

ANALYTICAL METHOD OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) IN SOIL AND AIR SAMPLES

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INTRODUCTION

Aromatic and aliphatic bromine compounds play an important role as industrial products. The special products are widely used as brominated flame retardants (BFRs) for polymeric materials. 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 coatings and so on. Also, these brominated compounds can be well known to the formation of polybrominated dibenzo-p-dioxin (PBDDs) and dibenzofurans (PBDFs) in the incineration process¹⁻⁵.

Because there is an increasing interest and concern about the behavior and fate of anthropogenic compounds in environment, we studied the environmental distribution of polybrominated diphenyl ethers (PBDEs). The main object is this study to establish the appropriate analytical method to minimize the interference such as PBDD, PEDF etc., and apply to the environmental samples of soil and ambient air samples. In this study, 7 kinds of PBDEs isomers were analyzed using GC/MSD and HRGC/HRMS to apply the environmental samples of the soil and ambient air sample in industrial area of Republic of Korea. From these study, the method detection limits were obtained⁶⁻¹⁰.

EXPERIMENTAL METHODS

The 7 kinds of PBDE isomers were analyzed to survey the distribution of environments in the soil and ambient air samples. The selected compounds are showed in *Table 1*, and the analytical procedure was represented in *Fig. 1*. The soil sample was collected by the Korean official soil test method, and the EPA To-9a using high volume sampler, which contained polyurethane foam¹¹, collected the ambient air sample. The PUF in ambient air sample was extracted with acetone : n-hexane, and soil samples were extracted with toluene for 24 hours in soxhlet. The multi-layer silica gel, florisil and activated carbon column cleanup were performed to remove the interference of extract. The experimental conditions of GC/MSD and HRGC/HRMS are represented in *Table 2*.

RESULTS AND DISCUSSION

Method detection limits(MDL) : The MDL of collected samples were 0.1~1.5 pg/g for soil and 0.003~0.030 pg/m³ for ambient air using HRGC/HRMS. The MDL of collected samples were 0.5~2.0 pg/g for soil and 0.02~0.15 pg/m³ using GC/MSD. The MDL is little difference between the brominated isomers between TriBDE to HpBDE, and the MDL was obtained by the following procedure represented in *Fig. 1*.

Table 1. PBDEs compounds for analysis

	IUPAC	Br congeners	IUPAC	RT(min)	
				GC/MSD	HRGC/MS
PBDEs	15	4,4'-DiBDE	15	10.733	5.868
	28	2,4,4'-TrBDE	28	12.744	7.115
	47	2,2',4,4'-TeBDE	47	14.755	8.855
	99	2,2',4,4',5'-PeBDE	99	16.629	10.652
	100	2,2',4,4',6'-PeBDE	100	16.218	10.206
	153	2,2',4,4',5,5'-HxBDE	153	18.594	12.358

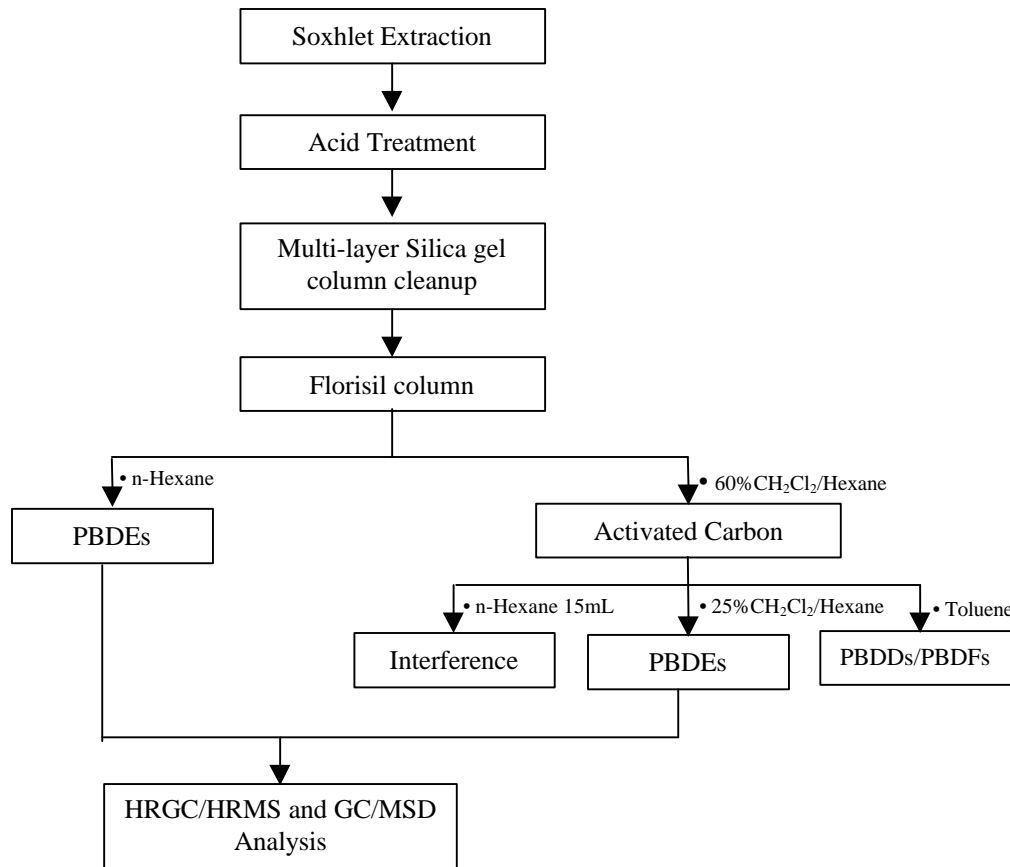


Fig. 1. Analytical procedure of PBDEs

Application of the establishing method in this study: The soil and ambient air sample were analyzed using GC/MSD as shown in *Fig. 1*. In the florisil column cleanup, the 5% water-containing florisil was used as packing material, and 100mL of n-hexane and 60% CH₂Cl₂/hexane were used as elution solvents. And then the second fraction introduced to the activated carbon column as cleanup process to separate the interference, PBDEs and PBDDs/PBDFs. The activated carbon was coated with silica gel. In activated column, the three different fractions are eluted. The first fraction is to remove the interference of PBDEs and PBDDs/PBDFs, and the second fraction is to analyze the PBDEs with 25% CH₂Cl₂/Hexane. This second fraction is combined with the florisil elution solvent and concentrated to analyze the PBDEs in the samples. The last fraction is to collected to analyze the PBDDs/PBDFs with toluene. The analytical results of ambient air detected less than pg/m³, and the spiked recovery was obtained between 50~120% for analyzed isomers, which is the same ranges of PCDDs/PCDFs in Korean official method. The PBDE isomers could be detected in ambient air and soil samples as shown in *Fig. 2*. The detected main isomers were IUPAC No. 47(2,2',4,4'-T₄BDE) and 99(2,2',4,4',5-P₅BDE). The isomer could be separated effectively, and applied the established method for analyzing the environmental samples.

Table 2. GC/MSD analytical conditions

	Items	Analytical conditions
GC/MSD	<ul style="list-style-type: none"> · Model · Injector · Column · Source Temp <ul style="list-style-type: none"> - MS Quad - MS Source · Carrier Gas · Injection Mode · Mode 	<ul style="list-style-type: none"> · HP6890/HP5793 · 280 · DB-5(30m×0.25 ID×0.25 thickness) 100 (1min, 10 /min) 300(19min) · 150 · 230 · He, 1mL/min · Splitless · SIM
HRGC/ HRMS	<ul style="list-style-type: none"> · Model · Injector · Column · MS Source Temp · Carrier Gas · Injection Mode · Ionization Volt · Acceleration Volt · Resolution 	<ul style="list-style-type: none"> · HP6890N/Autospec Ultima NT · 260 · DB-5(30m×0.25 ID×0.1 thickness) 140 (1.0min) 200 (20 /min) 290 (5 /min) · 290 · He, 1mL/min · Splitless · 40eV · 10kV · 12,000

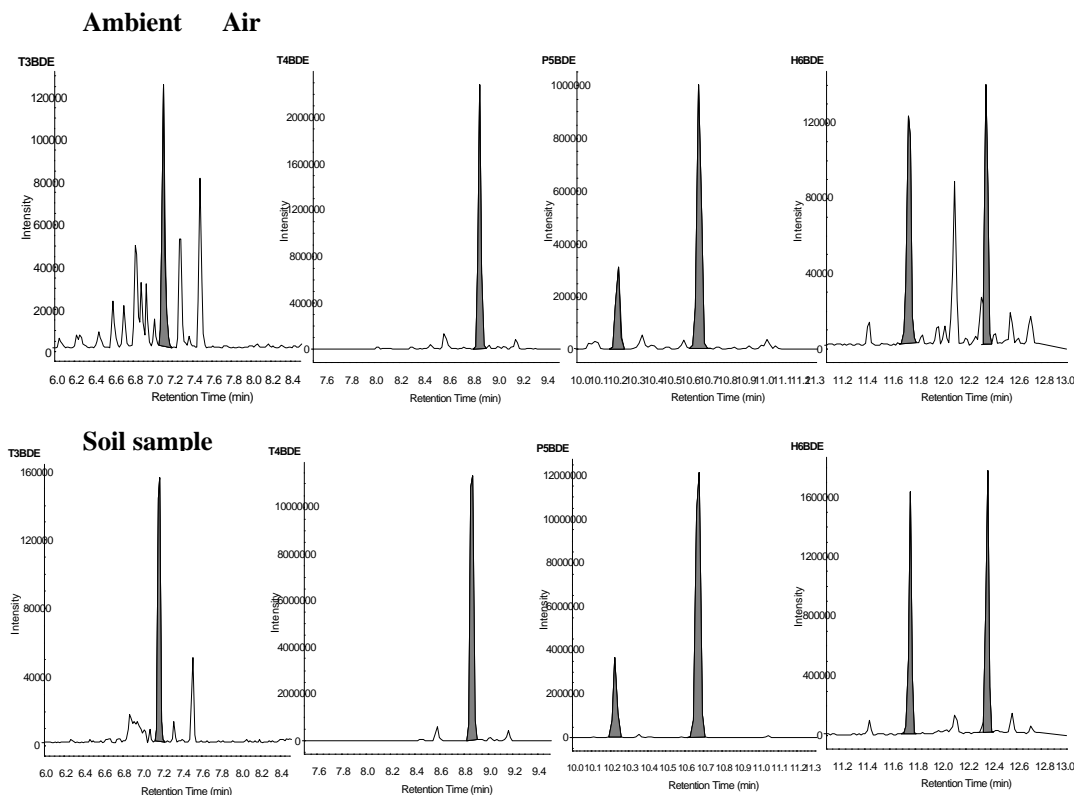


Fig. 2. PBDEs chromatograms of ambient air and soil samples

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