Emission characteristics of Polybrominated Dibenzo-p-dioxins and Dibenzofurans from the emission sources in Korea

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Introduction

Thermal treatment of plastics flame retarded with brominated compounds often lead to the formation of Polybrominated Dibenzo-p-dioxins and Dibenzofurans (PBDDs/PBDFs). During the production and recycling processes of plastics, PBDDs/PBDFs can be found in conciderable amounts. It has been known that the PBDDs/PBDFs share similar toxicity and bio-accumulatively with Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDDs/PCDFs). This study was performed to investigate emission characteristics of PBDDs/PBDFs from production and recycling processes, involving plastics and fibers which contain brominated flame retardants (BFRs).

Materials and methods

Four manufacturer factories and one recycling center were selected in order to investigate emission concentration and emission patterns of PBDDs/PBDFs in production and recycling process (Table 1). At each facility three flue gas samples were collected from the stack simultaneously. And four ambient air samples were collected from the work process. Collected samples were soxhlet-extracted with dichloromethane for 16 hours, and cleaned up using multi-layered silica gel chromatography. Whole PBDDs/PBDFs congeners of 13 kinds were analyzed by high-resolution gas chromatography/high-resolution mass spectrometry(Autospec Ultima, Micromass Co.) above 10,000 resolution with Dioxin 2 column (30 m×0.25 mm I.D×0.25μm film thickness) for 4-6 brominated congeners and DB-5MS column (10 m×0.32 mm I.D×0.25 μm film thickness) for 7-8 brominated congeners.

Results and Discussion

The respective PBDDs/PBDFs concentrations in the flue gas and ambient air from the manufacturer factories were 0.01~193.90 ng/Nm^3 (0.00~2.44 ng-TEQ/Nm^3) and 0.00~0.63 ng/m^3 (0.00~0.01 ng-TEQ/m^3). Table 3 shows the PBDDs/PBDFs concentrations in flue gas and ambient air of working process.

The dominant congeners of PBDDs/PBDFs were HpBDF and OBDF, and their TEQ values represented 90% of the total TEQ in flue gas samples, but the dioxins were not detected. And the dominant congeners were TBDF,

HpBDF and OBDF, and their TEQ values represented 90% of the total TEQ in ambient air of working process samples. Figure 1 shows emission pattern in flue gas and ambient air of working process.

In recycling factory, PBDDs/PBDFs were contained in a level of 0.03~0.05 ng/m^3 (0.00~0.00 ng-TEQ/m^3) in ambient air samples. The dominant congeners of PBDDs/PBDFs were HpBDF and OBDF, but 2,3,7,8-PBDD was not detected. Figure 2 shows emission pattern in ambient air at the crusher outlet.

***Table 1*. Investigate facilities in this study**

facility	product	flame retardants	remarks
A	ABS flame-retarded,	TBBPA, deca-BDE	production of plastic materials
B	PP compound	TBBPA-DBP, DBP-TBS, BPBPE	production of plastic materials
C	ABS flame-retarded, PP compound	TBBPA	production of plastic materials
D	parts of an automobile, electrics and electronics	BPS	production of plastic materials
E	-	-	recycling of electric waste

※ABS : Acrylonitrile-butadiene-styrene, PP : Polypropyrene, TBBPA : Tetrabromobisphenol A, Deca-BDE : deca-bromominated diphenyl ether, BPBPE : Bis-pentabromophenoxy ethane, TBBPA-DBP: Tetrabromobisphenol A bis(2,3-dibromopropyl ether), DBP-TBS : Bis(3,5-dibromo, 4(2,3-dibromopropoxy)phenyl sulfone), BPS : Brominated polystyrene

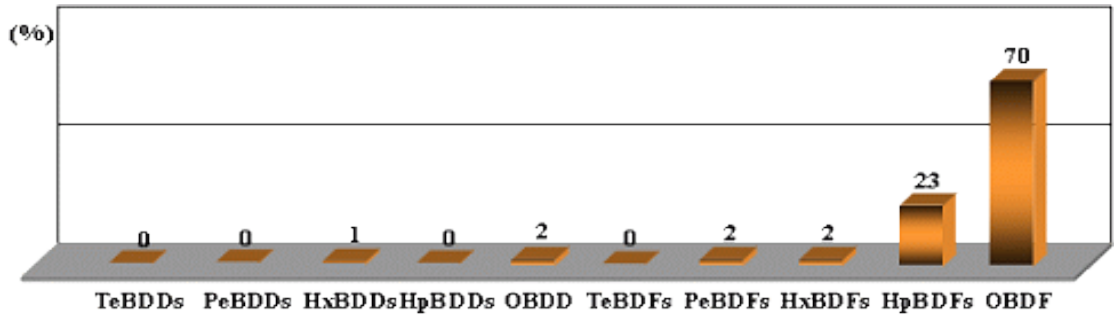
***Table 2*. Analytical conditions of PBDDs/PBDFs using HRGC/HRMS**

GC Conditions	MS Conditions
● HP6890	● Autospec Ultima Premier
● Injector temp : 280℃	● Source temp : 280℃
● Injection mode : Splitless	● Ion energy : 36eV
● Injection volume : 1 μL	● Resolution : above 10,000
● Flow rate : 1mL/min (He 99.999%)	● MS mode : SIM (5 Function, Magnet Switching)
● Column: Dioxin 2 (30m × 0.25mm I.D. × 0.25 μm film thickness)	
● Oven temp. : 100℃ (2 min) → 5℃/min → 310 ℃ (10 min)	
● **4Br ~6 Br** (481.6974~699.5495)	
● Column: DB5-MS (10m × 0.32mm I.D. × 0.25 μm film thickness)	
● Oven temp : 150 ℃ (2 min) → 15℃/min → 190 ℃ → 5℃/min → 280 ℃ (20 min) → 10 ℃/min → 310 ℃ (5 min)	
● **7 Br ~ 8 Br** (719.4248~827.3685)	

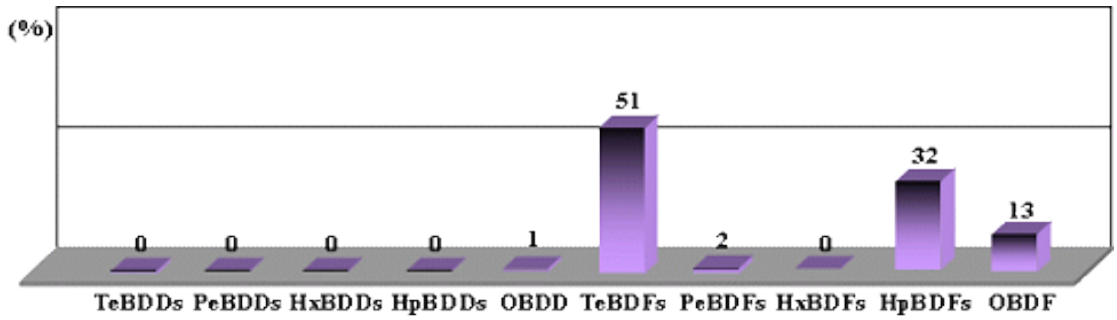
***Table 3*. PBDDs/PBDFs emission concentration in production and recycling process.**

		production process				recycling process
		A	B	C	D	E
flue gas	ng/Nm^3	68.349 (5.237~193.902)	14.991 (1.462~27.362)	41.697 (5.263~82.183)	0.273 (0.013~0.623)	-
	ng-TEQ/Nm^3	0.832 (0.028~2.435)	0.173 (0.056~0.283)	0.217 (0.025~0.478)	0.030 (0.001~0.076)	-
ambient air of working process	ng/m^3	-	0.011 (0.003~0.023)	0.412 (0.294~0.631)	0.001 (0.000~0.003)	0.038 (0.030~0.051)
	ng-TEQ/m^3	-	0.000 (0.000~0.000)	0.006 (0.004~0.009)	0.001 (0.000~0.001)	0.000 (0.000~0.000)

※ TEFs quoted are the I-TEFs that apply to the chlorinated analogues



(a) Flue gas



(b) Ambient air

***Figure 1*. Emission patterns of PBDDs/PBDFs of the production process.**

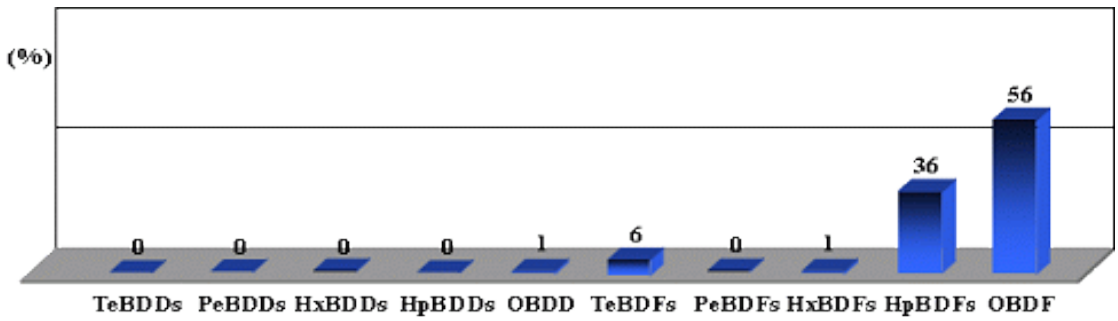


***Figure 2*. Emission patterns of PBDDs/PBDFs in ambient air at the crusher outlet of the recycling center.**

4. References

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