Hp3                    | 183                 | 440 ± 20                   | BDE-183                 | 456 ± 24                           |
|                | Hp4                    | -                   | 6 ± 1                      | BDE-183                 | -                                  |
|                | Hp5                    | -                   | 22 ± 2                     | BDE-183                 | -                                  |
|                | Hp6                    | 190                 | 14 ± 1                     | BDE-183                 | -                                  |
| Octa-BDE       | O1                     | -                   | 13 ± 1                     | BDE-203                 | -                                  |
|                | O2                     | 197, 204            | 246 ± 13                   | BDE-203                 | -                                  |
|                | O3                     | 203, 198            | 72 ± 4                     | BDE-203                 | 61 <sup>f</sup>                    |
|                | O4                     | 196                 | 95 ± 5                     | BDE-203                 | -                                  |
| Nona-BDE       | N1                     | 208                 | 4.0 ± 0.3                  | BDE-206                 | -                                  |
|                | N2                     | 207                 | 227 ± 14                   | BDE-206                 | -                                  |
|                | N3                     | 206                 | 16 ± 1                     | BDE-206                 | 17.3 ± 2.6                         |
| Deca-BDE       | D                      | 209                 | 18 ± 2                     | BDE-209                 | 20.0 ± 2.4                         |
| Total          | -                      | -                   | 1272 ± 58                  | -                       | -                                  |

<sup>a</sup>Refers to GC-ECD chromatogram. <sup>b</sup>PBDE congeners are numbered according to IUPAC scheme. <sup>c</sup>Ten independent samples were measured by GC/ECD. <sup>d</sup>The individual calibrants of PBDEs were prepared by gravimetry using high purity materials. <sup>e</sup>For certification, gas chromatography and isotope dilution mass spectrometry was used. <sup>f</sup>information value

compared with the certified value of the KRIS CRM. In this experiment, to determine each PBDE, the individual standard solutions of PBDE prepared by gravimetry using high purity neat compound were used. At present, the high purity compounds are not available for all isomers of PBDEs. Therefore, to determine some PBDEs, their high purity standard compounds are not available, the representative high purity standard in the same congener group was used. For example, to determine BDE-153 the standard solution of BDE-154 prepared by gravimetrically using high purity BDE-154 was used. As presented in Table 2, the analytical results of CRM by GC/ECD were comparable with the certified values of CRM.

## Conclusions

We examined the efficiencies of five combinations of organic solvents for extracting PBDEs in HIPS samples using shaking and ultrasonic extraction. Extraction with toluene/THF (1:1), toluene or dichloromethane yielded high extraction efficiencies for HIPS samples. The results demonstrate that the solvent used to extract PBDEs should be selected based on the properties of the plastic, and a suitable solvent can be selected by considering the solubility parameter of the target compound, plastic matrix and solvents. Under the optimized solvent condition, entire method was

validated using KRISS CRM (113-03-001).

**Acknowledgments.** This work was supported by the Korea Research Institute of Standard and Science (KRISS) under the project “Establishing Measurement Standards for Food and Environmental Analysis”, grant 12011026.

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