Comparison of Static and Dynamic Solvent Extraction of Polychlorinated Dibenzofurans from Fly Ash

Jeong Soo Yang,[*] **Jang Hwan Jeong**[*] **and Euy Kyung Yu**[★]

[+]*Department of Chemistry, Yonsei University, Seoul, 120-749, Korea*
[*]*Department of Applied Chemistry, Sejong University, Seoul, 143-747, Korea*
(Received May. 20, 2004, Accepted Jun. 5, 2004)

Abstract : In this study, static and dynamic solvent extractions are compared for more efficient extraction of polychlorinated dibenzofurans (PCDFs) from fly ash. Static solvent extraction rather than dynamic extraction showed a higher recovery of PCDFs, which was adsorbed strongly with fly ash. The effects of parameters, such as temperature, toluene-isopropyl alcohol mixture, static and dynamic time flow rate, and solvent volume on the extraction were investigated and the variations in average recoveries of PCDFs were explained. In both extractions, temperature was an effective parameter because the higher temperature gave the higher recoveries. In dynamic solvent extraction, dynamic time was more effective than flow rate and solvent volume for the extraction of PCDFs from fly ash. Multi-layer column chromatography on neutral and acidic silica gel with *n*-hexane was used for cleaning up the extracts. The quantification of the PCDFs extracted was performed using HPLC-UV.

Key words : Static solvent extraction, Dynamic solvent extraction, Fly ash, HPLC-UV

Introduction

The conventional measuring method of PCDD/Fs consists of four major steps; sampling, extraction, clean-up and determination. Compared to instrumental analyses, sample preparation is a long and critical step in analyzing organic contaminants in the environment. The extraction of organic compounds from solid materials can be attained using several established methods. Soxhlet extraction has been widely and successfully applied in the extraction of organic compounds from various matrix such as airborne particulate and soil samples.[1,2] However, Soxhlet extraction has some limitations, including considerable sample and solvent handling, lengthy extraction time, careful cleaning

and handling of expensive, fragile glassware and a bulky accessory apparatus.[3,4] Ultrasound-assisted extraction (UAE) is an alternative extraction technique that has been applied to extracting organic compounds such as DDT from soil, and the reported recovery efficiencies are slightly lower or equal to those of Soxhlet extraction.[5] New extraction techniques have been established in order to reduce the volume of solvents required for extraction, improve the precision of analyte recovery, and reduce extraction time and sample preparation costs. Such techniques include supercritical fluid extraction (SFE),[6,7] and enhanced-fluidity liquid extraction (EFLE)[8,9] and pressurized fluid extraction (PFE).[10]

Adjusting an extraction temperature has been an approach to increase extraction efficiencies. It was suggested that the desorption of the analytes from the environmental matrices requires overcoming the energy

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★ Corresponding author
Phone : +82-(0)61-393-8443   Fax : +82-(0)61-393-8444
E-mail : nykim@nisi.go.kr

barrier of desorption, which could be accomplished by increasing the extraction temperature.[11]

The extraction of organic compounds, such as PCDD/Fs, from fly ash, requires more efficient extraction methods and conditions because of lower recoveries caused by the strong analyte-matrix interaction.[12] For example, while activated carbon is sprayed into the flue gas of municipal waste incinerator for removal of PCDD/Fs, the carbon content of the fly ash raises up to 5% or more. In such case, the PCDD/Fs extraction efficiency turns to be very poor.[13]

This paper gives the PFE as a static solvent extraction method since the sample is allowed to statically, i.e., not flowing, extract for 5-10 minutes, with the expanding solvent vented to a collection vial. As the dynamic solvent extraction method, HPLC system, where column was replaced with extraction cell, was chosen since HPLC allows flowing extraction to be conveniently performed. The aim of this study is to compare extraction efficiency of PCDFs from fly ash between static and dynamic solvent extraction. PCDFs were chosen as the analytes because they had strong interaction with sample matrices such as fly ash and so that the extraction behaviors of PCDFs from fly ash were determined. To do so, we compared the static solvent extraction of PCDFs from fly ash with the dynamic solvent extraction and investigate the effect of temperature and static time on static solvent extraction, and the effect of temperature, flow rate, solvent volume and dynamic time on dynamic solvent extraction. Little data have existed that describe the relative efficiency of static and dynamic solvent extraction of PCDFs from fly ash. It should be noted that the purpose of this investigation is to compare extraction parameters on extraction efficiency rather than to obtain quantitative recoveries.

Experimental

PCDFs Standards and Fly Ash Sample

PCDFs consisting of 2,3,7,8-tetrachlorinated dibenzo-furans (TCDF), 1,2,3,7,8-pentachlorinated dibenzofuran (PeCDF), 1,2,3,4,7,8-hexachlorinated dibenzofuran (HxC-DF), 1,2,3,4,6,7,8-heptachlorinated dibenzofuran (HpCDF) and octachlorinated dibenzofuran (OCDF) were purchased from Accustandard (125 Market St. New Haven, CT). A stock solution containing a mixture of 0.5 μg/mL was prepared in toluene for each compound.

The fly ash was collected from the Mokdong municipal solid waste incinerator (Seoul, Korea). The sample was dried at room temperature and then at 110 ℃ in an oven to remove water content. 0.5 g of the sample was spiked at 50 ng/g with PCDFs prior to aging at 110 ℃ for 24h.

Reagents

All HPLC grade organic solvents (methanol, dichloromethane, n-hexane, toluene and acetonitrile) used were purchased from Burdick & Jackson (Muskegon, MI, USA). Isopropyl alcohol (IPA) was purchased from Kanto Chemical (Tokyo, Japan). Silica gel (230-400 mesh, Merck, Darmstadt, Germany) was initially rinsed with methanol twice, and then with dichloromethane twice. It were then activated at 180 ℃ for at least 12 hours. Anhydrous sodium sulfate (Merck, Darmstadt, Germany) was used to protect the packing materials in the multi-layer silica gel column.

Static Solvent Extraction

Static solvents were prepared by allowing an associated organic solvent to pressurized fluid extractor, Dionex ASE 200 (Dionex GmbH, Idstein, Germany) at 500 psi. Toluene and Toluene-IPA mixtures were used as extracting solvents. 0.5 g of fly ash sample was extracted with a stainless steel vessel with a volume of 7mL. The time for static extraction was 1, 5 or 10 min, after 5min of equilibration. Following the static extraction, the solvent within the vessel was flushed. As a final step, the vessel was purged with gaseous nitrogen. The extract was evaporated and then reconstituted with 2-3 mL of hexane solution for the following multi-layer silica gel column clean-up.

Dynamic Solvent Extraction

Dynamic solvents were prepared by allowing an associated organic solvent to Shimadzu Liquid Chromatograph HPLC pump system (Shimadzu, Japan). Samples were prepared by weighing 0.45 g of fly ash into an extraction cell fitted with stainless steel frit at the outlet. The cell is loaded into HPLC system. The sample was subjected to an equilibration step for 20 min, followed by a dynamic step for 3.5, 7.0 or 14 min. The experimental conditions used for dynamic extraction were the following: solvent, toluene-IPA mixture (100:0, 95:5, 90:10, 80:20, v/v); cell temperature, 60 or 80 ℃; solvent volume, 3.5, 7.0 or 14 mL; flow rate, 0.5, 1.0 or 2.0 mL/min. The short extraction times were purposely utilized so that sub-quantitative recoveries were achieved; thereby allowing one to compare directly the effect of temperature, flow rate, solvent volume and dynamic time on dynamic extraction of the target analytes. During the dynamic step, the extracts were driven to a round flask. The extract was evaporated and then reconstituted with 2-3 mL of hexane solution for the following multi-layer silica gel column clean-up.

Removal of Chromatographic Interferences

The clean-up of extracts was accomplished using a multi-layer silica gel column, which had been packed in this order, neutral (2 g), acidic (6 g), and neutral (4 g) silica gel. The column was eluted with 60 mL of n-hexane. The eluent was concentrated using a rotary evaporator to 2-3 mL and transferred into a 7-mL vial. Nitrogen evaporation was performed to remove n-hexane, and then 100 μL of acetonitrile was added for the quantification by HPLC-UV.

HPLC-UV Analysis Procedure

The amount of PCDFs in the liquid extracts was determined using a Kromasil KR100-5C18 column (250×4.6 mm, Eka Chemicals AB, Bohus, Sweden). The HPLC system used in this study was an M920 delivery pump (Young-Lin, Korea) equipped with an SPD-10A UV-visible detector (Shimadzu, Japan) and C-R6A integrator (Shimadzu). The injected volume was 20 μL, with the flow rate of the mobile phase at 1.0 mL/min at 40 ℃. An acetonitrile-water (90:10, v/v) solution was used to separate the analytes in 40 min. The chromatograms were then recorded at 250 nm (A.U.F.S.=0.005).

Results and Discussion

1. Static solvent extraction

Effect of Temperature

The effect of temperature on static solvent extraction of PCDFs from fly ash is shown in *Table* 1. Throughout all of toluene-IPA mixtures, the recoveries of PCDFs dramatically were increased with the temperatures. From the results, applied temperature was an important parameter for the higher recoveries because higher temperature enhanced the desorption of PCDFs from the active sites of the sample matrix. Langenfeld et al. suggested that the desorption of the analytes from the environmental matrices requires overcoming the energy barrier of desorption, which could be accomplished by increasing the extraction temperature.[11] The higher temperature also gives an increase in solubility and mass transfers resulting in higher extractabilities of solvent. In addition, the higher temperature breaks the equilibrium between analytes and matrix on adsorptive sites of matrix surface.[14]

Effect of Toluene-IPA Mixtures

The effect of toluene-IPA mixtures on static solvent extraction of PCDFs from fly ash is also shown in *Table* 1. In our previous works, the pressurized fluid extraction of PCBs and PCDDs from fly ash showed the higher recoveries at 95:5 (v/v) of toluene-IPA mixtures than the other mixtures (100:0, 90:10 & 80:20, v/v).[15] From the results, it was supposed that IPA increases the penetration of the toluene between the matrix by a swelling effect, and that toluene lowers the activation energy barrier of desorption. However, in this study, throughout all temperatures little difference was found between 100:0 (v/v) and 95:5 (v/v) of toluene-IPA while lowest recoveries were obtained at 80:20 (v/v).

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Table 1. Recovery and average recovery [mean±S.D. (%) (n=3)] of PCDFs from fly ash by static solvent extraction of the different temperatures and toluene-IPA mixtures

Temp. (℃)	40	60	80	100	120
Toluene:IPA (v/v)			100:0		
TCDF	21.5 (2.6)	29.3 (3.3)	41.0 (2.8)	55.7 (9.6)	69.8 (2.0)
PeCDF	22.6 (2.3)	32.1 (2.1)	54.6 (7.3)	68.8 (5.0)	83.6 (6.5)
HxCDF	25.1 (3.7)	36.8 (5.2)	56.7 (6.5)	72.8 (6.4)	79.0 (7.1)
HpCDF	32.6 (5.1)	47.6 (4.8)	62.3 (8.1)	75.3 (6.6)	79.6 (8.1)
OCDF	32.6 (4.1)	44.9 (4.9)	69.0 (8.1)	75.8 (5.6)	77.0 (6.4)
AVG	26.9 (3.5)	38.1 (3.9)	56.7 (6.5)	69.7 (4.6)	77.8 (5.9)
Toluene:IPA (v/v)			95:5		
TCDF	21.2 (5.8)	33.5 (0.8)	29.3 (9.0)	55.9 (12)	71.2 (7.3)
PeCDF	23.5 (3.7)	37.3 (1.2)	53.5 (9.7)	65.7 (7.6)	82.0 (7.0)
HxCDF	23.5 (3.2)	46.5 (5.6)	52.8 (7.3)	66.2 (6.0)	76.6 (6.3)
HpCDF	29.7 (3.7)	47.0 (1.6)	60.0 (9.8)	68.8 (5.0)	79.7 (6.1)
OCDF	24.9 (6.2)	47.7 (0.7)	64.5 (9.8)	67.6 (8.0)	78.6 (3.6)
AVG	24.6 (4.5)	42.4 (1.3)	52.0 (9.0)	64.8 (6.6)	77.6 (5.9)
Toluene:IPA (v/v)			90:10		
TCDF	19.6 (0.5)	30.5 (2.7)	36.2 (9.7)	54.0 (6.8)	68.3 (1.8)
PeCDF	21.1 (4.0)	35.6 (3.4)	48.6 (4.0)	63.1 (4.7)	78.0 (2.9)
HxCDF	20.0 (3.9)	34.6 (4.7)	46.7 (4.8)	63.0 (4.9)	70.0 (5.3)
HpCDF	25.8 (6.8)	42.7 (3.3)	53.6 (5.7)	65.7 (6.5)	71.8 (5.3)
OCDF	29.6 (5.2)	44.9 (2.1)	54.9 (5.7)	66.1 (7.6)	66.3 (3.6)
AVG	26.8 (3.8)	37.7 (3.2)	48.0 (6.0)	62.4 (3.3)	70.9 (2.9)
Toluene:IPA (v/v)			80:20		
TCDF	14.5 (1.9)	26.6 (0.7)	38.1 (3.0)	47.7 (9.7)	52.8 (1.5)
PeCDF	13.6 (3.1)	34.1 (0.5)	41.8 (3.8)	58.6 (4.4)	71.6 (4.3)
HxCDF	15.1 (2.1)	38.3 (3.3)	43.2 (4.8)	61.8 (8.1)	69.7 (4.8)
HpCDF	21.0 (2.3)	40.4 (1.7)	44.7 (5.7)	63.6 (6.5)	75.6 (3.8)
OCDF	24.2 (1.3)	40.8 (1.9)	45.1 (7.3)	63.3 (9.6)	75.1 (4.0)
AVG	17.3 (2.1)	36.0 (1.2)	42.6 (4.6)	59.0 (5.7)	69.0 (3.0)

Therefore, it could be supposed that IPA did not enhance the recovery by acting as the matrix-swelling solvent for the extraction of PCDFs from fly ash because the analytes did not adsorb strongly within sample matrix.

Effect of Static Time

The effect of static time on the variation in the average recoveries of PCDFs is shown in *Fig.* 1. The increase in static time from 1 to 5 min gave the increase in the average recoveries of PCDFs: 41 → 60%, at 100:0 (v/v) of toluene-IPA while the increase from 5 to 10 min did not. The trend was also confirmed at 95:5 (v/v) of toluene-IPA mixture. Therefore, 5 min of static time was sufficient for kinetic desorption of PCDFs from fly ash.
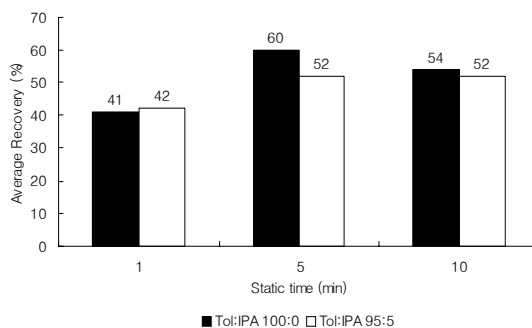

Fig. 1. Average recovery of PCDFs from fly ash by static solvent extraction of the different static times and solvent-compositions.

Table 2. Recovery and average recovery [mean±S.D. (%) (n=3)] of PCDFs from fly ash by dynamic solvent extraction of the different temperatures and solvent compositions

Temp. (℃)	60	80			
Toluene:IPA (v/v)	100:0	100:0	95:5	90:10	80:20
TCDF	20.3 (1.1)	34.8 (3.0)	31.5 (1.4)	31.9 (1.5)	30.3 (2.3)
PeCDF	22.6 (1.7)	40.6 (1.5)	36.8 (1.6)	36.7 (1.1)	36.7 (2.9)
HxCDF	27.4 (0.2)	50.1 (1.5)	41.4 (0.7)	43.7 (2.4)	43.5 (4.0)
HpCDF	34.1 (1.9)	57.9 (2.3)	53.2 (0.6)	52.9 (2.6)	52.3 (1.6)
OCDF	37.8 (1.0)	58.0 (3.2)	51.7 (1.0)	53.6 (1.1)	55.3 (1.4)
AVG	28.4 (0.6)	48.9 (1.8)	42.9 (0.3)	43.8 (1.4)	43.6 (2.4)

2. Dynamic Solvent Extraction

Effect of Temperature and Toluene-IPA Mixtures

Table 2 shows the effect of temperature and toluene-IPA mixture on dynamic solvent extraction of PCDFs from fly ash. When the temperature was increased from 60 to 80 ℃, the average recoveries of PCDFs were increased from 28.4 to 48.9%. It is due to the accelerated kinetic processes for the desorption of analytes from the sample matrix at the higher temperatures, compared to the conditions when solvents at lower temperature are used. The use of 100:0 (v/v) of toluene-IPA showed higher recoveries than the other mixtures as shown in *Table* 2. Likewise with static solvent extraction, therefore, temperature was important parameter and the small addition of IPA to toluene did not show elevated recoveries of PCDFs.

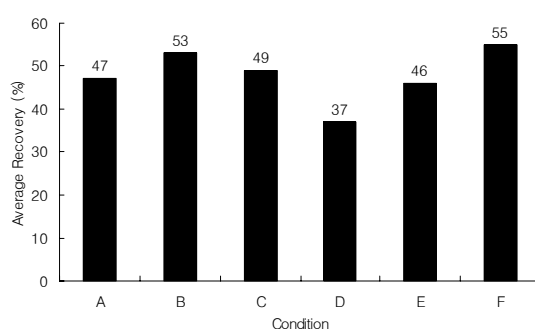*Effect of Flow Rate, Solvent Volume and Dynamic Time*

The experimental conditions that were used in this study are summarized in *Table* 3. Contrary to static solvent extraction, the dynamic solvent extraction is controlled by the flow of extracting solvent. *Fig.* 2 shows the effect of flow rate, solvent volume and dynamic time on the average recoveries obtained from dynamic solvent extraction.

From the comparison of condition B, C and D, although the constant solvent volume of 7.0 mL was used, the average recovery was decreased from 53 to 37% as the dynamic time was decreased by the increase of flow rate from 0.5 to 2.0 mL/min. The trend was also found from the comparison of condition E and F.

From the comparison of condition A and D, although the solvent volume was increased from 3.5 to 7.0 mL, the average recovery was decreased from 47 to 37% as dynamic time was decreased from 7.0 to 3.5 min by the increase of flow rate from 0.5 to 2.0 mL/min. The trend was also found from the comparison of condition B and E.

Table 3. Experimental conditions of dynamic solvent extraction at 100 ℃ and 100:0 (v/v) of toluene-IPA mixture

	Condition					
	A	B	C	D	E	F
Flow Rate (mL/min)	0.5	0.5	1.0	2.0	2.0	1.0
Solvent Volume (mL)	3.5	7.0	7.0	7.0	14	14
Dynamic Time (min)	7.0	14	7.0	3.5	7.0	14

Fig. 2. Average recovery of PCDFs from fly ash by dynamic solvent extraction of the different flow rates, solvent volumes and dynamic times (Experimental conditions corresponding from A to F are listed in *Table* 3).

From the comparison of condition A, C and E, although the flow rate and solvent volume were increased simultaneously, the little variation in average recovery was found at constant dynamic time of 7.0 min. The trend was also found from the comparison of condition B and F.

From above results, therefore, it is concluded that dynamic time is more effective parameter for elevated dynamic extraction of PCDFs from fly ash than flow rate and solvent volume because the recoveries were proportional to dynamic time. It implies that dynamic extraction of PCDFs from fly ash is mainly controlled by kinetic/desorption process rather than solubility/elution. When large amounts of fat are extracted from food products using SFE, a higher flow rate yields higher recoveries.[16] This indicates that the extraction is limited primarily by solubility considerations.[12,17] However, this phenomenon is not applied to samples whose interaction with analytes is strong since recoveries are more dependent on extraction time than on the volume of extraction fluid used.[18]

As the solvent volume and dynamic time were simultaneously increased at the constant flow rate, the average recoveries of PCDFs were increased as shown, respectively, from comparison of condition A and B, condition C and F, and condition D and E. The increases in recovery are due to the increase in dynamic time rather than solvent volume because dynamic time is the more important parameter than flow rate and solvent volume as mentioned above.

3. Comparison of static solvent extraction with dynamic solvent extraction

In this study, solvent extraction was divided into two types: the static and the dynamic. From the results of *Table* 1 and 2, the static and dynamic solvent extraction of PCDFs showed, respectively, 38.1 and 28.4% of average recoveries using 7 mL of toluene at 60 ℃. At the higher temperature of 80 ℃, the static and dynamic solvent extraction of PCDFs showed, respectively, 56.7 and 48.9% of average recoveries. Therefore, the static solvent extraction gave the higher recovery than dynamic solvent extraction at the same

volume of solvent and temperature. The static (no-flow) solvent extraction allows a better penetration of extraction fluid into the matrix than the dynamic (flowing) does. The dynamic extraction allows the higher solubility of analyte in the extracting solvent. Therefore, the above results imply that static solvent extraction rather than dynamic should be performed to overcome the strong analyte-matrix interaction such as PCDFs-fly ash because the extraction of PCDFs from fly ash is controlled by kinetic/desorption process.

First of all, temperature was most important parameter for the elevated recovery than extraction type because dynamic solvent extraction at 80 ℃ showed higher recovery than static solvent extraction at 60 ℃ as shown in *Table* 1 and 2 (average recovery, 48.9% vs. 38.1%).

4. Removal of Chromatographic Interferences

All the extracts were analyzed using HPLC-UV which is available to detect the amount spiked. Fly ash samples are loaded with a great variety of organic interferences. After the extractions, residual chromatographic interferences disturbed the separation and decrease the sensitivity of the HPLC-UV analysis procedure, resulting in uncertain quantification of PCDFs. To avoid such problems, multi-layer silica gel column clean-up was chosen. The extracts obtained from fly ash could be purified through the multi-layer silica gel column clean-up as shown in *Fig.* 3.

Conclusions

In this study, temperature was an effective extraction parameter because higher temperature showed the higher recoveries. The effect of matrix swelling by IPA did not enhance the recovery of PCDFs as little difference was found between 100:0 (v/v) and other mixtures of toluene-IPA. In static extraction, 5 min of static time was sufficient for kinetic desorption of PCDFs from fly ash. Dynamic time was more effective parameter for elevated dynamic extraction of PCDFs than flow rate and solvent volume because the recoveries were more directly influenced by dynamic time. From the comparison of
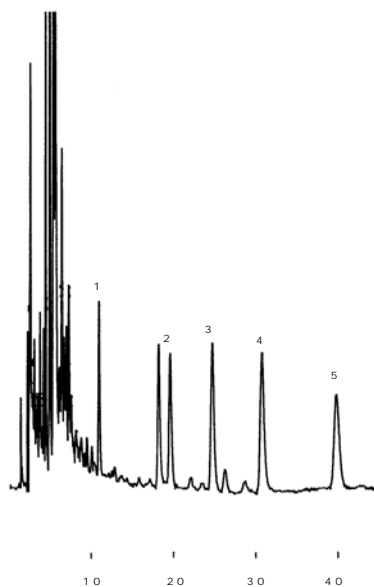
Fig. 3. HPLC UV Chromatograms of fly ash extract purified by multi-layer silica gel column clean-up. Peaks: 1=2,3,7,8-TCDF, 2=1,2,3,4,7,8-HxCDF, 3=1,2,3,4,6,7,8-HpCDF, 4=OCDF.

static and dynamic extraction, the static solvent extraction was more effective method than dynamic solvent extraction because the former gave the higher recovery than the latter at the constant volume of solvent and temperature. However, above all things, temperature was the most important parameter for the elevated recovery than extraction types.

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