

Application of Microwave-Assisted Extraction to the Analysis of PCBs and CBzs in Fly Ash from Municipal Solid Waste Incinerators

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Introduction

Annual emissions of dioxins first discovered in municipal solid waste incinerator (MSWI) fly ash and flue gas by Olie et al. in 1977 [1], were approximately 1743~1762 g-TEQ in Japan in 2001. Approximately 50%, or 812g-TEQ of dioxin emissions have been attributed to MSWI output [2]. The emitted concentrations of polychlorinated biphenyls (PCBs) and chlorobenzenes (CBzs), two classes of dioxin precursors [3], as well as those of co-planar PCBs, a type of dioxin, have been shown to be strongly correlated with dioxin levels. [4]

The extraction step has been, in generally, the least developed aspect of most analytical procedures, including procedures for the analysis of PCBs and CBzs. Although the Soxhlet extraction (SE) method for solid samples, developed in 1879 [5], is still employed today in many laboratories, during the past decade, several novel extraction techniques, such as supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and accelerated-solvent extraction (ASE), have been used to analyze PCBs, PAHs, and other persistent organic pollutants (POPs) from various matrixes.[6-8] These newer methods are less time-consuming and use much smaller amounts of organic solvents. The efficiency of MAE has been reported to be higher than that of SFE [8].

In the present study, MAE was used to analyze PCBs and CBzs in MSWI fly ash. Under different experimental conditions, the optimum solvent mixture, the optimum solvent volume, and the optimum irradiation time were established. Furthermore, the relative standard deviation (RSD) values were evaluated. Finally, MAE efficiencies were compared with those of SE. The main objective of the study, however, was to use water as a polar solvent in MAE. Because solvents with a high dielectric constant, such as water, have to be used in MAE to absorb the microwave energy and heat the solvent, the residual water after acid pretreatment could be used in MAE. Therefore, the air drying time, normally three days could be shortened with MAE following the required acid pretreatment.

Methods and Materials

Standards and Internal Standards Seventeen isomers of PCB (PCB-14, PCB-18, PCB-28, PCB-52, PCB-66, PCB-103, PCB-95, PCB-105, PCB-149, PCB-129, PCB-156, PCB-157, PCB-169, PCB-187, PCB-180, PCB-199, and PCB-194) and nine isomers of CBz (1,3-DiCBz; 1,3,5-TriCBz; 1,2,4-TriCBz; 1,2,3-TriCBz; 1,2,4,5-TetraCBz; 1,2,3,5-TetraCBz; 1,2,3,4-TetraCBz; PentaCBz; and HexaCBz) were used as native standards. ¹³C-PCBs (PCB-28, PCB-52, PCB-101, PCB-118,

and PCB-138) and ^{13}C -CBzs (1,4-DiCBz; 1,2,3-TriCBz; 1,2,3,4-TetraCBz; PentaCBz; and HexaCBz) were used as internal standards (ISs).

Samples

Spiked Fly Ash Fly ash-E was collected from an electrostatic precipitator (ESP) in a continuous stoker-type MSWI-E in Japan. The total organic carbon (TOC) of the fly ash-E was 4.61%. The elemental distribution in the fly ash-E was measured by XRF-1700 (Shimadzu, Japan). The ratios of the elements O, C, Cl were about 35.7%, 17.1%, and 14.8%, respectively. To eliminate metals from the fly ash-E, it was pretreated with 2 M hydrochloric acid (HCl) for 2 h. After air-drying for 3 days, SE was conducted three times to eliminate POPs in the fly ash-E. The PCB concentrations in the fly ash-E were reduced to 0 ng/g after the second SE. The CBz concentrations in the cleaned fly ash-E following the third SE were reduced to 0.74% of the original concentrations. The standards and ISs were then spiked into the cleaned fly ash-E.

Actual Fly Ash Fly ash-N was supplied by MSWI-N, which had two continuous stoker-type incinerators with a bag filter (BF) and a web scrubber (WS). The fly ash-N had a TOC of 0.27%. The distributions of the elements O, C, and Cl in the fly ash-N were about 33.7%, 5.1%, and 20.0%, respectively.

Analytical Procedures SE or MAE was conducted after spiking the standards and ISs into the cleaned fly ash. For actual fly ash analyses, SE was conducted after air-drying for 3 days, and MAE was conducted after air-drying for various times that depended on the water content (WC). The extracts were then concentrated to a volume of 4 ml using a rotary evaporator at 40 °C. Following clean-up on a multi-layer silica gel column, the solvent containing the target compounds was concentrated to a volume of 2 ml using a rotary evaporator at 30 °C. The volume of the solvent was further reduced to 100 μl by evaporation with compressed nitrogen gas. Finally, PCBs and CBzs were analyzed by GC-MS. The procedures for SE, MAE, clean-up, and GC-MS analyses are described below. All experiments were conducted three times.

Microwave-Assisted Extraction MAE was carried out using an MDS-2000 (CEM, Mathews, NC). This system allowed up to 12 extraction vessels to be irradiated simultaneously, in 1% increments, up to 2450 MHz of microwave energy at 100% power. The samples were placed in double-walled, lined digestion vessels with a volume of 110 ml. The principle of heating with microwave energy is based on the direct effect of microwaves on molecules by ionic conduction and dipole rotation. Polar molecules and ionic solutions strongly absorb microwave energy because they have a permanent dipole moment that is affected by microwaves. Therefore, in order to enhance the absorption of microwave energy, solvents with a high dielectric constant, such as water, methanol, and acetone, are preferred.

In the present study, 3.0 g fly ash were put into PFA vessels. For quantification, a standard solution (100 μl) and an IS solution (10 μl) of PCBs and CBzs were added into cleaned fly ash-E, and 10 μl of an IS solution of PCBs and CBzs were added into actual fly ash-N. The extraction was performed at 120 °C [8] with a heating time of 15 min or 25 min. After the extraction, the vessels were cooled to room temperature before being opened. The MAE solvent mixtures for spiked fly ash-E were hexane/acetone (1:1), toluene/acetone (1:1), toluene/ H_2O , methanol, or dichloromethane. The solvent mixtures for actual fly ash-N were toluene/acetone (1:1), toluene/acetone (5:3), and toluene/ H_2O .

Soxhlet Extraction The heating temperature was about 80 °C. Toluene (120 ml) was used as the extraction solvent, and 3.0 g fly ash was put into a cylindrical filter. For quantification, a standard solution (100 μl) and an IS solution (10 μl) of PCBs and CBzs were added into cleaned fly ash-E,

and 10 µl of an IS solution of PCBs and CBzs were added into actual fly ash-N. The extraction lasted for 18-24 h. Following extraction, the apparatus was air cooled for 30 min.

Clean-up The column for clean-up was filled with layers of KOH silica gel, 44% H₂SO₄ silica gel, 22% H₂SO₄ silica gel, AgNO₃ silica gel, and dried sodium sulfate. Hexane (50 ml) was used to pre-wash the multi-layered column [9], and 4 ml of extraction solvent that had been concentrated by rotary evaporation flowed through the column. The target compounds were eluted from the column with 120 ml hexane at 2.5 ml/min.

Gas Chromatography-Mass Spectrometry (GC-MS) Analysis The analysis was performed on an HP6890 series gas chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a splitless injector (purge delay 1 min, purge flow 60 ml/min). The carrier gas was helium at a constant flow rate of 1ml/min. The capillary column used was an HP-5MS (Hewlett Packard, Palo Alto, CA) with a length and inside diameter of 60m and 0.250 mm, respectively, and film thickness of 0.25 µm. The gas chromatograph was connected to an HP 5973 mass-selective detector (electron impact, 70 eV), operated under the selected ion-monitoring (SIM) mode using the molecular ion of each compound at 1.5-2 scan/s. The interface temperature was maintained at 295 °C for PCBs, and 280 °C for CBzs. To analyze PCBs, the temperature of the injector was maintained at 250 °C. The column temperature was initially held at 150 °C for 3 min, after which it was increased to 185 °C at a rate of 20 °C/min, and then to 245 °C at 2 °C/min. Finally, after being maintained at 245 °C for 3 min, the column was heated to 290 °C at a rate of 6 °C/min. To analyze CBzs, the temperature of the injector was maintained at 200 °C. The column temperature was initially held at 80 °C after which it was increased to 116 °C at a rate of 2 °C/min, and then to 122 °C at 1 °C/min. Finally, it was increased to 250 °C at a rate of 10 °C/min.

Results and Discussion

MAE Efficiencies with Different Organic Solvent Mixtures

Organic solvent mixtures of hexane/acetone, methanol, dichloromethane, and toluene/acetone were used for the MAE of spiked fly ash. The recoveries of PCBs and CBzs are shown in Table 1. DiPCBs extracted in a solvent of methanol or dichloromethane, and DiCBzs extracted with methanol had low recoveries, as shown in Table 1. Furthermore, Co-PCBs, especially PCB-169, were not extracted sufficiently in hexane/acetone, methanol, or dichloromethane. When

Table.1 Recoveries of PCBs and CBzs in spiked fly ash using different organic solvent mixtures

	Solvent mixture	Volume (ml)	MAE recovery (%) \pm RSD							
			Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	
MAE	CBzs	Hexane/Acetone (1/1)	30	89.4 \pm 4.2	81.4 \pm 6.7	82.7 \pm 6.0	102.4 \pm 4.8	95.6 \pm 10.6	X	
		Methnol	15	41.5 \pm 19.2	113.4 \pm 25.5	112.5 \pm 4.4	117.0 \pm 4.8	99.4 \pm 6.8		
		Dichloromathane	15	-	-	-	-	-		
		Toluene/Acetone(1/1)	30	103.3 \pm 1.3	120.1 \pm 3.6	105.2 \pm 12.1	115.7 \pm 5.2	110.8 \pm 3.8		
		Toluene/Acetone (1/1)	20	104.8 \pm 5.1	116.9 \pm 11.0	101.6 \pm 14.6	121.0 \pm 12.2	114.4 \pm 8.1		
	PCBs	Hexane/Acetone (1/1)	30	91.5 \pm 7.5	109.3 \pm 9.5	82.5 \pm 9.3	89.9 \pm 5.2	59.5 \pm 5.0	84.8 \pm 3.4	73.5 \pm 2.4
		Methnol	15	29.8 \pm 0.5	81.5 \pm 3.4	112.9 \pm 9.3	146.4 \pm 8.1	77.0 \pm 4.6	104.2 \pm 9.0	101.9 \pm 3.8
		Dichloromathane	15	42.1 \pm 2.5	90.5 \pm 10.5	84.4 \pm 3.9	122.7 \pm 16.9	66.0 \pm 3.2	91.9 \pm 5.2	90.2 \pm 4.9
		Toluene/Acetone(1/1)	30	99.5 \pm 3.0	97.6 \pm 4.3	99.0 \pm 3.3	95.9 \pm 3.5	98.9 \pm 3.2	100.6 \pm 3.5	84.5 \pm 3.4
		Toluene/Acetone (1/1)	20	91.3 \pm 3.2	95.2 \pm 4.7	92.0 \pm 5.1	95.0 \pm 3.6	89.0 \pm 5.9	92.6 \pm 2.0	84.8 \pm 9.6
SE	Co-PCBs	Congener	PCB-105	PCB-156	PCB-157	PCB-169				
		Hexane/Acetone (1/1)	30	54.3 \pm 5.3	39.9 \pm 4.9	63.7 \pm 9.8	31.3 \pm 4.3			
		Methnol	15	127.6 \pm 6.2	81.2 \pm 6.2	80.8 \pm 6.0	6.4 \pm 0.8			
		Dichloromathane	15	102.1 \pm 7.9	68.9 \pm 0.2	66.1 \pm 0.4	5.3 \pm 0.8			
		Toluene/Acetone(1/1)	30	106.5 \pm 3.9	107.6 \pm 3.7	104.2 \pm 3.9	90.2 \pm 2.1			
	Toluene/Acetone (1/1)	20	97.1 \pm 4.7	91.9 \pm 7.2	91.0 \pm 6.1	76.6 \pm 10.3				
	CBzs	Toluene	120	66.8 \pm 0.2	66.4 \pm 0.3	67.9 \pm 0.5	69.3 \pm 0.4	70.6 \pm 4.2		
		PCBs	120	89.3 \pm 1.5	79.4 \pm 1.6	93.8 \pm 3.2	89.5 \pm 2.7	97.3 \pm 3.0	96.0 \pm 2.8	100.9 \pm 3.6
		Congener	PCB-105	PCB-156	PCB-157	PCB-169				
		Co-PCBs	Toluene	120	95.0 \pm 3.3	98.0 \pm 3.6	98.0 \pm 3.2	101.1 \pm 3.2		

dichloromethane was used as a solvent, no CBzs were extracted from fly ash-E. Toluene performed

better than hexane, methanol, or dichloromethane as a non-polar solvent for MAE of both PCBs and CBzs. The principle “like dissolves like” could explain this result. Based on these results, toluene was used as the non-polar solvent in the following experiments.

Effect of Irradiation Time on MAE

As shown in Fig.1, when irradiation time was decreased from 25 to 15 min, the extraction efficiencies increased slightly for PCBs in both spiked fly ash and actual fly ash. The lower recoveries at 25 min were originally attributed to analyte degradation as resulting from prolonged exposure to heat or to volatility at high temperatures [10]. An irradiation time of 15 min was therefore used for the remainder in this study.

Effect of Water Content on MAE Spiked Fly Ash

Water was used as a polar solvent in MAE instead of acetone. The fly ash containing water was extracted properly in the solvent toluene when the toluene/H₂O mixture was used as the solvent. The amounts of water were expressed by the water content (WC) parameter in the fly ash.

The recoveries of each PCB and CBz homologue did not vary much with WC (Table 2). When the WC reached 90%, the recovery of the non-polar substance of PCB-169 decreased. When the WC was increased, however the RSDs increased. For example, when the fly ash contained 90% water, the average

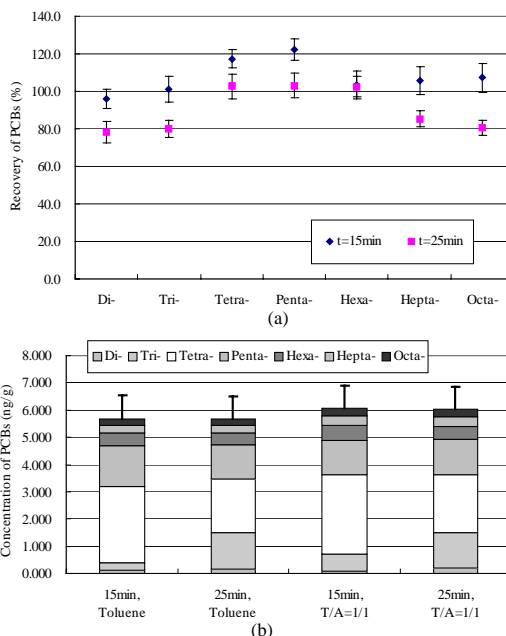


Fig.1 Recoveries and concentrations of PCBs in fly ash at different irradiation time using MAE with a toluene/acetone solvent mixture (n=3).

Table.2 Recoveries of PCBs and CBzs in spiked fly ash when water using as the polar solvent (n=3)

	Solvent mixture	Volume (ml)	WC (%)	MAE recovery (%)±RSD							
				Di-	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-	
CBzs	Toluene/H ₂ O	15/0.75	20	115.3±1.8	87.5±6.8	113.7±1.7	105.8±3.1	99.9±1.7	X		
	Toluene/H ₂ O	15/2	40	115.6±4.0	95.5±5.2	110±2.9	115.3±6.6	100.6±0.7			
	Toluene/H ₂ O	15/5	60	102.3±3.1	94.4±1.7	99.9±7.3	105.3±17.7	113±18.6			
	Toluene/H ₂ O	15/27	90	113.7±7.3	126±16.5	146.6±31.7	141.8±37.3	152.8±44.7			
	Toluene/H ₂ O	10/5	60	102.3±4.1	96.6±3.8	96.3±4.2	92.2±7.1	77.2±9.2			
	Toluene/H ₂ O	15/0.75	20	96.2±8.3	99.1±8.9	101.7±4.2	87.8±3.5	108.7±2.7			91.3±3
MAE PCBs	Toluene/H ₂ O	15/2	40	95.7±3.4	96.1±4.1	96.1±7.2	86.6±1.5	104.7±1.7	89.7±1.3	86.5±2.0	
	Toluene/H ₂ O	15/5	60	89.9±9.2	102.4±10.6	93.8±7.0	90.6±8.6	86.5±7.6	92.2±6.6	95.6±7.6	
	Toluene/H ₂ O	15/27	90	69.6±10.3	91.4±14.3	92.9±18.4	99.5±27.9	93.2±21.8	103.3±15.8	112.7±13.6	
	Toluene/H ₂ O	10/5	60	72.3±3.2	90.8±2.3	75.7±3.3	92.8±5.5	66.9±4.2	82.3±4.5	83.7±5.9	
	Congener				PCB-105	PCB-156	PCB-157	PCB-169			
	Co-PCBs	Toluene/H ₂ O	15/0.75	20	107.3±5.1	111.5±2.8	108.3±3.1	121.4±1.0			
Toluene/H ₂ O		15/2	40	100.8±2.0	106.5±1.8	103.4±2.4	119.7±2.4				
Toluene/H ₂ O		15/5	60	92.4±9.0	93.9±9.6	86.0±6.2	72.4±9.5				
Toluene/H ₂ O		15/27	90	98.5±13.6	101.4±16.3	94±28.3	76.9±38.7				
Toluene/H ₂ O		10/5	60	80.1±5.2	68.0±5.1	66.9±5.2	32.5±4.6				
SE	CBzs	Toluene	120	66.8±0.2	66.4±0.3	67.9±0.5	69.3±0.4	70.6±4.2			
	PCBs	Toluene	120	89.3±1.5	79.4±1.6	93.8±3.2	89.5±2.7	97.3±3.0	96.0±2.8	100.9±3.6	
	Congener				PCB-105	PCB-156	PCB-157	PCB-169			
	Co-PCBs	Toluene	120		95.0±3.3	98.0±3.6	98.0±3.2	101.1±3.2			

RSD of PCBs was about 15%, while that of CBzs was approximately 20%. From these experimental results, the extraction recoveries were deemed stable with a WC below 60%.

Actual Fly Ash

Following acid pretreatment, the WC of fly ash-N was adjusted to 20%, 40%, 60%, or 90% by varying the drying time. The concentrations of PCBs and CBzs in fly ash-N with different water contents are shown in Fig.2. The extraction efficiencies increased gradually with the reduction of WC. For PCBs, the extraction efficiencies by MAE were improved remarkably by reducing the WC of fly ash-N. On the other hand, no significant effects of WC were noticed for CBzs extraction. Nevertheless, the fly ash-N with a high WC had higher values for DiCBzs.

The Effect of Solvent Mixture Volume on MAE

Spiked Fly Ash

MAE with an Organic Solvent Mixture

Toluene/acetone solvent mixtures of 20 ml and 30 ml produced similar recoveries of PCBs, Co-PCBs, and CBzs, as shown in Table 1. This indicates 20ml of toluene/acetone was sufficient for the extraction of PCB and CBz from fly ash-E. The RSD values of TetraCBzs and PentaCBz using 20 ml of solvent were about 25%, however, indicating that the experimental repeatability under these conditions was not very good. In the other cases, the RSD values for PCBs were less than 5% and those for CBzs, except those repeated above, were less than 10%. The RSD values for PCBs were lower than those for CBzs.

MAE with Water as a Polar Solvent

The recoveries of PCBs, Co-PCBs, and CBzs from fly ash with a WC of 60% using different volumes of toluene are shown in Table 2. The recoveries of Co-PCBs and other homologues of CBzs increased as the volume of toluene increased.

The residual fly ash was extracted by SE after MAE with 10 ml toluene, shown in Fig.3, indicate that PCB-169, a non-polar substance, was not extracted well by MAE. This could have been due to the facts that non-polar substances are difficult to heat with microwave energy and that water acts as a barrier in MAE. As a results, it was difficult to transfer PCB-169 from fly ash with a high WC to the solvent using MAE. The recovery of PCB-169 with 10

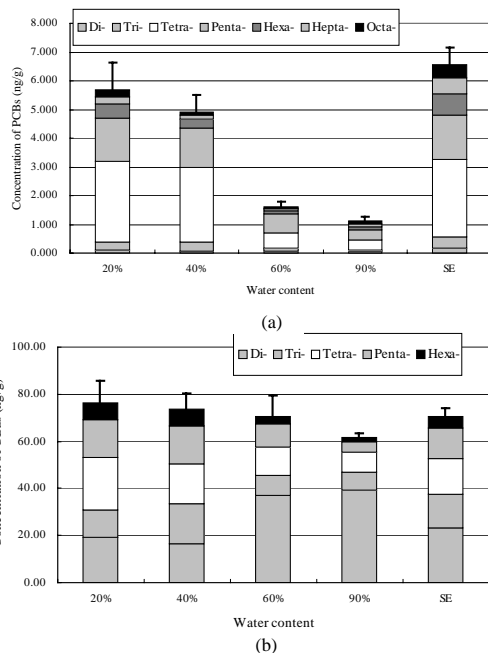


Fig.2 Concentrations of PCBs and CBzs in actual fly ash with different water contents (n=3).

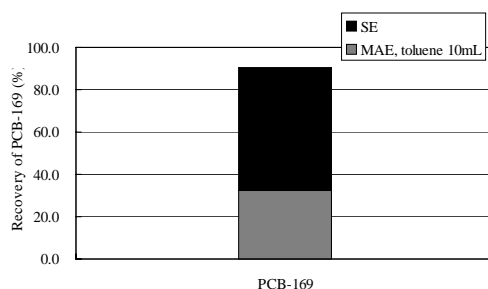


Fig.3 Recovery of PCB-169 in spiked fly ash with a water content of 60% using MAE and SE

ml toluene was significantly less than that with 15 ml toluene. The recoveries of other Co-PCBs also increased by 10%-25% with 15 ml toluene, as shown in Table 2. Therefore, an additional 5 ml toluene influenced the recoveries of Co-PCBs in fly ash with a WC of 60%, even though 10 ml toluene was sufficient for extracting most PCBs and CBzs as indicated below.

Actual Fly Ash

The Combined Effects of Different Volume and Ratio on MAE

The concentrations of PCBs and CBzs extracted by MAE with different solvent mixtures, e.g., 30 ml (1/1), 50 ml (1/1), 30 ml (5/3), and 40 ml (5/3) of toluene/acetone, are shown in Fig.5. The controlling for solvent ratio, a low solvent volume resulted in high MAE efficiencies. This could have been due to inadequate stirring of the solvent by the microwaves [11,12]. On the other hand, with a volume of 30 ml, the toluene/acetone ratio of 5/3 produced higher efficiencies than did a ratio of 1/1.

Comparison of MAE Efficiencies and SE

Spiked Fly Ash

The recoveries of PCBs by SE were about 80-100%, as shown in Table 1 and 2; by MAE were about 90-110%. The recovery of PCB-169 from fly ash-E containing 60% water, however, was about 70%. The recoveries of CBzs by SE were approximately 60-70%, which are lower than the recoveries by MAE (about 90-120%). The homologues of CBzs are easily volatilized during the SE process because CBzs have low boiling points of about 180-320 . On the other hand, CBzs are difficult to volatilize using the closed vessels required for MAE. Thus, MAE had higher efficiencies than did SE for CBz analysis.

The RSD values of PentaCBz and HexaCBz in fly ash with WC of more than 60% were high using MAE. Under all the experimental conditions, including those of SE, the RSD values of all PCBs and CBzs, except PentaCBz and HexaCBz, were less than 15%. The repeatability of the extraction of higher CBz homologues from fly ash containing water was therefore poor.

With water as the polar solvent, however, the recoveries of PCBs and CBzs varied little. Therefore, with the exception of the non-polar substance PCB-169, MAE produced almost the same efficiencies with a solvent mixture of either toluene/acetone or toluene/H₂O. Moreover, MAE had higher efficiencies than did SE in spiked sample analyses.

Actual Fly Ash

Both PCBs and CBzs, especially the lower homologues, were extracted better by MAE than by SE, as shown in Fig.4.

The large amount of solvent needed for SE (120 ml of toluene was used in this study) meant that more time was required for the rotary evaporation process. Less than 30 ml of solvent was used in MAE, so the concentration process was faster approximately 20 h of extraction time.

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