

## ANALYTICAL METHOD OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN ELECTRICAL PLASTIC WASTE

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### 1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one of the flame retardant compounds that are widely used in electrical and electronic (E&E) plastic applications. The use of flame retardant compounds has significantly reduced fire hazardous over the years. From these materials polybrominated pollutants are easily released into the surrounding environments. Brominated flame retardants (BFRs) containing PBDEs are now acknowledged to be widespread environmental contaminants. EU directives on waste set target for recycling of E&E waste plastics.<sup>1-5</sup>

The test method for determining PBDE in plastics can be divided by soxhlet extraction, dissolution, and dissolution-precipitation according to different polymer materials. Unlike detecting trace levels in environmental samples, separation of analyte from polymer is the most important procedure in case of plastic materials. However, there is no clearly described test method about plastic materials. The aim of this study is to evaluate the development of analytical method of detecting PBDEs. To achieve this purpose, four types of plastic materials from the manufacturing factory and seven plastic wastes were used.<sup>1-6</sup>

### 2. Materials and Methods

#### 2.1 Plastic material

Four plastic waste samples for method optimization were used. These polymer samples obtained from commercial polymer products containing PBDEs. Waste materials were consisted of HIPS (High Impact Polystyrene), PP (Polypropylene), PC (Polycarbonate), and ABS (Acrylonitrile Butadiene Styrene). Actual values of PBDEs in polymer samples were determined by continuous 3<sup>th</sup> iterative test and sum of seven congeners (BDE-47, 49, 66, 99, 100, 153, 154).

#### 2.2 Analysis for PBDEs

Analytical method was established of tri- to heptabrominated diphenyl ethers. In this study, soxhlet extraction and dissolution-precipitation method are used for separating analyte from polymer materials. Only non-soluble materials with selected solvents were extracted by soxhlet extractor and grinded by cooling and milling. In case of dissolution-precipitation method, recommended solvents with polymer materials are applied for dissolving polymer material such as THF (tetrahydrofuran), chloroform, DCM (methylene chloride), toluene and so on. First, approximately 0.5 ~ 1g of plastic powder were dissolved in 10mL of adequate solvent after adding 25 ng <sup>13</sup>C<sub>12</sub> labeled 3,3',4,4'-tetrabromodiphenyl ether (TetraBDE) as internal standard (Cambridge Isotope Laboratories (CIL)) for one or two days at room temperature. Then, n-hexane was gradually added for the solvent exchange by a gentle nitrogen stream, and polymer constituents and additives were precipitated, simultaneously. The flowchart of cleanup procedure is showed in Fig. 1.

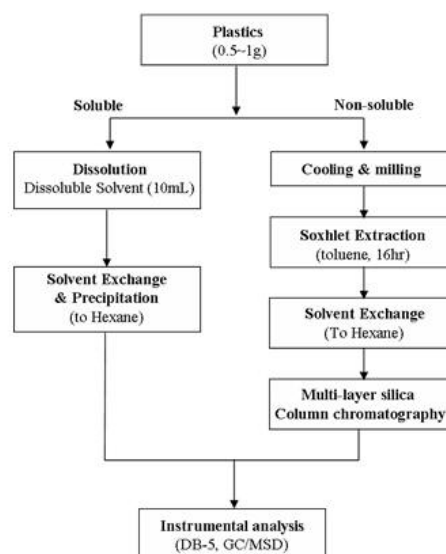


Fig. 1. Clean-up procedure of plastic samples

### 3. Results and Discussion

#### 3.1 Method optimization

##### 3.1.1 Extraction

For analytical method optimization, several solvents were applied to extraction efficiency and it has been found that the DCM, Toluene, THF, and mixtures acetone/hexane (1:4, v/v) gave similar concentrations, while the use of the ethyl ether acetone/ethyl ether (1:4, v/v), acetone/hexane (1:1, v/v), DCM/hexane (1:1, v/v) resulted in significantly lower values (Fig. 2). Therefore, the final optimized analytical method for extraction solvents of PBDEs were selected the Toluene, DCM, THF and acetone-hexane mixture.

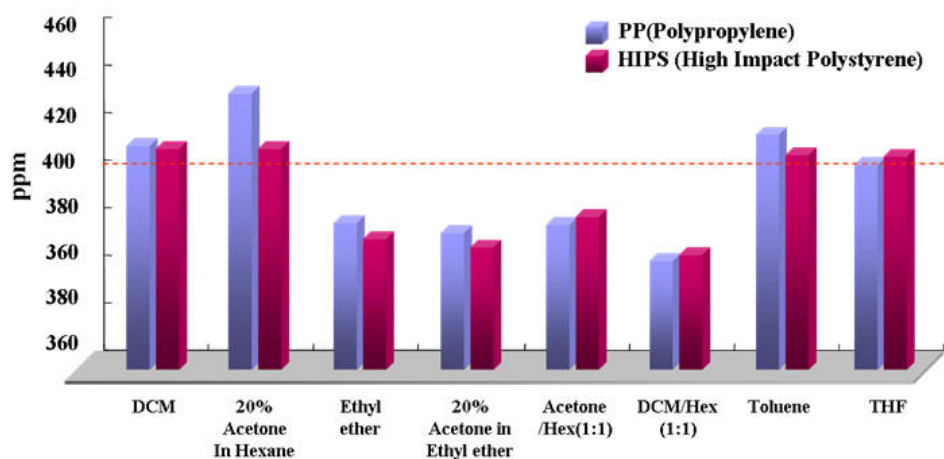


Fig. 2. Comparison of the effect of solvent on the soxhlet extraction from PP and HIPS polymer material

##### 3.1.2 dissolution-precipitation

Dissolved polymer in selecting solvents is precipitated by solvent exchange with a non-polar solvent such as hexane. This extraction was subjected to instrumental analysis without extra clean-up procedure because almost polymer material is removed by precipitation. Several solvents were tested to study effects of differences of dissolving solvents (Fig. 3).

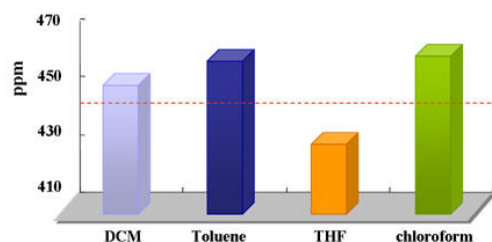


Fig. 3. Comparison of the effect of solvent on the dissolution-precipitation from PC polymer material

##### 3.1.3 Column chromatography clean-up

Sample extract clean-up was carried out by packed silica column chromatography. The use of multi-layer silica column in combination with basic and acidified silica for clean-up resulted in cleaner extracts than silica or Florisil. To optimize the volume of column elution, fraction test of multilayer silica and Florisil column were studied. These results are shown in Fig. 4. The elution amount of multilayer silica and Florisil column were determined with 300 mL and 70 mL of hexane, respectively. In this study, the collected fraction fractions extended from 300 mL to 350 mL of elutes for PBDEs in multilayer silica column cleanup. The collected fractions were evaporated to incipient dryness by gentle stream nitrogen at 40 °C.

##### 3.1.3 Gas chromatogram-mass spectrometry

The oven temperature program was from 100 (held for 2 min) to 330 °C (held for 10 min) at 10 °C /min. The operating conditions were as follows: an ion source temperature of 300 °C, ionization mode EI at 70 eV, transfer line temperature of 300 °C, H<sub>2</sub> at 1 mL/min constant flow, 2μL of injection. Confirmation criteria for the detection and quantification of PBDEs should include the following: (a) retention time for all m/z monitored for a given analyte should maximize simultaneously ±1 s, with signal-to-noise ratio (S/N) > 3 and (b) the ratio

between the two monitored ions should be within 15% of the theoretical value.

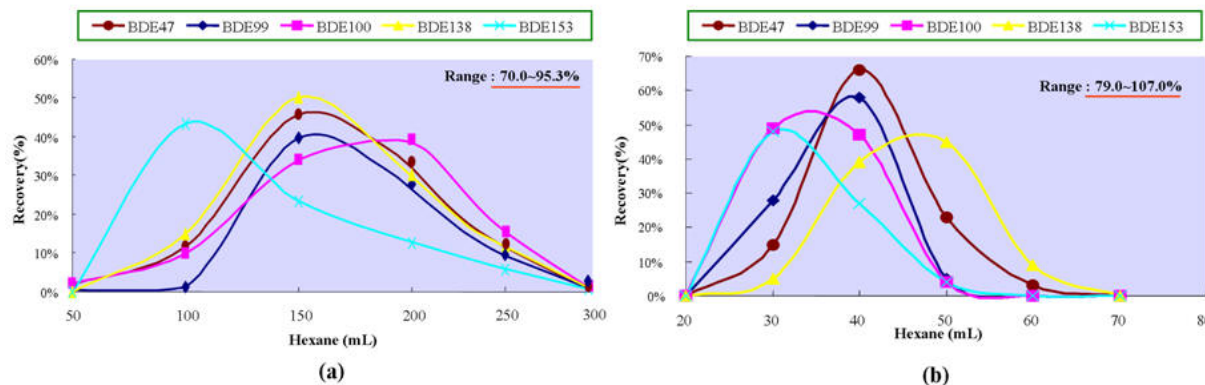


Fig. 4. Results of fraction test at (a) multi layer silica and (b) Florisil column.

### 3.2 Examination of the applicability in plastic waste

#### 3.2.1 Reference material analysis

Four kinds of plastic material, which known concentration, were analyzed to make sure the proposed method. These materials were obtained from electrical equipment analytical labs in large scale company to prepare the control of RoHS regulation. The recoveries and the repeatability were similar to those reported by other laboratory analytical results. The recovery ranges showed from 96% to 102%.

#### 3.2.2 Concentration of PBDEs in waste plastics

To examine the applicability of the proposed method, seven plastic wastes samples collected in different polymer materials. The plastic waste samples were analyzed as shown in Fig. 5. The analytical results of 8 individual congeners (BDE-47, 49, 66, 99, 100, 153, 154, and 209) in the waste plastics are shown in Fig. 6. The most predominant congener is BDE 47 and followed BDE 99 which is similar to the sediment cores as shown in Fig. 6.

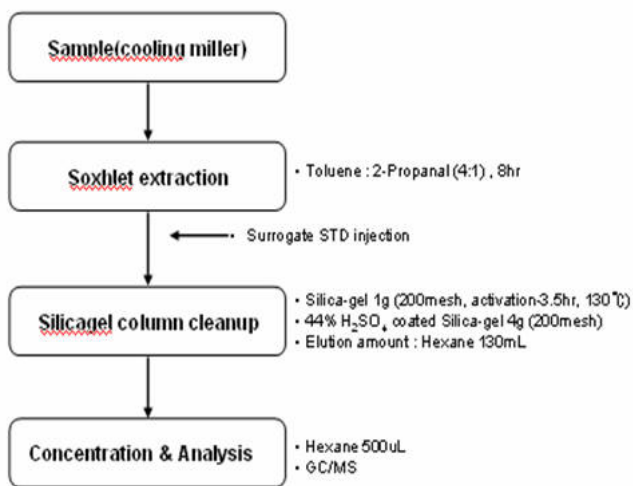


Fig.5. Analytical method of plastic samples

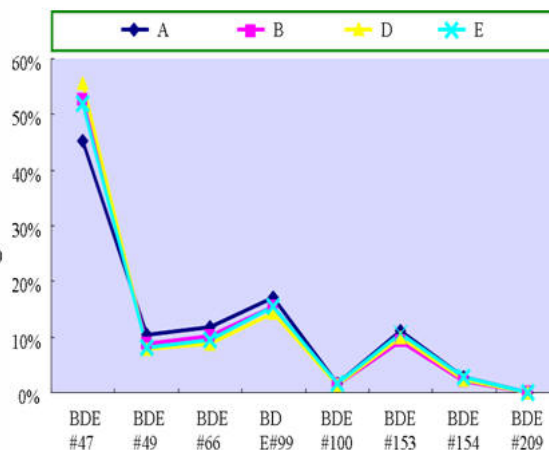


Fig. 6. Profiles of PBDEs in waste plastics

Range of PBDE in waste plastics was detected from N.D. to 1028 ppm. The profile of PBDEs in these samples was similar to each other independently of their concentration (Fig. 7). The fig. 8 showed the

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chromatogram of one of the plastic waste sample. As shown in this figure, the selected PBDEs congeners did not detected in the sample.

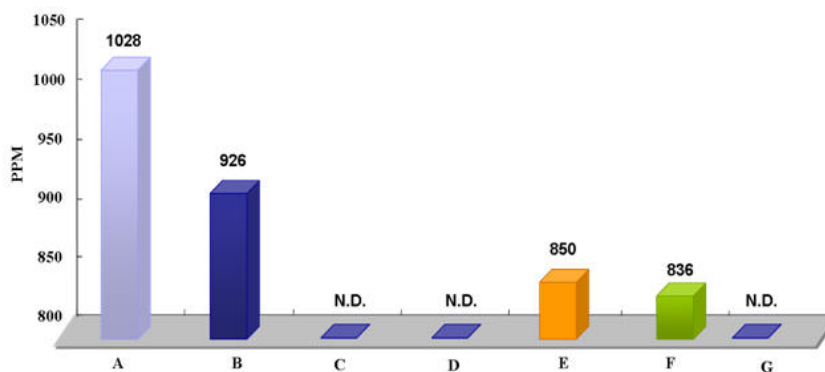


Fig. 7. Concentration of PBDEs in waste plastics

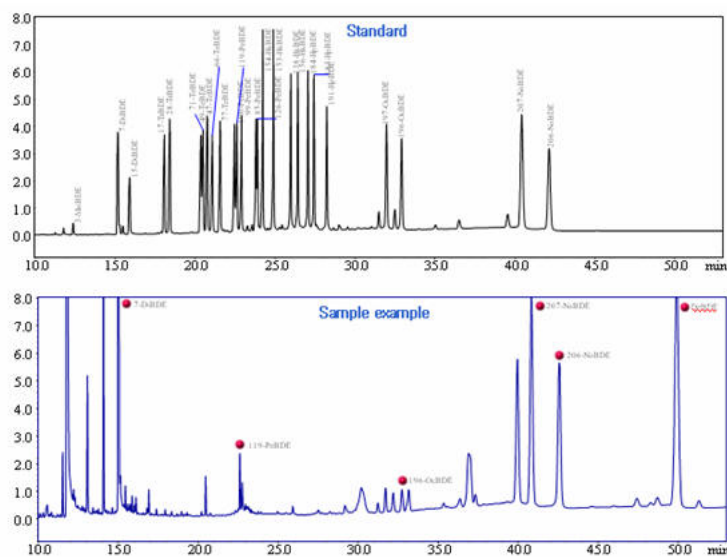


Fig. 8. Chromatogram of plastic waste samples

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