Isotope Dilution Analysis of Polybrominated-Diphenyl Ethers and -Biphenyls fom Waste Electric and Electronic Equipments (WEEE) with HRGC-HRMS

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Introduction

Waste Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC)**[1]** propose hose involved in manufacturing, selling, distributing, recycling or treating electrical and electronic equipment to reduce the waste arising from electrical and electronic equipment (EEE); and improve the environmental performance of all those involved in the life cycle. These strict regulations enforced based on the restriction of the use of certain EEE containing lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs) to the environment Directive (2002/95/EC)**[2]** by Release of Hazardous Substances (RoHS). After WEEE and RoHS enforcement, importance of analyzing WEEE chemicals deserves immediate attention**[3]**. Consequently in this study, PBDEs and PBBs new analytical methodology were developed; standard operating procedure was conducted and briefly discussed.

Materials and Methods

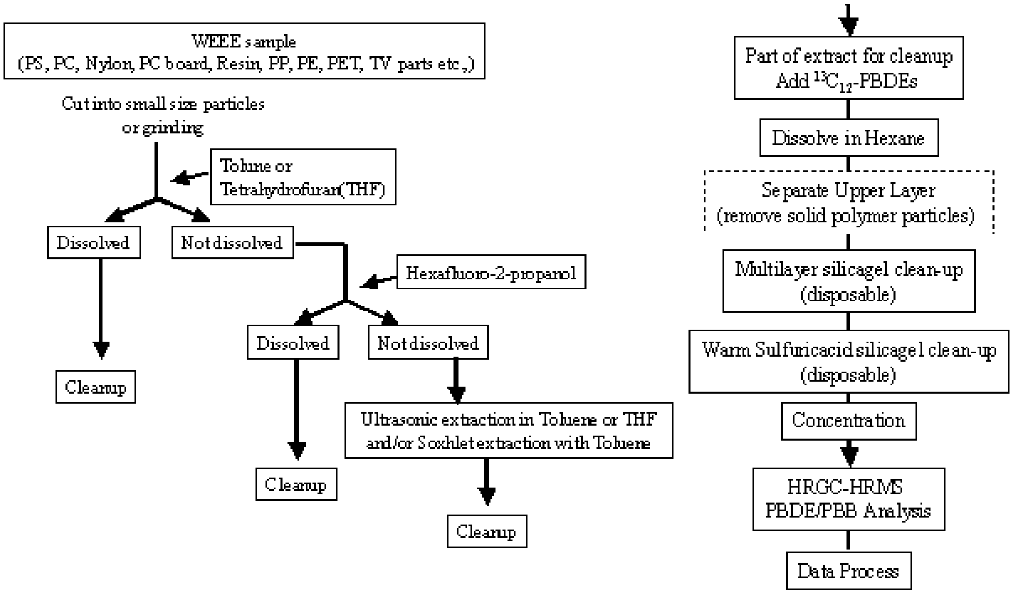

Figure 1. The flow chart shows old and new cleanup method of plastic samples

All analysis was performed under conditions optimizing the prevention of photo light. The cleanup method of plastics has been flow-charted in Figure 1. The identification and quantification of analytes were conducted in HRGC-HRMS after major modifications**[4]** (Table 1). A detailed analysis condition and the monitor ions were shown elsewhere**[4]**.

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Identification and quantification: Identification of all compounds was confirmed, and the concentrations were measured using an external quantification standard possessing known amounts of all target compounds, and recovery and surrogate standard mixtures were used for the analyses. Particularly, $^{13}C_{12}$-labeled PBDE congeners and were commercially available for the quantification which served as internal standards. Whereas, $^{13}C_{12}$-labeled PBB congeners were not commercially available and therefore, $^{13}C_{12}$-labeled PBDE congeners were used for the PBB quantitation. The criteria for peak identification of target compounds for MS were as follows: (1) The S/N ratio was greater than 3. (2) The compounds eluted at the same GC retention time (•}0.05 or 0.1 min) as the standards compounds. (3) The internal standard recoveries were between 50% to 120% (except DeBDE which showed >120%). (4) The isotope ratios of two or three ions monitored for each compound were •}15% of the theoretical value. Quantification was undertaken by the internal standard method relative to a multilevel calibration for all compounds.

Table 1. HRGC-HRMS programming/conditioning for PBDEs and PBBs analysis.

MS	Micromass Autospec Ultima (Waters)
Ionization mode	EI
Ionization Volt.	30-40eV
Trap current	500µA
Accel. Volt.	8kV
Ion source Temp.	300°C
Interface Temp.	300°C
Resolution	M/△M > 10,000 (10% Valley)
GC	HP 6890 Series GC System (HEWLETT PACKARD)
Injector	7683 Series Injector (Agilent)
Auto Sampler	7683 Series Auto Sampler (Agilent)
Column	DB-5MS 30m x 0.25mm i.d. (0.1 µm)
Injector	On-column injector
Injection Volume	2µL
Injector Temp	120°C(0.1 min)-100 °C/min-300°C(15 min)
Column Temp	120°C(1 min)-10 °C/min-300°C(25 min)
He flowrate	1.0 mL/min

Results and Discussion

Methodology Development: The studies on cleanup and analytical methods for plastic samples are rare. In this study, we propose to establish cleanup and analytical methods of PBDE and PBBs from plastic samples by high sensitivity and selectivity method using HRGC-HRMS. Particularly, the method describes the simple analysis of PBDEs and PBBs with rapid pre cleaning method as well as with low cost and low background level by using disposable glassware. Figure 1, shows the removal of un-necessary steps of sample cleanup that we adopted in earlier years.

Standards: Totally, 20 major native PBDE and 22 major native PBB standards were respectively used from MoBDE/MoBBs, DiBDEs/DiBBs, TrBDEs/TrBBs, TeBDEs/TeBBs, PeBDEs/PeBB, HxBDEs/HxBBs, HpBDE, DeBDE/DeBB with five points calibration 0.4 to 130 pg/mL. The labeled MoBDE-3, DiBDE-15, TrBDE-28, TeBDE-47, PeBDE-99, HxBDEs-153/154/139, HpBDE-183 and DeBDE-209 were used for this group. In addition, in second group, native OBDEs, NBDEs were also analyzed separately. The labeled HxBDE-139, OBDE-197 and NBDE-207 used for second group standards.

Grouping: Totally 9 grouping were established according to the selected ion monitoring. MoBDEs to PeBDEs and MoBBs to HxBBs were monitored in two or more parent ion [M]$^+$ group while, HxBDEs to DeBDE and PeBBs to DeBB were monitored in two or more fragment ion [M-2Br]$^+$ group. The detailed grouping of PBDEs and PBBs are illustrated elsewhere[5].

RRF and RSD: The individual isomers/congeners average (n=15) relative response factor (RRF) and relative standard deviation (RSD) for PBDEs and PBBs has been determined in two ion monitoring but their Ion-1 data has been plotted in Table 2. The major PBDE/PBB congeners analyzed were plotted in first row while, internal standard used for the quantification comes in second row followed by mass number (*m/z*) for native and internal standards, RRF and RSD, respectively.

Detection limit: The instrument detection limits (IDL) and instrument detection quantification (IDQ) after 5 injections of isotope dilutions have been summarized in Table 2. The concentrations of the standard for the detection limit quantification were set as 0.42 pg/mL.

Extraction**:** Various plastic samples which include TV parts (product of 1980•fs), personal computer casing, plastic cables, polyethylene (PE), polypropylene (PP), polyethylene terphenyl (PET), polystyrene (PS), resins, nylon, etc., was analyzed in this study. Tetrahydrofuran (THF) and hexafluoro-2-propanol unable to dissolve PE, PP, nylon, PC boards. While, TV cover, PS, resin, TV parts was dissolved in THF and nylon, PET, PS, TV parts was dissolved in hexafluoro-2-propanol. The samples that not dissolved in either solution were subjected in to a THF sonification extraction and further cleanup procedures.

Analytical Results**:** Various PBDE congeners were detected in plastic samples while PBB were not detected (<1 mg/g) in any samples. Personal computer casing contained DiBDE, TrBDE, TeBDE, PeBDE, HxBDE, HpBDE, OBDE, NBDE, DeBDE homologues at concentration (ng/g) of 7, 11, 28, 86, 11,000, 77,000, 44,000, 14,000, 240,000, respectively. Particularly, following congeners are predominantly noticed with the decreasing order (concentration wise) of HpBDE-183, HxBDEs-153, 154, 138, PeBDEs-99, 119, TeBDE-47, PeBDE-100, TeBDEs-49, 66, TrBDEs-28, 17, DiBDEs-7 and 15. Similar results were also reported elsewhere[6]. The methodology blank also contained DiBDE-15, TrBDE-28, TeBDEs-49, 47, PeBDEs-100, 99 and HpBDE-183 at trace levels (0.33-6.5 ng/g). Several other samples showed PBDE concentrations at parts per million orders. Based on this method, PBDEs could be detected in 50 mL of 0.25-g plastic sample that extracted. However, PBBs were not detected (except HxBB) in any of the sample.

Literature Cited

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