

ANALYSIS

ANALYTICAL METHOD OF POLYBROMINATED DIBENZO-*p*-DIOXIN AND DIBENZOFURANS (PBDDs/PBDFs) IN FLUE GAS, AMBIENT AIR AND SOIL SAMPLES

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Introduction

Polybrominated flame retardants (BFRs) are under discussion because of the formation of polybrominated dibenzo-*p*-dioxin (PBDDs) and dibenzofurans (PBDFs) for a long period. The BFRs such as polybrominated biphenyls (PBBs), brominated diphenyl ethers (PBDEs), tetrabromobisphenol-A (TBBPA) and hexabromocyclododecane (HBCD) are common additive flame-retardants used in high impact polystyrene, polyurethane foam and textile coatings¹⁻⁵.

Municipal and chemical waste incinerators are the most important sources of halogenated dibenzo-*p*-dioxins and dibenzofurans in environments. Polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) play an important role as environmental contaminants such as PCDDs/PCDFs, PCBs, POPs and so on. The brominated compounds are one of the unregulated pollutants, which is highlighted the new pollutants of environmental contamination, recently. In this study, the analytical method of 10 kinds of PBDDs/PBDFs was established and applied to the flue gas, ambient and soil. The improvement method using multi-layer silica gel, florisil and activated carbon column are described, which allows an almost complete separation of PBDEs from PBDDs/PBDFs, and the analytical instruments were used HRGC/HRMS⁶⁻⁹.

Methods and materials

The 10 kinds of PBDDs/PBDFs (*Table 1*) were analyzed to establish the analytical method of the flue gas samples in MSWI³. The various cleanup processes and elution solvents were used to take the highest recovery efficiency. The instrument consisted of a HP6890N Autospec Ultima NT equipped with split injector, and a 30-meter DB-5 column (30m×0.25 mm ID×0.1 mm thickness). The GC oven temperature program was 140°C for 1min, temperature-ramped to 200°C at 20°C/min, and temperature-ramped 290°C/min at 5°C/min. The experimental conditions are represented in *Table 2*.

RESULTS AND DISCUSSION

Column cleanup : In silica gel column cleanup, PBDDs/PBDFs eluted until 80mL of n-hexane, and the recovery was obtained 73 ± 105%. In multi-layer silica gel column cleanup, the recovery was obtained 56 ± 125%, and the PBBs, PBDEs and PBDDs/PBDFs standard mixture can be eluted to different fraction with various elution solvents. The PBDDs/PBDFs eluted the second fraction, and PBDEs and PBBs eluted the first fraction with n-hexane and 60% dichloromethane with n-hexane in florisil column. Also, the PBDEs elution time depend largely on the amounts of AgNO₃-silicagel.

Table 1. PBDDs/PBDFs compounds for analysis

	Compound	HRGC/HRMS (RT : min)	¹² C	
			Quantitation ion	Confirmation ion
PBDDs	2,3,7,8-TeBDD	11.096	497.6923	499.6923
	1,2,3,7,8-PeBDD	13.286	577.6008	579.5988
	1,2,3,4,7,8-HxBDD	16.208	655.5113	657.5093
	1,2,3,6,7,8-HxBDD	16.226	655.5113	657.5093
	1,2,3,7,8,9-HxBDD	16.477	655.5113	657.5093
PBDFs	2,3,7,8-TeBDF	10.911	481.6974	483.6954
	1,2,3,7,8-PeBDF	12.897	561.6059	563.6039
	2,3,4,7,8-PeBDF	12.236	561.6059	563.6039
	1,2,3,4,7,8-HxBDF	15.775	639.5164	641.5144
	1,2,3,4,6,7,8-HpBDF	17.428	717.4270	719.4250

Table 2. HRGC/HRMS analytical conditions

Items	Analytical conditions
· HRGC/HRMS Model	· HP6890N/autospec Ultima NT
· Injector	· 260□
· Column	· DB-5(30m × 0.25□ ID × 0.1□ thickness) 140□(1.0min) → 200□(20□/min) → 290□(5□/min)
· MS Source Temp	· 290□
· Carrier Gas	· He, 1mL/min
· Injection Mode	· Splitless
· Ionization Volt	· 40eV
· Acceleration Volt	· 10kV
· Resolution	· 12,000

In alumina clean process, the standard mixture(PBBs, PBDEs, PBDDs/PBDFs) eluted the first fraction of 2% dichloromethane with n-hexane in the range of 0□100mL, and the IUPAC No. 15 of PBBs compounds eluted in the second fraction of 50% dichloromethane with n-hexane. Also, the low brominated compounds of PBDEs and PBBs eluted to the rear fraction. In activated carbon column cleanup, the PBBs and PBDEs eluted to the first fraction (n-hexane) and second fraction (toluene), but PBDDs/PBDFs only eluted to the second fraction. The analytical method of environmental samples was established as shown in *Fig. 1*.

Analysis of flue gas, ambient air and soil samples: The samples were collected in large-scale industrial area in Republic of Korea, which has the possibility of PBDDs/PBDFs contamination. The method detection limits of each isomer in flue gas were obtained 0.01 pg/m³ for TeBDD/F, 0.10 pg/m³ for PeBDD/F and HxBDD/F, and 0.3 pg/m³ for HpBDD/F, which was obtained by applying the established methods as shown in *Fig. 1*. The MDL of collected samples were 0.1~0.8 pg/g for soil and 0.003~0.030 pg/m³ for ambient air using HRGC/HRMS. The 2,3,7,8-substituted PBDDs/PBDFs were not detected in the flue gas, but non-2,3,7,8-substitute PBDDs/PBDFs was

detected. The some isomers of PBDDs/PBDFs could be detected in soil and ambient air samples by establishing method of this study. The representative chromatograms of each matrix showed in *Fig. 2, Fig. 3 and Fig. 4.*

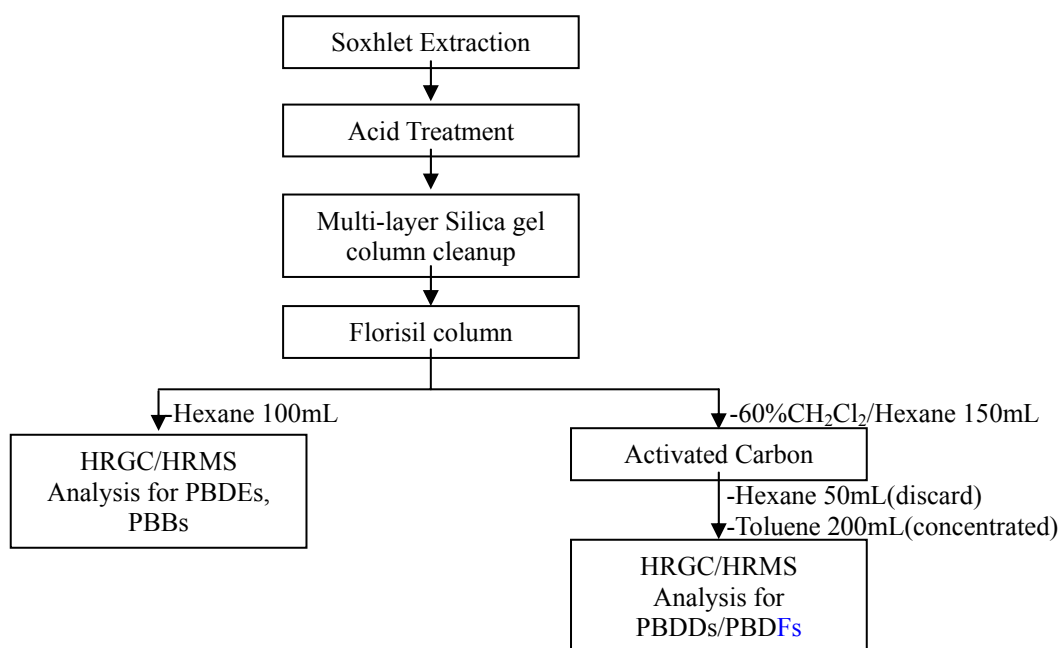


Fig. 1. Established analytical method of PBDDs/PBDFs

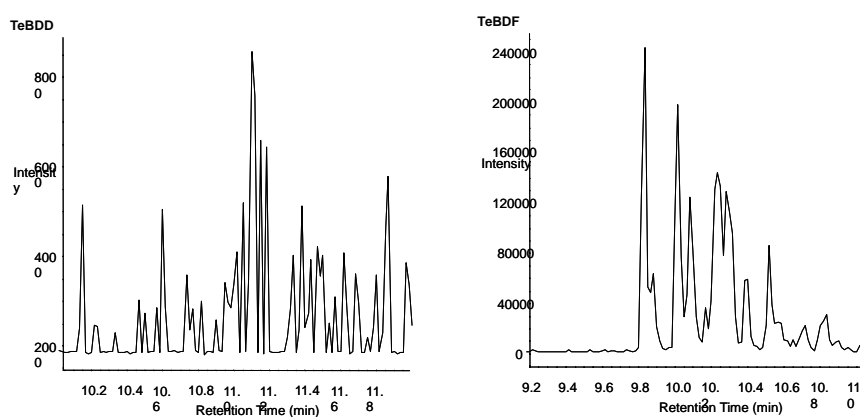
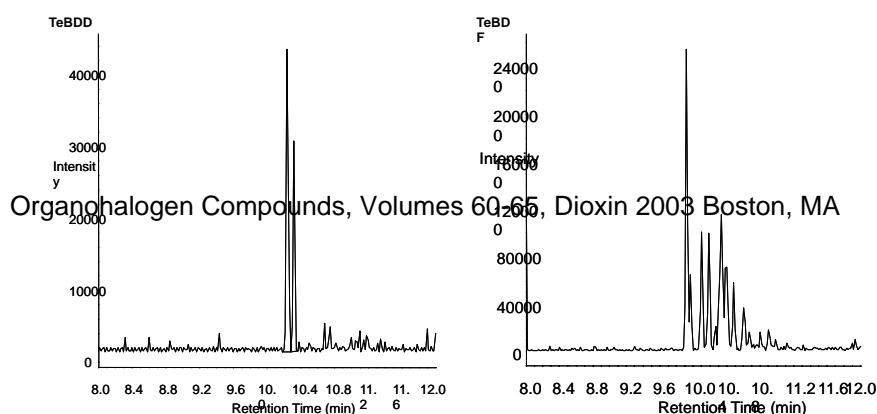


Fig. 2. HRGC/HRMS chromatogram of TeBDDs/TeBDFs in flue gas



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Fig. 3. HRGC/HRMS chromatogram of TeBDDs/TeBDFs in ambient air

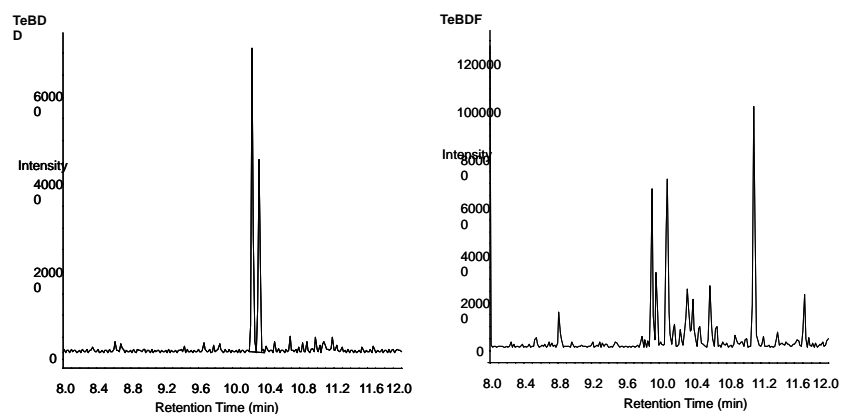


Fig. 4. HRGC/HRMS chromatogram of TeBDDs/TeBDFs in soil

References

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