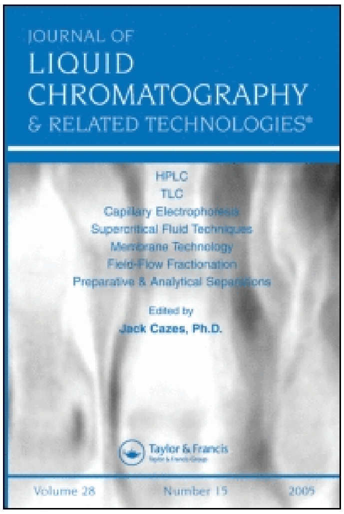

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EFFECT OF SOLVENT ON EXTRACTION OF POLYCHLORINATED BIPHENYLS AND POLYCHLORINATED DIBENZODIOXINS FROM CHARCOAL

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ABSTRACT

The effect of solvent on the extraction of two polychlorinated biphenyls (PCBs) and five polychlorinated dibenzodioxins (PCDDs) from charcoal is investigated and the variations in recoveries of these analytes are explained. The extraction is performed using chromatographic elution, ultrasound-assisted extraction (UAE) of probe- and bath-type, supercritical fluid extraction

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(SFE), and enhanced-fluidity liquid extraction (EFLE). In each of the extraction methods used, only the use of isopropanol-toluene mixtures shows higher recoveries than the use of toluene alone.

Higher recoveries are obtained using EFLE, compared with other extraction methods, even though the same amount, i.e., 30mL, of extraction solvent is used, because higher temperature is applied under higher pressure. After each extraction, chromatographic interferences are removed through a multilayer silica gel column clean-up. The quantification of PCBs and PCDDs is performed using HPLC-UV.

INTRODUCTION

Soxhlet extraction has been widely and successfully applied in the extraction of organic compounds from various matrices, such as airborne particulate and soil samples(1,2). However, Soxhlet extraction has some limitations,(3,4) including considerable sample and solvent handling, lengthy extraction time, careful cleaning and handling of expensive, fragile glassware, and bulky accessory apparatus. 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 than, or equal to, those of Soxhlet extraction(5).

In the last few years, 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).

Solid matrices, including soil and fly ash, undergo strong interactions with polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs), making them more resistant to extraction,(10,11) especially when carbon content within the matrix exists.(11) Therefore, the extraction of PCBs and PCDDs from a carbonaceous matrix such as charcoal requires more efficient conditions.

In general, toluene has been known to be a good solvent for the extraction of PCBs and PCDDs from various solid matrices(12,13). However, the effect of a mixture containig 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 effects of solvent mixture on the extraction of PCBs and PCDDs from charcoal.

EXPERIMENTAL

Standards and Chemicals

Reagent-grade standards of 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) were obtained from Ultra Scientific (250 Smith Street, North Kingstown). Stock solutions of PCBs and PCDDs were prepared in toluene.

Charcoal was obtained from Shinhwa Industry (Sunchon, Korea). The charcoal of 48-170 mesh was air-dried. Charcoal, 0.5 g, was spiked at 500 ng/g with a 5 µg/mL stock solution of 4B and 5B, and at 45 ng/g with a 0.45 µg/mL stock solution of 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. 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. All solvents were HPLC grade from J.T.Baker (Phillipsburg, NJ, USA).

Extraction Using Chromatographic Elution

The glass chromatography column (20×2 cm I.D.), which had a stopper and a plug of glass wool, was packed with 1 g of anhydrous sodium sulfate, followed by 0.5 g of charcoal sample. The column was eluted with 30 mL of toluene, or 30 mL of 5 % isopropanol in 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 Fisher Scientific (Pittsburgh, PA, USA) Solid State/Ultrasonic FS-28 (bath type) and 60 Sonic Dismembrator (probe type). Liquid solvent, 10 mL, (toluene or 5 % isopropanol in toluene) was added to 0.5 g of charcoal sample. The mixture was sonicated in a bath-type sonicator for 30 min at 40 ºC, followed by being centrifuged for 5 min. The solvent supernatant was transferred to a round flask and the residue was subjected to the same procedure twice more. The collection was concentrated to 2-3 mL by a rotary evaporator. UAE of a probe-type was also performed using the procedure described above, except for a 5 min extraction time.

Supercritical Fluid and Enhanced-Fluidity Liquid Extraction

Supercritical fluid extraction (SFE) and enhanced-fluidity liquid extraction (EFLE) were carried out using a Suprex Model SFE/50 (ISCO, Lincoln, NE) extractor. Sample, 0.5 g, and glass wool (filler) were put into an extraction vessel of 5mL, which was then maintained at 100 °C. 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 modifier (toluene or 10 % isopropanol in toluene) added to CO_2 were 10 % volume for SFE and 30 % for EFLE, respectively. The sample was subjected to static step for 5 min, followed by dynamic step for 30 (SFE) or 60 (EFLE) min. During the dynamic step, the extracts were driven to a glass bead column trap at -10 ºC. The trap was rinsed with 4.0 mL of dichloromethane that was pumped through it at 0.5 mL/min and 25 ºC. The eluent was collected in a 7 mL vial.

The experimental conditions that were used in this study are summarized in Table 1.

Table 1. Experimental Conditions of Extraction Methods

Method Number	Extraction Method	Extraction Solvent	Solvent Amount (mL)	Extraction Temperature (°C)	Extraction Time (min)
1	Elution	Toluene	30	25	60
2	Bath-UAE	Toluene	30	40	90
3	Probe-UAE	Toluene	30	75	9
4	SFE	Toluene	6 (CO_2: 60[a])	100	60
5	EFLE	Toluene	9 (CO_2:30[b])	100	30
6	Elution	Toluene+Isopropanol (95+5, v/v)	30	25	60
7	Bath- UAE	Toluene+Isopropanol (95+5, v/v)	30	40	90
8	Probe- UAE	Toluene+Isopropanol (95+5, v/v)	30	75	9
9	SFE	Toluene+Isopropanol (90+10, v/v)	6 (CO_2: 60)	100	60
10	EFLE	Toluene+Isopropanol (90+10, v/v)	9 (CO_2:30)	100	30

[a,b] The amounts of supercritical CO_2 used in SFE and EFLE, respectively.

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 Procedure

The amount of PCBs and PCDDs in the liquid extracts was determined on a Shodex C18-5B (250×4.6mm, 5µm; 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).

RESULTS AND DISCUSSION

From Table 2, it can be seen that the addition of isopropanol to toluene increased the recovery of the analytes, compared with the use of toluene alone in each of the extraction methods.

Extraction Using Chromatographic Elution

The elution using toluene showed the recovery of 13-24 % for PCBs and PCDDs, while the isopropanol-toluene mixture showed 33-42 % (compare the values of methods 1 and 6 in Table 2).

Whenever isopropanol was added to toluene, an increased dispersion of charcoal particulates was observed, while 100% toluene led to an aggregation of particulates. Therefore, isopropanol might increase the penetration of the toluene, which desorbs PCBs and PCDDs inside the charcoal matrix.

As the elution volume of isopropanol-toluene mixture was increased from 30 to 100 mL, the recoveries of PCBs and PCDDs were raised from 33-42 % to 61-75 %, where their standard deviation was 0.3-1.1 (result not shown). The elu-

Table 2. Recoveries and Standard Deviation (n=3) of PCBs and PCDDs According to Method Number from Table 1

Method	1	2	3	4	5
4B	12.9(0.9)	41.5(0.5)	79.3(2.9)	83.1(1.5)	84.0(2.1)
5B	19.8(1.2)	48.0(0.6)	80.8(0.8)	79.3(2.1)	79.3(1.0)
4D	17.1(0.9)	41.8(1.1)	81.7(1.2)	79.4(2.4)	88.1(1.9)
5D	16.7(0.4)	40.8(0.5)	81.6(2.1)	87.4(2.3)	89.6(1.6)
6D	23.3(0.7)	49.7(0.5)	80.4(2.0)	90.3(2.0)	94.8(1.8)
7D	22.8(0.5)	52.8(0.8)	83.3(0.6)	84.1(2.2)	93.2(1.4)
8D	24.0(0.6)	53.9(2.5)	86.9(1.7)	82.4(2.3)	96.4(1.4)
Method	**6**	**7**	**8**	**9**	**10**
4B	33.9(0.3)	73.0(1.1)	85.7(2.9)	92.1(1.4)	96.2(1.6)
5B	40.8(1.6)	78.5(0.9)	85.6(3.5)	96.4(2.4)	101.8(4.4)
4D	34.0(0.1)	61.6(1.9)	91.2(4.7)	85.9(1.2)	93.8(2.2)
5D	33.1(0.5)	58.9(0.8)	82.2(2.5)	90.3(2.3)	98.5(0.5)
6D	39.7(0.3)	67.5(0.5)	93.0(6.9)	92.0(1.2)	99.5(2.8)
7D	37.6(0.4)	67.6(1.7)	84.8(2.8)	86.8(2.1)	97.2(1.2)
8D	42.2(0.4)	64.8(2.2)	87.6(4.3)	83.4(1.4)	99.2(2.1)

4B, 5B, 4D, 5D, 6D, 7D, and 8D were abbreviated in the experimental section.

tion of the larger volume was time-consuming and laborious because the elution of 100 mL required 200 min.

Ultrasound-Assisted Extraction (Bath- and Probe-Type)

The results of UAE using the toluene and isopropanol-toluene mixture for the bath- and the probe-type are compared in method 2, 3, 7, and 8 of Table 2. When isopropanol was added to toluene, the recoveries of PCBs and PCDDs were increased from 41-54 % to 59-79 % in methods 2 and 7 of Table 2. In the probe-type UAE (methods 3 and 8 of Table 2), the isopropanol-toluene mixture also showed increased recoveries compared with toluene alone. Previously, it was reported that, for UAE of PCDDs from XAD-2 resin, the solvent mixture of acetone-toluene (1:1, v/v) produced higher recoveries than toluene alone(13). The ultrasonic energy of the probe-type apparatus was stronger than the bath-type, so that a higher temperature was obtained with probe-type (40°C vs. 75°C in Table 1). As the result, the UAE of the probe-type procedure showed higher recoveries than that of the bath-type.

Supercritical Fluid and Enhanced-Fluidity Liquid Extraction

The extractions using two modifiers, toluene and a mixture of isopropanol and toluene, are compared using SFE and EFLE, respectively (see the values in methods 4, 5, 9, and 10 of Table 2). In the case of both SFE (methods 4 and 9) and EFLE (methods 5 and 10), it is supposed that isopropanol increases the penetration of the toluene inside the matrix by a swelling effect and that toluene lowers the activation energy barrier of desorption.

The variance in recoveries depended upon whether the isopropanol was added to toluene or not. The addition of isopropanol to toluene, comparing methods 4 and 9, resulted in a larger increase in the recoveries of PCBs than of PCDDs. This also can be observed in methods 5 and 10. When methods 5 and 9 were compared, more PCBs were extracted in method 9, while more PCDDs were extracted in method 5. Therefore, although less volume of modifier was used, the increase of extraction fluid polarity by the addition of isopropanol led to the increase in recovery of PCBs more polarisable than PCDDs. For the extraction of PCDDs, a larger amount of modifier, i.e., EFLE, was required. From a comparison of the values of SFE and EFLE shown in Table 2, the recoveries were increased at a higher modifier concentration; (the proportions of modifier to CO_2 are 10 and 30% in SFE and EFLE, respectively) whether toluene was mixed with isopropanol or not (compare the values of methods 4 and 5, and methods 9 and 10), although the CO_2 volume of SFE was larger.

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 the strong analyte-charcoal interaction which is better desorbed using toluene than isopropanol.

When comparing all the extraction methods in Tables 1 and 2, applied temperature was found to be the main contributor to the recovery variation of PCBs and PCDDs. In SFE and EFLE, a higher temperature, i.e., 100°C, was obtained by raising the pressure to 30.4 MPa. As the temperature was increased, the kinetics of the desorption process were also increased, resulting in the higher extraction recoveries(22,25).

After SFE and EFLE, the partial quantification of the extracts could be performed without multi-layer silica gel clean-up. However, the HPLC peaks of two PCBs and TCDD showed overlapping with the neighbouring interference (see (b) of Figure 1). It made their quantification inaccurate. Nonetheless, from a comparison of Figure 1(a) with 1(b), SFE and EFLE were found to be the cleaner and more selective extraction methods.

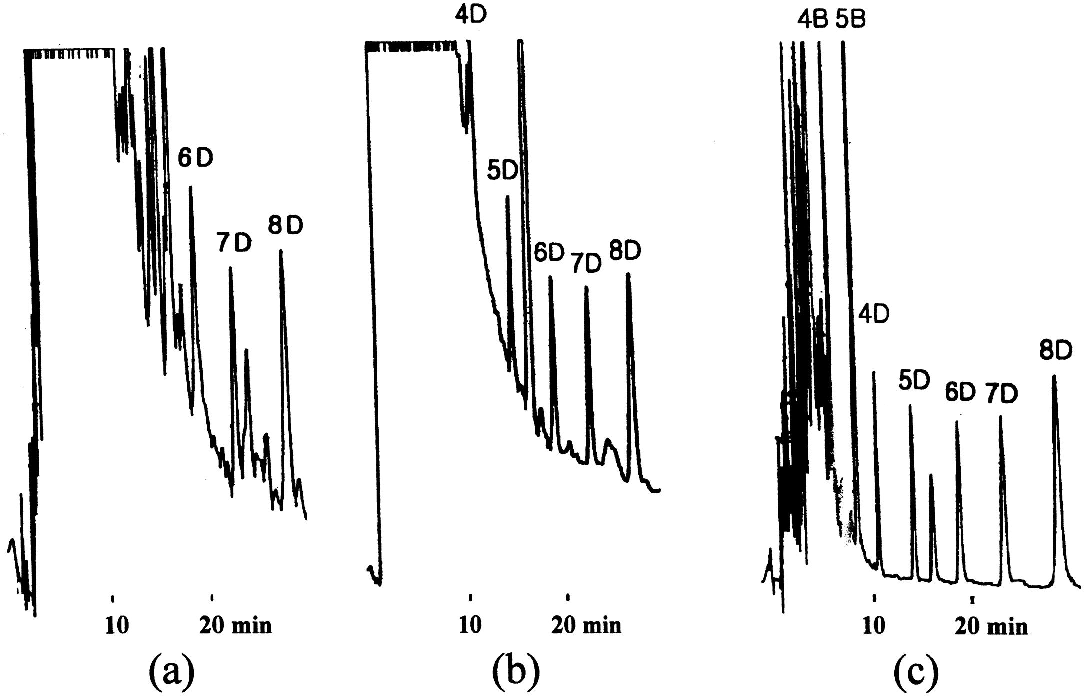

Figure 1. Chromatograms of charcoal extracts. (a) Ultrasound-assisted extraction (probe-type), no multi-layer silica gel column clean-up. (b) Supercritical fluid extraction, no multilayer silica gel column clean-up. (c) Supercritical fluid extraction, multilayer silica gel column clean-up. Peaks: 4B= 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.

CONCLUSION

The effect of solvent on analyte desorption was compared for UAE, SFE, and EFLE. The recoveries of PCBs and PCDDs increased upon the addition of isopropanol to toluene in each of the extraction methods. The addition of isopropanol to toluene resulted in a larger increase in the recoveries for PCBs than for PCDDs. By using solvents at higher temperatures rather than other extraction methods, EFLE achieved rapid extractions, reduced solvent expenditure, and had higher recoveries. The extraction solvent and temperature were important for the efficient extraction of PCBs and PCDDs from charcoal.

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