

Determination of PBDEs and PBDD/DFs in the Environmental Samples

Matsuda M¹, Takechi Y¹, Nose K², Okimoto M¹, Harada C¹, Kawano M¹, Kadota Y¹, Morita M¹

¹ Department of Environment Conservation, Ehime University,
Tarumi 3-5-7, Matsuyama, Ehime 790-8566, Japan

² Diagnostic Division, Otsuka Pharmaceuticals Co., Ltd.,
224-18 Ebisuno, Hiraishi, Kawauchi-cho, Tokushima, 771-0195 Japan

Introduction

Polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are toxic chemicals produced unintentionally. They seem to be induced mainly by brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) which are widely used for electrical appliances as to improve incombustibility¹⁾²⁾³⁾⁴⁾. 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 tissue⁵⁾.

There is a possibility that workers in these factories are exposed to PBDD/Fs through respiring dust and indoor air. The fire site another work environment that may be PBDD/Fs pollution. Generation of PBDD/Fs is concerned because that an electric appliance including BFRs may burn in the fire accident spot. The air of fire spot has an influence on a firefighter performing a firefighting and the police performing an inspection of the scene.

In this study, we analyse sample of various workplace environment, and necessitate to collected analysis data to prevent worker health damage. Therefore we analysed dust samples of TV sets. And we performed monitoring investigation of the work environment where pollution by PBDD/DFs is expected such as in a recycling factory and the fire accident spot.

We needed improvement of the analysis sensitivity to analyze the low concentration sample such as blood sample or air sample. For the analysis of PBDD/DFs we used in most cases the capillary column of 0.1 μm film thickness, but tested performance of 0.1 μm, 0.05 μm and 0.01 μm film thickness for higher sensitivity.

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. The dust sample was dried in a desiccator for overnight before analysis.

Air Samples:

Location of air samples are E-waste depot, E-waste recycling factory, the Ehime University campus. We used quartz fiber filter (QF) and polyurethane foam (PUF) for the sampling materials.

Fire accident Samples:

Fire accident samples are the soot and burning refuse. The soot sample was wiped off it which stuck to firefighting clothes and the soot which stuck to a sash. We collected soot sample using alcohol cotton and solid sample using tweezers.

Comparing of capillary column performance:

We examined three kinds of capillary columns. The isomer which compared the sensitivity is eight isomers of 4-6 brominated PBDD/DFs. We specially ordered a thin film thickness column in GL Sciences Inc.. Capillary column and other measurement condition are showed in table 1. We compared instrumental detection limit(IDL) and S/N ratio.

Table 1 Capillary column and other measurement condition

GC-MS Condition		Hewlett Packard 6890 series JEOL JMS-800D (EI mode)
Gas chromatograph	Column	VF-5ms (30m×0.25mm i.d.×0.1μm) InertCap 0.01 (30m×0.25mm i.d.×0.01μm) InertCap 0.05 (30m×0.25mm i.d.×0.05μm)
	Column Temp	VF-5ms 150°C(3min)→10°C/min→180°C →5°C/min→300°C(5min) InertCap0.01 120°C(1min)→10°C/min →260°C(15min) InertCap0.05 120°C(1min)→15°C/min →280°C(21min)
	Injection Temp	260°C
	Mass resolution	10,000 or more
Mass spectrometer	Ionization Energy	38ev
	Ionization Current	500μA
	Ion source Temp	260°C
	Photo multiplier voltage	0.35kV
	Detection method	SIM method with Lockmass mode

PBDD/Fs and PBDEs analyses:

PBDD/Fs and PBDEs were extracted by soxhlet extraction equipment using toluene over 16 hours. In case of air samples, they were extracted from the QF by soxhlet extraction equipment using toluene over 16 hours, and they were extracted from the PUF by soxhlet extraction equipment using acetone over 8 hours.

The extracts were spiked with $^{13}\text{C}_{12}$ -labeled internal standards (made by CIL, EDF-5382) and were treated with concentrated sulfuric acid. Then the extracts were purified by a two-layer column chromatography²⁾ (44% sulfuric acid silicagel: 2g and Florisil:3g) and by an active carbon column chromatography (silicagel with active carbon:0.3g). The first fraction of both column chromatography was used for PBDEs analysis, and the second fraction of column chromatography was used for PBDD/Fs analysis. The column chromatography effluents were spiked with $^{13}\text{C}_{12}$ -labeled standards (made by CIL, PBDEs: EO-5427, PBDD/Fs: EDF-5383), and then concentrated to a small volume(50μl), 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.

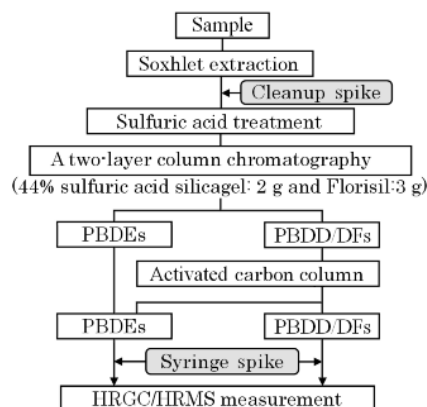


Figure 1. Analytical procedure

Results and Discussion

TV dust samples:

The analysis of PBDD/DFs and PBDEs is shown in Figure 2.

PBDD/Fs were detected in all samples examined, and the range of concentration was 2100 pg/g-40,000 pg/g. PBDEs were detected in all samples examined, and the range of concentration was 690 ng/g-4,100 ng/g.

PBDDs were not detected while PBDFs were detected in all dust sample. DecaBDE was detected predominantly in those samples. In them, OBDD and Hexa~OBDFs were detected at high levels.

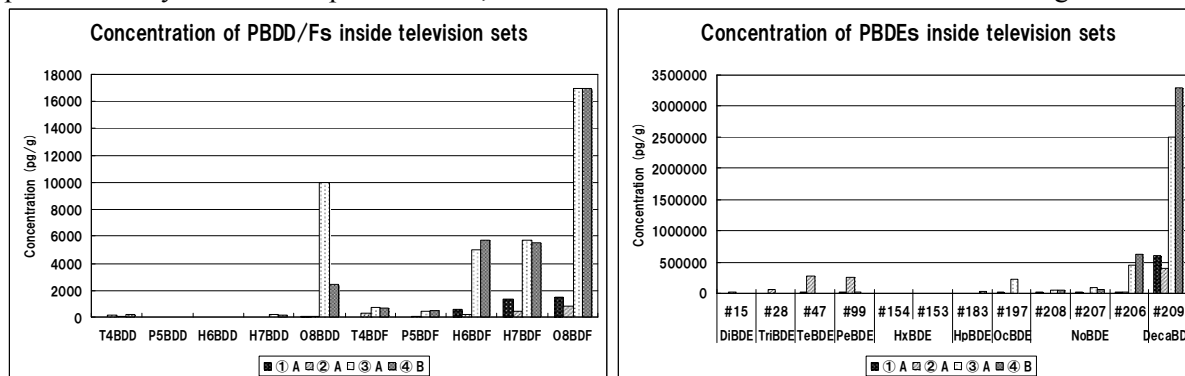


Figure 2 Concentration of PBDD/DFs and PBDEs inside television sets

Air Samples:

The results of analysis of PBDD/DFs and PBDEs in air samples were shown in Figure 3. 2378-substituted PBDDs were not detected while 2378- substituted PBDFs were detected in all air sample. This tendency resembled with a dust sample in the television sets. PBDFs were detected in filter more than in PUF. This supports that PBDD/Fs in the atmosphere sample exist predominantly as a particle phase.

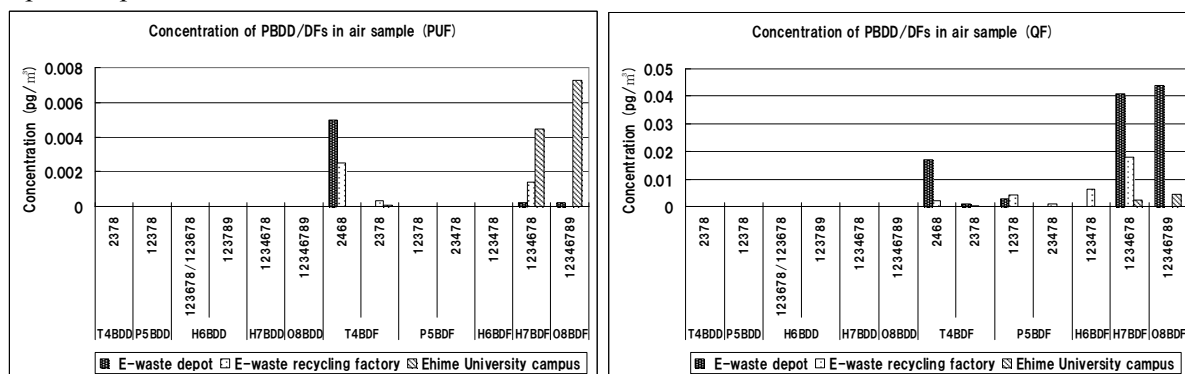


Figure 3 Concentration of PBDD/DFs in air sample

Di-HxBDEs which are in a gas phase are detected by PUF. Hp-DecaBDEs which are in a particle phase are detected by QF. The result of QF of E-waste depot and E-waste recycling factory closely resembled each other with a tendency of PBDEs detected in a dust sample in the television sets.

However, it was not in PUF. Therefore, measurement of PBDEs in gas phase seemed important as well as that of particle phase.

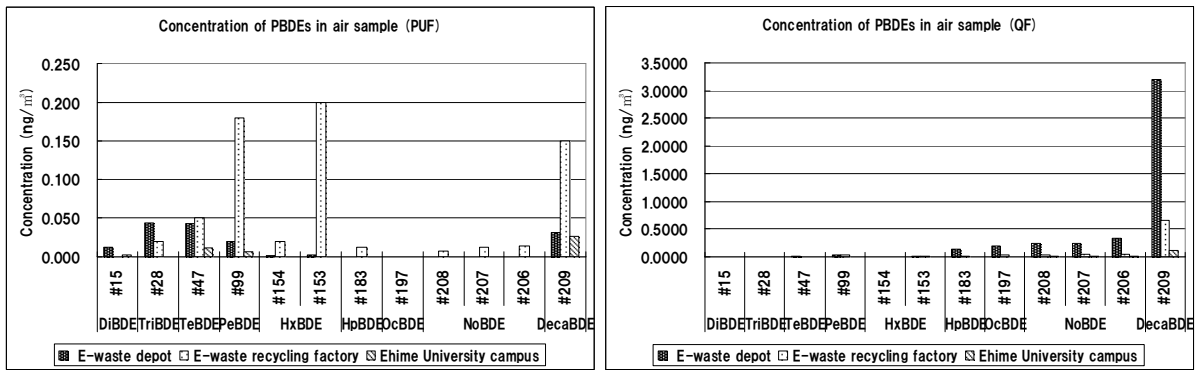


Figure 4 Concentration of PBDEs in air sample

Acknowledgement

This work was supported by MEXT KAKENHI(Grant-in-Aid for Scientific Research (C) No.21510033) . We thank GL sciences Inc. for supplying thin film thickness capillary columns.

References

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