

### Quantitative analysis of polybrominated biphenyls (PBBs) in Japanese waste samples

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#### Introduction

Polybrominated biphenyls (PBBs) were produced as flame retardants (FRs) of acrylonitrile butadiene styrene or polyurethane in electronic equipment, plastics, building materials and carpets, under brand names such as FireMaster®BP-6, FF-1 (Michigan Chemical Corp., St. Louis, Mich., USA), Bromkal (Chemische Fabrik Kalk, Cologne, Germany), Adine (Ugine Kuhlmann now Atochem, Paris, France)<sup>2</sup>. Commercial PBBs products are mixtures of various brominated biphenyls (BBs) mainly containing HxBBs, Oc/NoBBs, and DeBB. The most predominant congener in FireMaster®BP-6 is 2,2',4,4',5,5'-HxBB (BB-153). The second predominant congener is 2,2',3,4,4',5,5'-HpBB (BB-180). Accordingly, these two congeners account for about 75% of the mixture. PBBs products in world wide were not explicit but a cumulative volume sold in USA by period of production, from 1970 to 1974, was 5,800,000 kg. An accidental contamination of the food chain in Michigan with PBBs was occurred in 1973. Although PBBs products have been voluntarily controlled since this accident, PBBs have been detected from environmental and biological samples.

In Japan, PBBs have been detected from environmental samples, though PBBs have not been produced in Japan<sup>3</sup>. Especially, BB-153 was mostly contaminated. The reasons of PBBs existed in Japanese environmental samples were explained as follows; (1) from impurities of other brominated FRs produced in Japan, *e.g.* PBDEs, (2) from usage of imported technical PBBs from abroad, and (3) from imported products contained PBBs, *e.g.* industrial and electrical products<sup>3,5</sup>. For grasping the emission and sources of PBBs in Japan, analysis of PBBs in industrial, electrical products and their wastes is important, but the analysis is very difficult and complicated at the point of separation and refinement of PBBs from matrix, *i.e.* plastic and wastes. The analysis method for PBBs has not been established under actual state. Therefore, the emission and sources of PBBs in Japan have not been clear. Until now, Takasuga's report for PBBs analysis in various plastics from waste of electrical and electronic equipment was the only one in Japan, but PBBs were not detected in this report<sup>4</sup>.

In this study, we tried to establish a method for quantitative analysis of PBBs and to understand of PBBs concentration in Japanese waste samples by four kinds of waste sample, (a) incinerable waste, (b) bulky waste, (c) automobile shredder residue (ASR), and (d) office dust. Additionally, two technical PBBs, FireMaster®BP-6 and Dow FR-250, were analyzed at the same time for comparing to the components of homologues and congeners of PBBs with the waste samples. And the relationships between the concentration of PBDEs<sup>6-8</sup> and PBBs were discussed.

#### Materials and Methods

##### Samples.

Four kinds of waste sample analyzed were as follows; (a) incinerable waste; general household garbage which made from kitchen refuse, paper waste, waste cloth, plant waste, small branch, vinyl, plastic, disposable diaper, etc., (b) bulky waste; shredder residue of the bulky waste which made from electronic waste, carpet, bedclothes, furniture, etc., (c) ASR, and (d) office dust; it was caught by sweep in office room which has wooden floor and some electric appliances such as computer and TV.

##### Chemicals.

S-11116-R6 which was mixture of 22 unlabeled PBBs congeners, *i.e.* 2-MoBB (BB-1), 3-MoBB (BB-2), 4-MoBB (BB-3), 2,2'-DiBB (BB-4), 2,4-DiBB (BB-7), 2,5-DiBB (BB-9), 2,6-DiBB (BB-10), 4,4'-DiBB (BB-15), 2,2',5-TrBB (BB-18), 2,3',5-TrBB (BB-26), 2,4,6-TrBB (BB-30), 2,4',5-TrBB (BB-31), 2,2',4,5'-TeBB (BB-49), 2,2',5,5'-TeBB (BB-52), 2,2',5,6'-TeBB (BB-53), 3,3',4,4'-TeBB (BB-77), 3,3',5,5'-TeBB (BB-80),

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2,2',4,5',6-PeBB (BB-103), 2,2',4,4',5,5'-HxBB (BB-153), 2,2',4,4',6,6'-HxBB (BB-155), 3,3',4,4',5,5'-HxBB (BB-169) and 2,2',3,3',4,4',5,5',6,6'-DeBB (BB-209), FireMaster®BP-6 and Dow FR-250 were purchased from Accu Standard Inc. (Connecticut, USA). <sup>13</sup>C-labeled standard of BDE-138 used as cleanup spike was purchased from Wellington Labs. Inc. (Ontario, Canada). All solvents and reagent used for extraction and cleanup were dioxin analysis grade, which were purchased from the Kanto Chemical Co., Inc. (Tokyo, Japan).

### Analytical method.

#### Clean up.

The analysis throughout the extraction and cleanup processes was performed by using amber glassware or by wrapping the glassware in aluminum foil for avoiding the occurring PBBs decomposition by light. Each sample (1g) was extracted by soxhlet extraction with toluene for 16 hours. The extracted solution was concentrated and dissolved in hexane after adding <sup>13</sup>C-labeled internal standard, 100pg/μL BDE-138, as cleanup spike (20μL). After that, it was cleaned up by sulfuric acid treatment, washing with water, and copper treatment. And after that, it was concentrated for cleanup by “the connected multilayer silica gel column” which component from “Column A (anhydrous sodium sulfate, 22% H<sub>2</sub>SO<sub>4</sub>/silica, anhydrous sodium sulfate, Florigil, anhydrous sodium sulfate)”, and “Column B (carbon impregnated silica gel)”. The connected multilayer silica gel column was initially pre-washed with n-hexane (70 ml), and PBBs was eluted with next n-hexane (70 ml) (This elution is called “the elution A”). Moreover, only column B, 25% dichloromethane in n-hexane (15 ml) was passed through for extraction of PBBs. This is “the elution B”. The elution A and B was mixed and concentrated for 10% of fuming sulphuric acid treatment. After that, it was washed by water and concentrated to 100μL for PBBs analysis by HRGC/HRMS. The sample cleanup procedure was shown in Figure 1.

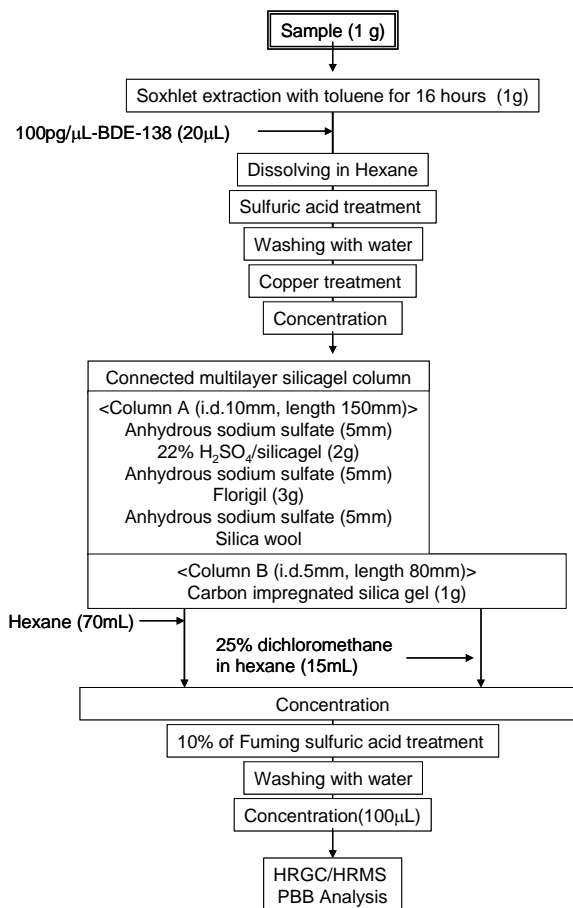


Figure 1 Sample cleanup procedure

#### HRGC/HRMS Analysis.

All cleaned up samples were analyzed by HRGC/HRMS (Agilent HP6890 and Micromass Autospec 3000; resolution >10,000) which equipped ENV5-ms column (SGE; 30 m x 0.25 mm i.d.); the column temperature was programmed from 110°C to 200°C at a rate of 15°C/min, to 260°C at 5°C/min, and finally to 300°C at 10°C/min with a final hold time of 16.5 min. The injection port temperature was 260°C. PBBs were determined by isotope dilution quantification. The measuring condition of HRGC/HRMS and monitoring ions as SIM were shown in Table 1.

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Table 1 Measuring condition of HRGC/HRMS

GC			
column:	ENV-5ms, 30 m x 0.25 mm i.d, 0.1 $\mu$ m		
oven:	110 °C (2 min hold)- 15 °C/min- 200 °C- 5 °C/min- 260 °C- 10 °C/min-300 °C (16.5 min hold)		
carrier gas:	He, 1.0ml/min, Constant flow		
inlet:	Splitless		
inlet temp.:	260 °C		
MS			
ion source temp.:	260 °C		
ion source voltage:	38eV		
MS resolution:	10,000		
monitoring ions:	Homologue	Monitoring ions	
		Quantitative ions	Confirmative ions
	MoBBs	231.98870	233.98670
	DiBBs	311.89720	309.89920
	TrBBs	389.80770	391.80570
	TeBBs	469.71620	467.71820
	PeBBs	547.62660	549.62460
	HxBBs	627.53510	625.53710
	HpBBs	705.44560	707.44360
	OcBBs	785.35410	783.35610
	NoBBs	863.26450	865.26250
	DeBB	943.17300	941.17500

### Identification and Quantification.

Identification of PBBs congeners was as follows; First, the mixed standard solution of 22 PBBs congeners was analyzed by using the same method as the waste samples, and the retention times (R.T.) of 22 congeners were obtained by standardized data within reference to the data<sup>5</sup>. Next, each sample was identified by the R.T. Additionally, FireMaster®BP-6 and Dow FR-250, as the technical PBBs, were analyzed for getting the R.T. of predominant congeners in them as unknown PBBs peak for identification of PBBs in the waste samples. The criteria for peak identification of PBBs congeners by HRGC/HRMS were as follows;

- (i) The S/N ratio was greater than 3.
- (ii) The isotope ratios of two selected ions for monitoring were  $\pm 25\%$  of the theoretical value.
- (iii) The congener in the waste samples was eluted at the same R.T. ( $\pm 0.02$ min) with the standard congeners which contained in S-11116-R6, FireMaster®BP-6 and Dow FR-250.

PBBs congeners were identified by IUPAC numbering systems of PCBs. And, quantification was undertaken by the absolute calibration method with using S-11116-R6 as standard solution.

### Results and Discussion

PBBs were detected from all waste samples. The total concentration of PBBs were 0.27- 0.76 ng/g (Table 2).

Table 2 Concentration of PBBs and PBDEs

	(a)Incinerable waste	(b)Bulky waste	(c)ASR	(d)Office dust
PBBs (ng/g)	0.27	0.76	0.43	0.53
PBDEs (ng/g)	100*	140000 <sup>+</sup>	310000 <sup>#</sup>	1900 <sup>#</sup>
PBBs/PBDEs	$2.7 \times 10^{-3}$	$5.4 \times 10^{-6}$	$1.4 \times 10^{-6}$	$2.8 \times 10^{-4}$

\* Ref.6, <sup>+</sup>Ref.7, and <sup>#</sup>Ref.8

The compositions of homologues of PBBs are shown at Figure 2. The composition of PBBs in office dust (d) was similar with FireMaster®BP-6. The predominant homologue of incinerable waste (a), bulky waste (b), ASR (c), and office dust (d) were HxBBs, PeBBs, HxBBs, and HxBBs, respectively. BB-153 was detected from all samples as the most predominant congeners in 22 congeners which were contained in S-11116-R6. The

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concentrations of BB-153 in incinerable waste (a), bulky waste (b), ASR (c), and office dust (d) were 0.13, 0.20, 0.19 and 0.38 ng/g, respectively. And these compositions to total PBBs concentration were 49, 26, 44, and 72%, respectively. The concentrations of PBDEs in the waste samples whose values were from Ref. 6, 7, and 8 were also shown in Table 2. The ratios of PBBs concentration to PBDEs concentration were  $1.4 \times 10^{-6}$ -  $2.7 \times 10^{-3}$ . The concentrations of PBDEs were much higher than PBBs.

The recovery rate of BDE-138 as cleanup spike incinerable waste (a), bulky waste (b), ASR (c), and office dust (d) were 11, 26, 9.2, and 39%, respectively. The low recovery rate might be caused by several times of fuming sulphuric acid treatment in order to remove the extracted resinoid in the concentrated solution. Further improvement for cleanup is necessary to raise the recovery rate and to analyze more accurately.

In this study, PBBs which had not been produced in Japan were detected in the range of 0.27- 0.76 ng/g from the waste samples. The imported PBBs or products contained with PBBs were suspected as the sources, while the concentrations were over  $10^3$  times lower than those of PBDEs. Detailed investigation is necessary to identify the sources.

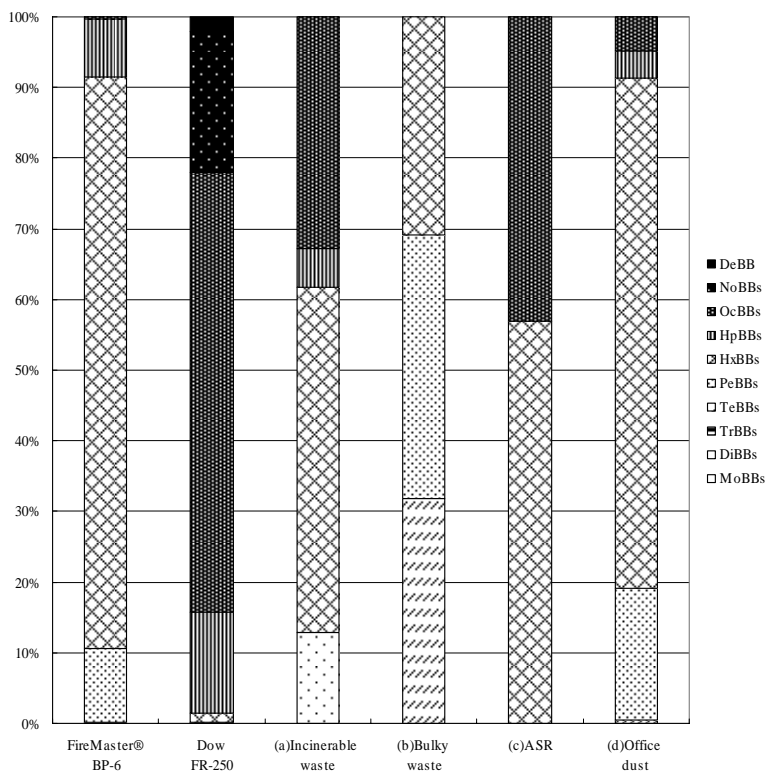


Figure 2 Composition of homologues of PBBs

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