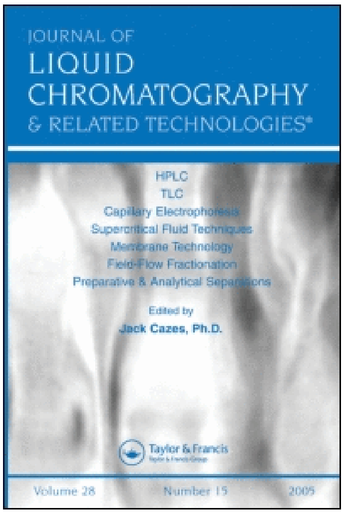

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EFFECT OF SOLVENT AND TEMPERATURE ON EXTRACTION OF POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED DIBENZODIOXINS FROM FLY ASH

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ABSTRACT

The effect of solvent and temperature on the extraction of two polychlorinated biphenyls (PCBs) and five polychlorinated dibenzodioxins (PCDDs) from fly ash is investigated and the variations in recoveries of these analytes are explained. The extraction is performed using chromatographic elution, ultrasound-assisted extraction (UAE), enhanced-fluidity liquid extraction (EFLE), and pressurized fluid extraction (PFE). In each of the extraction methods used, only the use of isopropanol-toluene mixtures (5:95 or 10:90, v/v) shows higher recoveries than the use of toluene alone. Applied temperature is an important factor for the higher recoveries throughout all the extraction methods. After each extraction,

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chromatographic interferences are removed through a multilayer silica gel column clean-up. The quantification of PCBs and PCDDs is performed using HPLC-UV.

INTRODUCTION

Ultrasound-assisted extraction (UAE) is an extraction technique that has been used to extract organic compounds from environmental solid samples. The reported recovery efficiencies are slightly lower, or equal to those, in a Soxhlet extraction.(1) New extraction techniques have been established in order to reduce the volume of solvents required for extraction, to improve the precision of the analyte recovery, and to reduce extraction time and sample preparation costs. Such techniques include supercritical fluid extraction (SFE),(2,3) enhanced-fluidity liquid extraction (EFLE),(4,5) and pressurized fluid extraction (PFE).(6,7)

Adjusting an extraction temperature has been an approach to increase extraction efficiencies.(8,9,10) Raising the extraction temperature can lead to an increase in the kinetics of the extraction desorption process. Increased temperature can disrupt the strong analyte-matrix interactions in the active sites of the sample matrix, or lessen analyte-matrix interactions by overcoming the activation energy barrier for the desorption process.

The extraction of organic compounds, such as PCBs and PCDDs, from fly ash, requires more efficient conditions because of low recoveries caused by the strong analyte-matrix interaction.(11) In general, toluene has been known as a good solvent for the extraction of PCBs and PCDDs from various solid matrices.(6,12,13) However, the effect of a mixture containing a small proportion of polar solvent to toluene on the extraction of PCDDs from a solid matrix, has rarely been studied. The purpose of this study is to investigate the effect of solvent mixtures on the extraction of PCBs and PCDDs from fly ash. In addition, the effect of temperature on UAE, EFLE, and PFE, is also investigated.

EXPERIMENTAL

Standards and Chemicals

The following reagent-grade standards were obtained from Ultra Scientific (250 Smith Street, North Kingstown): 2,2',4,5'-tetrachlorinated biphenyl (4B), 2,3,4,5,6-pentachlorinated biphenyl (5B), 1,2,3,4-tetrachlorinated dibenzodioxin (4D), 1,2,3,4,7-pentachlorinated dibenzodioxin (5D), 1,2,3,4,7,8-hexachlorinated dibenzodioxin (6D), 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin (7D), and octachlorinated dibenzodioxin (8D). Stock solutions containing a mixture of PCBs of 5.0 μg/mL and PCDDs of 0.45 μg/mL were prepared in toluene for each compound. All solvents were HPLC grade from J.T.Baker (Phillipsburg, NJ, USA).

Fly ash was obtained from the Mokdong municipal waste solid incinerator (Seoul, Korea). The fly ash was air-dried to remove water content. An aliquot of fly ash of 0.5g was spiked at 500 ng/g level with a stock solution of 4B and 5B, and at 45 ng/g with 4D, 5D, 6D, 7D, and 8D.

Silica gel (230-400 mesh, Merck, Darmstadt, Germany) was first rinsed with methanol twice, and then with dichloromethane twice. Consecutively, it was activated at 180°C for at least 12 hours. Anhydrous sodium sulfate (Merck, Darmstadt, Germany) was used to protect the packing materials in the multilayer silica gel column.

Extraction Using Chromatographic Elution

The glass chromatography column (20 × 2 Cm I.D.), which had a stopper, was packed with 1 g of anhydrous sodium sulfate, followed by 0.5 g of fly ash sample. The column was eluted with 30 mL of toluene, or mixtures of isopropanol and toluene. The extract was evaporated and then reconstituted with 2-3 mL of hexane solution for the following multilayer silica gel column clean-up.

Ultrasound-Assisted Extraction

The extraction was performed using a *60* Sonic Dismembrator (Fisher Scientific, Pittsburgh, PA, USA). 10 mL of liquid solvent was added to 0.5 g of fly ash sample. The mixture was sonicated for 3 min; it was then centrifuged for 5 min. The solvent supernatant was transferred to a round flask and was concentrated to 2-3 mL by a rotary evaporator. The extract was evaporated using nitrogen gas, and then reconstituted with 2-3 mL of hexane solution for the following multilayer silica gel column clean-up.

Enhanced-Fluidity Liquid Extraction

Enhanced-fluidity liquid extraction (EFLE) was carried out using a Suprex Model SFE/50 (ISCO, Lincoln, NE) extractor. 0.5 g of sample was put into an extraction vessel of 5mL. Carbon dioxide was pressurized at 30.4 Mpa (300 atm), and passed through the extraction vessel at a flow rate of 1.0 mL/min. The concentrations of the modifier (toluene or mixtures of isopropanol and toluene) added to the CO_2 fluid were 3 mL for static modification and 13.3% for dynamic modification. The sample was subjected to the static step for 5 min, and then to the dynamic step for 20 min.

During the dynamic step, the extracts were driven to a glass bead column trap at -10ºC. The trap was rinsed with 4.0 mL of dichloromethane that was pumped through it at 0.5 mL/min and 25ºC. The eluent was collected in a 7 mL vial. The extract was evaporated, and then reconstituted with 2-3 mL of hexane solution for the following multilayer silica gel column clean-up.

Pressurized Fluid Extraction

PFE was carried out using a Dionex ASE 200 (Dionex GmbH, Idstein, Germany) at 13.8 MPa. Toluene and mixtures of isopropanol and toluene were used as extraction solvents. 0.5 g of sample was extracted with a stainless steel vessel with a volume of 7 mL. The time for static extraction was 5 min, after 5 min 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 multilayer silica gel column clean-up.

Multilayer Silica Gel Column Clean-up

The clean-up of extracts was accomplished using a multilayer silica gel column,(14) which had been packed in this order: neutral (2 g), acidic (6 g), and neutral (4 g) silica gel. The column was eluted with 50 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

The amount of PCBs and PCDDs in the liquid extracts was determined using a Shodex C18-5B (250 x 4.6 mm, 5 µm; Shoko, Kyoto, Japan) column. The HPLC system used in this work was a Shimadzu Liquid Chromatograph equipped with an SPD-10A UV-visible detector and C-R6A integrator. The injected volume was 20 µL, and the flow rate of the mobile phase was 1.0 mL/min. The temperature was 40°C. An acetonitrile/water (93:7, v/v) solution was used to separate the analyte within 30 min. Chromatograms were recorded at 250 nm (A.U.F.S.=0.005).

Table 1. Extraction Solvent and Temperature Applied to Four Extraction Methods

Extraction Method	Extraction Solvent: Proportion of Toluene to Isopropanol (%)	Extraction Temperature (°C)
Elution	100, 95, 90, 80	25
UAE	100, 95, 90, 80	3, 40, 75
EFLE	100, 95, 90, 80	80, 100, 120
PFE	100, 95, 90	70, 100, 130

RESULTS AND DISCUSSION

The extraction solvent and temperature applied to four extraction methods in this study are summarized in Table 1.

Extraction Using Chromatographic Elution

The results of elution using the toluene and isopropanol-toluene mixtures are compared in Table 2. The elution using toluene showed an average recovery of 42.7% for PCBs and PCDDs, while the isopropanol-toluene mixture (5:95, v/v) showed 44.2%.

Whenever isopropanol was added to toluene, an increased dispersion of fly ash particulates was observed, while 100% toluene led to an aggregation of particulates. As the percent volume of isopropanol to toluene was increased from 10

Table 2. Recovery [mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by Elution of the Different Solvent-Compositions

Proportion[a]	100%	95%	90%	80%
4B	44.8(2.0)	45.4(2.1)	43.2(3.7)	42.5(3.5)
5B	51.3(2.8)	52.2(3.0)	49.0(3.4)	46.9(5.1)
4D	39.9(3.0)	40.8(4.6)	39.7(4.6)	36.5(5.2)
5D	36.8(2.4)	38.1(2.6)	35.0(2.6)	34.3(4.4)
6D	39.1(1.5)	39.4(3.0)	38.5(2.0)	35.8(4.5)
7D	39.6(2.5)	42.8(2.9)	40.6(2.8)	37.7(5.1)
8D	47.6(2.4)	50.7(2.8)	48.1(3.0)	44.7(6.4)

[a] Percent volume proportion of toluene to isopropanol, Condition: Flow rate 0.5mL/min, Elution volume 30mL.

to 20%, the average recoveries of PCBs and PCDDs were decreased from 42.0% to 39.8%. Therefore, isopropanol might increase the penetration of the toluene, which desorbs PCBs and PCDDs between the fly ash particulates.

Ultrasound-Assisted Extraction

The results of UAE using the toluene and isopropanol-toluene mixtures at three different temperatures are compared in Table 3. As isopropanol was added to toluene, the recoveries of PCBs and PCDDs were decreased at the same temperature. For example, average recoveries of PCBs and PCDDs were decreased from 69.8 to 58.9% at 75°C. It was previously reported that, for UAE of PCDDs from XAD-2 resin,(12) the solvent mixture of acetone-toluene (1:1, v/v) produced higher recoveries than toluene alone and that, for PCBs and PCDDs from charcoal,(15) the solvent mixture of isopropanol-toluene (90:10, v/v) produced higher recoveries than toluene alone. This difference might be because, unlike XAD-2 and charcoal, fly ash particulate does not have a porous structure and, instead of isopropanol, ultrasonic energy increases the penetration of the toluene between the matrix particulates.

For higher extraction recoveries, temperature had to be adjusted. As temperature was increased from 3 to 75°C, for example, using100% toluene, the average recovery was increased from 24.1 to 69.8%.

Enhanced-Fluidity Liquid Extraction

The extractions using two modifiers, toluene and mixtures of isopropanol-toluene, are compared using EFLE at 100°C (see Table 4). Among four compositions of solvents, a mixture of isopropanol-toluene (10:90, v/v) gave higher recoveries of PCBs and PCDDs. From the results, it is also supposed that isopropanol increases the penetration of the toluene between the matrix by a swelling effect, and that toluene lowers the activation energy barrier of desorption. For EFLE, temperature was also an important factor. Under composition of 90%, a temperature of 100°C gave higher recoveries than the other two temperatures (see Table 4).

Pressurized Fluid Extraction

The results of PFE using the toluene and mixtures of isopropanol-toluene at three different temperatures are compared in Table 5. Among the three compositions of solvents, the mixture of isopropanol-toluene (5:95, v/v) gave a higher

Table 3. Recovery [mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by UAE of the Different Temperatures and Solvent-Compositions

Temp(°C)	75			
Proportion	100%	95%	90%	80%
4B	60.5(1.3)	59.9(2.6)	58.5(0.2)	55.6(2.3)
5B	71.9(1.0)	70.9(2.0)	66.5(0.3)	64.7(1.0)
4D	60.8(0.8)	60.9(2.5)	53.1(0.6)	55.8(0.4)
5D	70.1(0.8)	59.1(2.9)	55.7(1.1)	54.4(0.5)
6D	73.5(0.3)	63.9(4.0)	57.7(0.6)	56.4(0.7)
7D	74.4(0.5)	63.5(3.2)	61.5(0.8)	58.9(0.6)
8D	77.8(0.9)	71.2(2.8)	67.9(0.7)	66.4(1.1)
Temp(°C)	40			
4B	32.8(1.2)	33.3(3.6)	33.0(4.9)	37.0(5.5)
5B	41.5(2.2)	41.7(3.2)	37.4(5.9)	41.4(6.0)
4D	56.5(2.1)	52.0(3.5)	31.5(1.4)	32.4(7.4)
5D	35.9(2.8)	33.4(3.3)	31.0(5.2)	32.0(3.8)
6D	36.4(2.7)	36.3(3.7)	31.2(6.1)	32.7(3.4)
7D	42.2(2.8)	38.7(2.8)	34.1(5.9)	35.2(4.2)
8D	46.9(3.2)	45.2(3.4)	38.7(6.9)	37.7(3.9)
Temp(°C)	3			
4B	20.0(0.3)	19.5(1.0)	22.0(0.4)	18.8(4.2)
5B	28.0(0.1)	25.5(1.4)	28.0(0.9)	20.9(3.3)
4D	24.0(0.2)	19.0(1.6)	26.0(1.1)	16.0(3.1)
5D	23.0(2.9)	17.8(1.9)	24.0(2.1)	12.9(2.9)
6D	20.9(0.1)	17.4(0.6)	21.0(1.1)	19.0(3.2)
7D	24.8(0.4)	23.7(1.0)	24.1(1.1)	12.9(3.0)
8D	28.0(2.8)	21.0(2.9)	22.0(3.2)	17.0(2.4)

Condition: Time 3min, Solvent volume 10mL.

average recovery of 85.7% (Solvent composition of 100 and 90% gave an average recovery of 71.7 and 69.9%, respectively). Just like EFLE, a temperature of 100°C gave higher recoveries than 70 and 130°C.

Effect of Solvent and Temperature

In each of the extraction methods, a larger proportion of isopropanol to toluene, i.e. > 10%, lowered the extraction recoveries. This can be explained by

Table 4. Recovery [mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by EFLE of the Different Temperatures and Modifier-Compositions

Temp(°C)	80	100				120
Md Proportion [a]	90%	100%	95%	90%	80%	90%
4B	84.1(2.5)	37.7(10)	87.2(1.2)	93.4(5.9)	44.4(14)	62.9(3.1)
5B	63.9(2.4)	41.4(2.0)	65.1(0.3)	84.0(5.5)	48.7(9.9)	45.7(2.5)
4D	66.1(3.9)	55.7(16)	80.9(0.7)	92.4(0.5)	60.3(5.4)	60.3(5.1)
5D	52.9(6.9)	36.5(1.5)	62.1(2.9)	74.5(0.7)	57.5(14)	41.6(3.4)
6D	61.8(5.9)	36.8(1.5)	72.1(3.9)	81.3(6.3)	60.5(9.6)	46.9(4.4)
7D	57.2(3.7)	34.0(1.6)	65.9(3.6)	89.4(1.3)	55.2(11)	38.4(5.5)
8D	55.6(4.5)	37.0(5.1)	64.4(3.2)	94.0(2.5)	43.9(8.4)	39.3(3.4)

[a] Percent volume proportion of toluene to isopropanol, Condition: Pressure 30.4 Mpa, Flow rate 1.0mL/min, St/Dy time 5/20 min, St/Dy MD 3.0mL/13.3%.

the strong interaction, which is better overcome using toluene than isopropanol, between analyte and fly ash.

When comparing all the extraction methods from Tables 2 to 5, applied temperature was found to be the main contributor to the recovery variation of PCBs and PCDDs. In EFLE and PFE, a higher temperature - i.e. 100°C - was obtained by raising the pressure. As the temperature was increased, the kinetics of the desorption process were also increased, resulting in the higher extraction recoveries.(9) In our previous work,(12,15) the optimum temperature for SFE, EFLE, and PFE of PCBs and PCDDs from different sample matrix, such as

Table 5. Recovery [mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by PFE of the Different Temperatures and Solvent-Compositions

Temp (°C)	70	100			130
Proportion	95%	100%	95%	90%	95%
4B	68.4(6.9)	82.6(2.0)	90.5(1.8)	80.7(7.6)	75.6(10)
5B	65.5(1.7)	66.6(1.8)	81.0(2.5)	62.6(0.5)	74.1(1.6)
4D	77.9(0.3)	70.5(4.3)	82.6(3.3)	68.7(1.6)	79.9(3.3)
5D	78.4(1.0)	73.4(4.4)	87.5(2.8)	71.3(2.2)	80.3(2.2)
6D	70.7(1.4)	70.2(2.0)	86.6(4.0)	67.1(1.6)	80.5(0.9)
7D	66.3(1.4)	68.6(2.6)	85.0(2.2)	68.9(1.8)	76.2(1.2)
8D	72.9(2.5)	70.1(2.5)	86.9(3.2)	70.3(1.5)	78.0(1.5)

Condition: Pressure 13.8 MPa, Time 5 min.

XAD-2 and charcoal was also 100°C. Therefore, it is found that extraction temperature is independent of sample matrices and extraction methods.

Removal of Chromatographic Interferences

Figure 1 represents an HPLC chromatogram of the eluate of multilayer silica gel column clean-up. After the extractions, the quantification of the extracts could not be performed without multilayer silica gel clean-up; chromatographic interferences made the quantification of them inaccurate. Previously, it was also

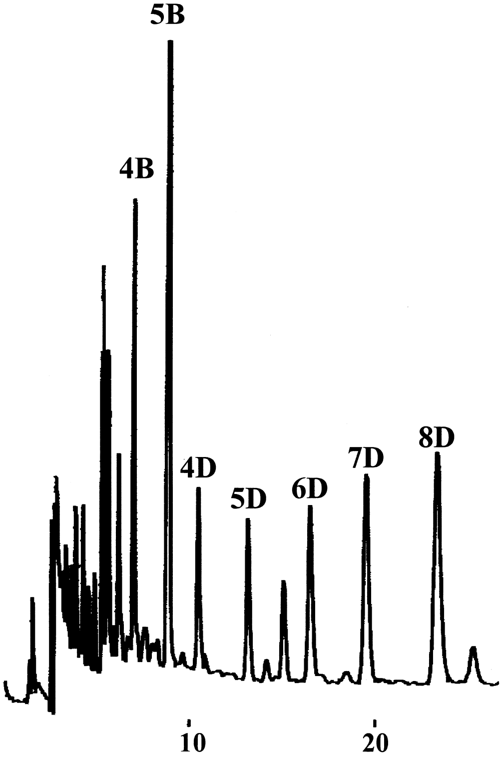

Figure 1. HPLC chromatogram of eluate of multilayer silica gel column clean-up after PFE. Peaks: 4B= 2,2,4,5-tetra chlorinated biphenyl, 5B= 2,3,4,5,6-penta chlorinated biphenyl, 4D= 1,2,3,4-tetra chlorinated dibenzodioxin, 5D= 1,2,3,4,7-penta chlorinated dibenzodioxin, 6D= 1,2,3,4,7,8- hexa chlorinated dibenzodioxin, 7D= 1,2,3,4,6,7,8-hepta chlorinated dibenzodioxin, 8D= octa chlorinated dibenzodioxin.

reported that the interference could be removed using multilayer silica gel column clean-up.(15,16)

CONCLUSION

The effect of solvent and temperature on analyte desorption was compared for elution, UAE, EFLE, and PFE. The recoveries of PCBs and PCDDs increased upon the addition of isopropanol to toluene in each of the extraction methods, except for UAE. Unlike the effect of solvents, the effect of temperature on recoveries of PCBs and PCDDs was independent of sample matrices and extraction methods. The extraction solvent and temperature were important for the efficient extraction of PCBs and PCDDs from fly ash.

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