

# DETERMINATION OF PBDD/Fs IN DUST SAMPLE INSIDE TELEVISION SETS IN THE RECYCLING FACTORY

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## Introduction

Polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are toxic chemicals produced unintentionally. They seem to be sourced mainly from brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) which are widely used for electrical appliances as to improve incombustibility<sup>1)2)3)4)</sup>. A part of PBDD/Fs emitted from resin at elevated temperature, in television set can be source of human contamination. Choi et al. reported the presence of tetrabrominated dibenzofurans (TBDFs) in human adipose tissue<sup>5)</sup>. Recent RoHS directory aimed to prevent such contamination.

Television sets manufactured before the regulation of RoHS directory may contain significant amounts of PBDEs and are being passed to recycling factory and waste incineration facility. There is a possibility that workers in these factories are exposed to PBDD/Fs through respiring dust inside television sets. It is for this reason that we started to analyse the dust sample in used television sets to determine a PBDD/Fs levels and congener compositions. In addition, we performed a heating tests using PBDE to understand which PBDD/Fs are produced.

## Materials and Methods

### Dust Samples:

Ten dust samples inside television sets were collected at two recycling factory in Matsuyama-city, Ehime-prefecture, Japan. They were gathered from a printed circuit board, backcover and cathode-tube. Sample details are listed in Table 1. The dust sample was dried in a desiccator for overnight before analysis.

Table.1 Sample number and the related data

Sample number	①	②	③	④	⑤
Maker(company)	A	A	B	C	D
Manufactured year	'83	'86	'87	'93	'97
Sample weight	0.91g	0.52g	0.42g	0.14g	2.02g
Sample number	⑥	⑦	⑧	⑨	⑩
Maker(company)	D	E	F	C	G
Manufactured year	'98	'97, '00 <sup>※1</sup>	'00	'00, '01, '03 <sup>※2</sup>	'01, '03 <sup>※1</sup>
Sample weight	0.20g	0.17g	0.49g	0.24g	0.18g

※1・・・Sample from two television sets.

※2・・・Sample from three television sets.

### PBDD/Fs standards:

Twelve unlabeled 2,3,7,8-substituted isomers (2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF) and twelve <sup>13</sup>C<sub>12</sub>-labeled(2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8/1,2,3,6,7,8-HxBDD, 1,2,3,7,8,9-HxBDD, OBDD, 2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF) isomers were obtained from Cambridge Isotope Laboratories.

### PBDD/Fs analyses:

PBDD/Fs were extracted from the samples by soxhlet extraction using toluene over 16 hours. The extracts were spiked with <sup>13</sup>C<sub>12</sub>-labeled internal standards and were treated with concentrated sulfuric acid. Then the extracts were purified by a two-layer column chromatography<sup>2)</sup> (44% sulfuric acid silicagel: 2g and Florisil:3g) and by an

active carbon column chromatography(silicagel with active carbon:0.3g). The column chromatography effluents were spiked with  $^{13}\text{C}_{12}$ -labeled standards (syringe spike), and then concentrated to a small volume( $50\ \mu\text{l}$ ), and subjected to the analysis using HRGC (6890 series, Agilent, USA)/HRMS (JMS-800D, JEOL, Japan). HRGC/HRMS was run at high resolution of 12,000 and measured in selected-ion monitoring (SIM) mode. Because  $^{13}\text{C}_{12}$ -labeled HpBDD was not available, recovery correction of HpBDD was made using  $^{13}\text{C}_{12}$ -HxBDD.

### Thermolysis of PBDE:

An aliquot PBDEs(100mg) or deca-BDE were placed on a quartz boat in a heating quartz tube. The quartz heating tube was heated in an electric tube furnace at  $300^\circ\text{C}$  under air flow(200ml/min) for two hours. The gas which came out from a quartz tube was cold-trapped. After heating, products wererecovered from trap and quartz tube with hexane as solvent.

Prior to the thermolysis examination, PBDD/Fs in PBDEs were analysed as they may occur as impurities in PBDE. Synthetic PBDEs was dissolved in hexane, and deca-BDE was dissolved in toluene, and they were analyzed for PBDD/Fs. The analysis of thermolysis of deca-BDE and PBDEs was performed by a method shown in "PBDD/Fs analyses" mentioned above.

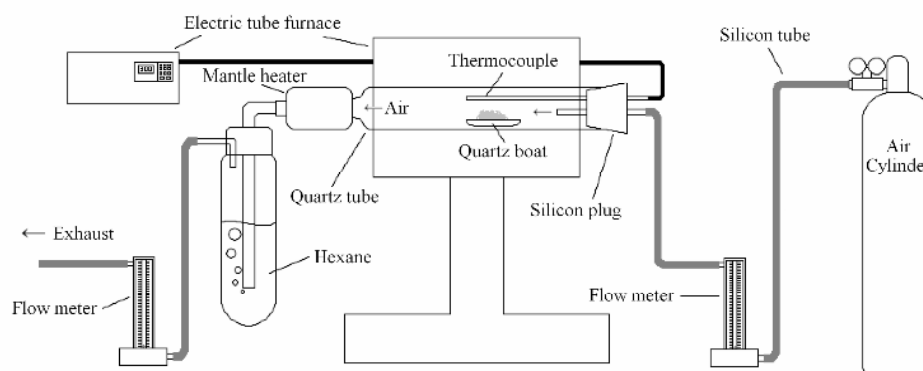


Fig 1 Thermal degradation apparatus for PBDEs and deca-BDE

### PBDEs:

Three PBDEs with different bromine substitution number were prepared by bromination of diphenyl ethers for thermal degradation experiment. PBDEs① was a mixture of the 1~3 brominated compound. PBDEs② was a mixture of the 3~5 brominated compound. PBDEs③ was a mixture of the 4~6 brominated compound.

### Results and Discussion

The results of analysis of PBDD/Fs in dust samples inside television sets were shown in Table 2. The congener compositions were indicated in Figure 2.

Table 2 Concentrations of PBDD/Fs in dust samples inside television sets (pg/g)

Sample Number	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	
Maker(company)	A	A	B	C	D	D	E	F	C	G	
PBDDs	T4BDD	N.D.	5.9	N.D.	1000	290	41	13	320	1900	210
	P5BDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	H6BDD	N.D.	11	N.D.	N.D.	23	N.D.	5.1	N.D.	N.D.	N.D.
	H7BDD	N.D.	N.D.	N.D.	N.D.	5.2	9.6	5.4	N.D.	N.D.	5.7
	O8BDD	N.D.	15	N.D.	26	8.7	12	44	N.D.	5.3	140
	ΣPBDDs	0	32	0	1000	320	62	67	320	1900	350
PBDFs	T4BDF	270	550	94	100	12	60	300	29	75	280
	P5BDF	440	930	56	120	27	110	360	34	53	460
	H6BDF	540	670	33	190	110	140	420	29	34	630
	H7BDF	780	4100	260	1100	470	700	3600	120	260	5000
	O8BDF	520	1900	420	31000	260	690	5000	390	860	8000
	ΣPBDFs	2500	8100	870	33000	880	1700	9600	600	1300	14000
ΣPBDD/Fs	2500	8200	870	34000	1200	1700	9700	910	3000	15000	

PBDD/Fs were detected in all samples examined, and the range of concentration was 870 pg/g-34,000 pg/g. The results of the television dust sample may be classified in four category depending on the period manufactured: in 1980's, in the first half of the 1990's, in the latter half of the 1990's and 2000's. In the samples produced 80's product, PBDDs were not detected while PBDFs were detected. The results of 80's in this study were similar with a report by sakai et al.<sup>3)</sup> In the samples produced in the first half of 90's, OBDF was detected at high levels. When PBDD/Fs was analysed in deca-BDE, OBDD is detected as a major impurity of deca-BDE. It is suggested that the sample produced in the first half of the 1990s is contaminated from deca-BDE.

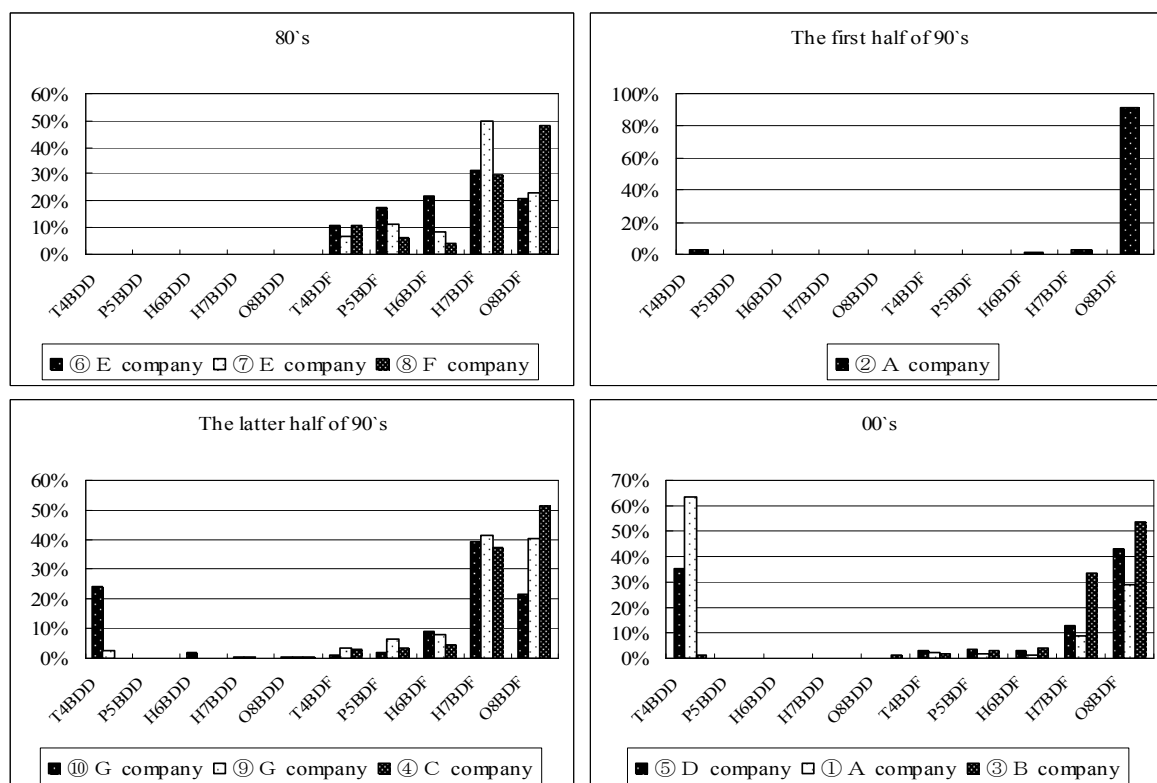


Fig 2 Concentration of PBDD/Fs in dust samples inside television sets classified in category of four generation.

Table 4 Concentrations of PBDD/Fs produced by thermolysis of PBDE and deca-BDE. (ng/g)

	PBDE①		PBDE②		PBDE③		Deca-BDE		
	After thermolysis	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis	Before thermolysis	After thermolysis	Before thermolysis	
PBDDs	T4BDD	15	130	110	71	74	13	6.3	18
	P5BDD	4.9	79	240	79	64	23	13	22
	H6BDD	1.1	45	750	82	65	29	630	23
	H7BDD	0.17	24	140	44	21	54	5000	5.9
	O8BDD	1.8	26	53	18	57	180	4700	93
ΣPBDDs	23	300	1300	290	280	300	10000	160	
PBDFs	T4BDF	25	150	61	110	110	120	19	49
	P5BDF	5.2	1300	690	1400	510	240	36	160
	H6BDF	0.85	950	2000	1400	680	270	64	110
	H7BDF	0.82	220	820	410	160	270	2300	2600
	O8BDF	1.8	210	180	69	490	410	7800	6400
ΣPBDFs	34	2800	3800	3400	2000	1300	10000	9300	
ΣPBDD/Fs	57	3100	5000	3700	2200	1600	21000	9500	

In the samples produced in the latter half of 90's, TBDDs were detected in significantly high level in addition to PBDF. There is possibility that another source of PBDD/Fs is existing other than deca-BDE. This figure seems to be continued to 2000's products. In order to understand congener patterns of PBDD/Fs, we analysed brominated diphenyl ethers all the different brominated substitution. Table 4 and Fig 3 represent the analytical result of deca-BDE before and after thermolysis.

The congener patterns of dust samples in late 90's and 2000's are different from these thermal decomposition product patterns. It suggests the presence of different PBDD source other than PBDE.

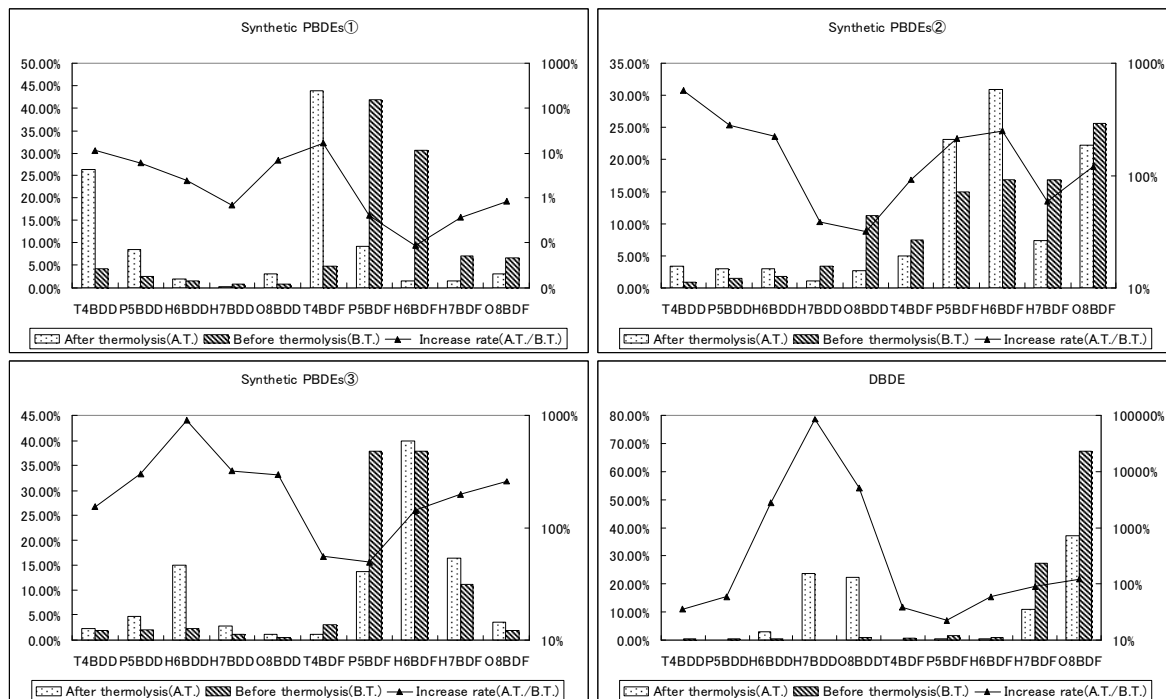


Fig 3 Differences of PBDD/Fs congener profiles before and after thermolysis

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### References

- 1、 Kono Y, Fukuzawa E, Miyazaki M, Nomura T, Komatsu K, Watanabe I, Sakai S. *Environment International* 29 (2003) 665– 682
- 2、 Nose K, Hashimoto S, Takahashi S, Noma Y and Sakai S, *Chemosphere* 68 (2007) 120–125
- 3、 Sakai S, Honda Y, Takatsuki H, Watanabe J, Aoki I, Nakamura K, et al. *Organohalogen Compounds* 52 (2001)35–38
- 4、 Tamade Y, Shibukawa S, Osaki H, Kashimoto S, Yagi Y, Sakai S, et al. *Organohalogen Compounds* 56(2002)189– 192
- 5、 Choi J, Fujimaki S, Kitamura K, Hashimoto S, Ito H, Suzuki N, Sakai S, and Morita M, *Environmental Science and Technology* 37 (5)( 2003) 817 -821