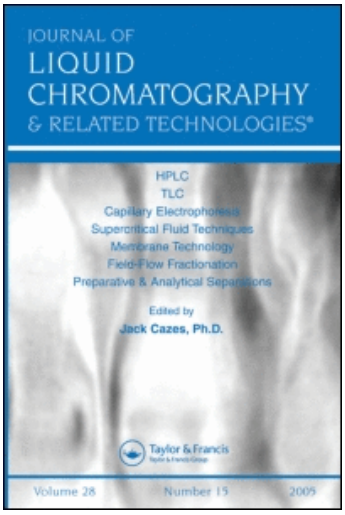

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J. S. Yang[a]; W. -S. Kim[a]; D. W. Lee[a]; E. K. Yu[b]
[a] Department of Chemistry, Yonsei University, Seoul, Korea [b] Department of Chemistry, Sejong University, Seoul, Korea

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ENHANCED-FLUIDITY LIQUID EXTRACTION OF PCBs AND PCDDs FROM FLY ASH. EFFECT OF STATIC/DYNAMIC MODIFICATION AND FLOW RATE

J. S. Yang,[1] W.-S. Kim,[1] D. W. Lee,[1,*] and E. K. Yu[2]

[1] Department of Chemistry, Yonsei University, Seoul, 120-749, Korea
[2] Department of Chemistry, Sejong University, Seoul, 143-747, Korea

ABSTRACT

The extraction of two polychlorinated biphenyls (PCBs) and five polychlorinated dibenzodioxins (PCDDs) from municipal solid waste incinerator (MSWI) fly ash is investigated using enhanced-fluidity liquid (EFL) conditions. Static/dynamic modification, static time, and flow rate are investigated, and trends and controlling factors in the recoveries of analytes are explained. Static modification, rather than dynamic, is more effective in the recovery of some analytes, which consist of hexa chlorinated dibenzodioxin (6D), hepta chlorinated dibenzodioxin (7D), and octa chlorinated dibenzodioxin (8D), and which adsorb more strongly with a matrix.

Throughout the investigation of static time from 0 min to 15, the optimal time is found to be 5 min. Modification volume con-

* Corresponding author. E-mail: leedw@alchemy.yonsei.ac.kr

trolled by flow rate has little effect on recovery. After extraction, HPLC chromatographic interference is removed through a multilayer silica gel column clean-up. The quantification of the PCBs and PCDDs extracted is performed using HPLC-UV.

Enhanced-fluidity liquid extraction (EFLE) is a promising technique for the efficient extraction of analytes that are difficult to isolate from an adsorptive matrix such as fly ash.

INTRODUCTION

Supercritical fluid extraction (SFE) with CO_2 is a favorable method for the extraction of organic compounds from solid matrices because of its low critical point, low toxicity, and cost.[1–3] However, pure CO_2 sometimes fails to extract many organics efficiently from environmental solid samples. This demonstrates that CO_2 may be insufficient to either solvate some organics or interact with the analyte-matrix complex.[4] Even analytes that are quite soluble in CO_2 may not be efficiently extracted if interactions with the matrix are strong.[5]

To improve the extraction of organic compounds with pure CO_2, several approaches using modified SFE have been studied because modifiers can either increase the solubility of the target analyte or interact with active sites on the sample matrix, which can help CO_2 to efficiently extract the analyte.[1,6–9] In general, modified SFE efficiencies are improved compared to extraction using pure CO_2. The effect of the modifier depends on the analyte and the matrix.

Despite the use of modified SFE, less than quantitative recoveries have sometimes still been found.[10,11] Because of its carbon content, a solid matrix such as fly ash, has undergone strong interactions with polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs), making it more resistant to extraction.[12] Enhanced-fluidity liquid extraction (EFLE) has been applied to improve SFE and modified SFE from a strong analyte-matrix interaction.[13,14] An enhanced-fluidity liquid (EFL) is prepared by combining a commonly associated organic solvent with a large proportion of supercritical CO_2.

EFLs were previously studied for the extraction of phenolics from river sand.[15] While the SFE experiments resulted in approximately 65–104% recoveries, quantitative recoveries were obtained with the enhanced-fluidity liquid mixture of 18:2:80 mol % methanol-water-CO_2 for the eleven analytes studied. Liquid mixtures of CO_2 and polar modifiers were used for the extraction of phenolic and nitroaromatic pollutants from polygosil octadecyl poly siloxane stationary phase material.[16] Extraction fluid mixtures consisting of 10 and 20 mol % methanol in CO_2 were examined at 25, 45, and 65°C.

When large amounts of fat are extracted from food products, a higher flow rate yields higher recoveries.[5,17] This indicates that the extraction is limited primarily by solubility considerations.[4,5] However, this phenomenon is not be

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]

SFE is divided into two modes: the static and the dynamic.[19,20] The static (no-flow) mode allows a better penetration of extraction fluid into the matrix than the dynamic (flowing) mode does. The dynamic mode allows the higher solubility of analyte in the supercritical fluid.

The matrix that is considered in this study is municipal solid waste incinerator (MSWI) fly ash. Since fly ash is a carbonaceous particle adsorbing strongly with PCBs and PCDDs, it is difficult to extract them from it. A comparison of the efficiency of static and dynamic modification on EFLE of PCDDs from fly ash has rarely been done. In this study, a comparison of recoveries with supercritical fluid and liquid conditions is made. The addition of larger proportions (20–50 vol %) of modifier (isopropanol-toluene mixture) to CO_2 fluid volume is investigated as a means of extending the range of SFE for the extraction of PCBs and PCDDs.

It should be noted that, the purpose of this investigation is to compare several parameters on EFLE rather than to obtain quantitative recoveries. The relative contributions of static and dynamic modification to recovery are considered. The effect of static time and modifier volume controlled by flow rate was also compared. Finally, the relative interaction between fly ash and analytes, including PCBs and PCDDs, are discussed in order to explain trends in extraction recoveries.

EXPERIMENTAL

Standards and Chemicals

PCBs consisting of 2,2′,4,5′-tetrachlorinated biphenyl (4B), 2,3,4,5,6-pentachlorinated biphenyl (5B), and PCDDs consisting of 1,2,3,4-tetrachlorinated dibenzodioxin (4D), 1,2,3,4,7-pentachlorinated dibenzodioxin (5D), 1,2,3,4,7,8-hexachlorinated dibenzo-dioxin (6D), 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin (7D), OCDD (8D) were obtained from Ultra Scientific (250 Smith Street, North Kingstown). 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. Aliquot fly ash of 0.5 g 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.

Enhanced-Fluidity Liquid Extraction (EFLE)

All extractions were performed using a Suprex Model SFE/50 (ISCO, Lincoln, NE, USA) extractor. The sample was put into a 5 mL-size extraction vessel. Carbon dioxide was conditioned at a pressure of 30.4 Mpa and a flow rate of 0.5, 1.0, or 2.0 mL/min, respectively, to compare the effect of flow rate. A mixture of isopropanol and toluene (10:90, v/v) was used to modify CO_2.

The static and dynamic modification volumes to CO_2 at various ratios were also compared. The sample was subjected to a static step for 5 min, followed by a dynamic step for 15 min. The short extraction times were purposely utilized so that subquantitative recoveries were achieved, thereby allowing one to directly compare the effect of modifications, flow rate, and static time on EFLE of the target analytes.

During the dynamic step, the extracts were driven to a glass bead column trap at −3°C. The trap was rinsed with 4.0 mL of toluene that was pumped through it at 0.5 mL/min and 25°C. 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.

Multilayer Silica Gel Column Clean-Up

The clean-up of extracts was accomplished using a multilayer silica gel column,[21] which had been packed in the order of 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 of 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 refilled 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 × 4.6 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 at the temperature of 40°C. An acetonitrile-water (93:7, v/v) solution was used to separate the analytes within 30 min. Chromatograms were recorded at 250 nm (A.U.F.S.=0.005).

RESULTS AND DISCUSSION

Table 1 shows the recovery variations of PCBs and PCDDs with a respective volume of static and dynamic modifier. Justly, the recoveries were propor-

Table 1. Recovery [Mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by the Different Volumes of Modifier Under Static and Dynamic Modification

Type of Modification	Static					Dynamic			
Modifier Volume (mL)	0.125	0.25	0.5	1.0	2.0	0	0.15	1.5	4.5
4B	87.6(7.7)	89.2(8.5)	92.7(9.7)	97.4(9.6)	98.3(8.8)	22.3(2.2)	35.0(6.8)	83.5(6.6)	94.7(15.0)
5B	53.8(5.1)	52.2(6.5)	69.1(2.4)	74.9(6.0)	77.3(7.9)	7.6(0.4)	14.4(2.5)	60.9(5.3)	70.8 (3.6)
4D	6.9(0.7)	8.5(0.3)	19.6(1.1)	37.9(3.6)	51.7(5.4)	-	-	14.7(3.1)	40.4 (6.0)
5D	1.3(1.3)	6.0(2.0)	20.4(4.0)	36.2(6.1)	54.0(6.3)	-	-	10.0(2.1)	40.0 (5.9)
6D	-[a]	2.9(1.7)	17.6(3.0)	39.1(6.4)	57.8(5.0)	-	-	-	38.1 (5.2)
7D	-	-	10.3(2.8)	31.6(8.7)	49.9(6.8)	-	-	-	24.7 (3.8)
8D	-	-	12.2(2.1)	33.0(7.3)	53.6(7.4)	-	-	-	21.2 (3.0)

[a] "-" means "not quantified". Conditions: Pressure 30.4MPa, Temperature 100°C, Flow rate 1.0mL/min, St/Dy time 5/15min,

tional to modifier volumes in both the static and dynamic modifications. PCDDs were rarely detected in a supercritical fluid condition (lower modifier volume) but extraction was improved considerably in an enhanced-fluidity liquid condition (higher modifier volume). From a comparison of a static modification of 1.0 mL to a dynamic one of 4.5 mL, although the dynamic modifier volume was larger than static, the average recovery of PCBs and PCDDs was almost similar.

The recoveries of 4B, 5B, 4D, and 5D (4B–5D) were higher in the dynamic modification of 4.5 mL than in the static modification of 1.0 mL, while those of 6D, 7D, and 8D (6D–8D) were higher in the static than in the dynamic. These indicate that the effect of static modification is more important for the extraction of analytes that have lower recoveries.

The effect of the dynamic modifier volume controlled by three flow rates on SFE and EFLE is shown in Table 2. Two extraction fluids of 10% (SFE) and 50% (EFLE) modifier in CO_2 volume were used. Comparing SFE with EFLE at a constant flow rate, as expected, EFLE yielded more recoveries. Although modifier volume increased with flow rate in both SFE and EFLE, the recoveries had little difference in these flow rate conditions, except for 0.5 mL/min. These indicate that analyte-matrix interaction is strong, as mentioned in Langenfeld et. al.[18]

The effect of static time on SFE and EFLE under static and dynamic modifications is shown in Table 3. Regardless of modification type, at a constant static time, recoveries of analytes increased with modification volume. In static modifi-

Table 2. Recovery [Mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by the Different Flow Rates Under SFE and EFLE Conditions

Rate of Dynamic Modification[a] (%)	10 (SFE)			50 (EFLE)		
Flow Rate (mL/min)	0.5	1.0	2.0	0.5	1.0	1.6
Resulting Modifier Volume (mL)	0.75	1.5	3.0	3.75	7.5	12
4B	27.7(3.2)	83.5(6.6)	95.1(7.5)	85.8(8.4)	97.4(5.1)	97.9(10.1)
5B	8.3(0.5)	60.9(5.3)	71.6(4.2)	22.9(4.8)	75.1(6.8)	74.2 (2.1)
4D	-	14.7(3.1)	13.2(5.7)	-	50.6(7.8)	48.5 (2.0)
5D	-	10.0(2.1)	16.5(5.9)	-	50.2 (10)	56.4 (2.0)
6D	-	-	8.7(8.7)	-	52.3 (11)	57.6 (1.1)
7D	-	-	-	-	38.7 (11)	41.4 (1.9)
8D	-	-	-	-	36.3 (12)	36.6 (1.9)

[a] Percent volume proportion of modifier to supercritical CO_2. Condition: Pressure 30.4MPa, Temperature 100°C, St/Dy time 5/15min.

Table 3. Recovery [Mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash in the Different Modification Types, Volumes of Modifier and Static Times*

Type of Modification	Static												Dynamic							
Md Vol. (mL)	0.5				2.0				4.0				1.5				7.5			
St Time (min)	0	5	10	15	0	5	10	15	0	5	10	15	0	5	10	15	0	5	10	15
4B	91.1	92.7	92.9	91.8	89.9	98.3	97.4	98.2	90.1	98.3	96.9	97.4	90.5	83.5	91.5	90.6	95.4	97.4	98.6	98.1
	(2.0)	(9.7)	(10)	(2.3)	(6.7)	(8.8)	(3.3)	(7.8)	(7.3)	(3.8)	(6.2)	(6.8)	(4.1)	(6.6)	(10)	(0.1)	(5.3)	(5.1)	(4.4)	(0.5)
5B	65.3	69.1	67.4	65.2	63.3	77.3	54.9	55.5	59.2	74.7	51.5	46.0	52.3	60.9	59.4	65.3	70.1	75.1	68.2	75.4
	(1.5)	(2.4)	(3.4)	(1.3)	(7.3)	(7.9)	(2.3)	(3.7)	(3.9)	(6.1)	(3.1)	(5.3)	(3.5)	(5.3)	(6.1)	(1.1)	(6.0)	(6.8)	(6.1)	(4.9)
4D	17.4	19.6	21.4	22.8	42.9	51.7	37.7	63.6	43.5	53.9	41.8	56.6	18.7	14.7	21.1	17.2	48.6	50.6	42.6	33.2
	(1.2)	(1.1)	(0.3)	(1.4)	(4.8)	(5.4)	(6.4)	(4.5)	(4.7)	(6.5)	(4.8)	(4.1)	(3.1)	(3.1)	(5.2)	(0.7)	(5.6)	(7.8)	(2.3)	(1.4)
5D	16.8	20.4	20.1	21.4	44.7	54.0	41.4	50.5	48.9	64.4	50.9	51.6	7.2	10.0	12.6	11.6	44.4	50.2	37.5	35.9
	(0.1)	(4.0)	(0.7)	(1.3)	(3.9)	(6.3)	(1.2)	(3.2)	(3.6)	(3.2)	(5.2)	(1.3)	(0.8)	(2.1)	(3.2)	(1.6)	(4.0)	(10)	(2.1)	(5.2)
6D	5.4	17.6	16.7	17.5	54.8	57.8	45.7	57.8	53.9	73.3	59.5	74.3	-	-	13.1	8.6	49.7	52.3	46.4	46.9
	(5.4)	(3.0)	(0.1)	(0.1)	(1.3)	(5.0)	(7.0)	(3.7)	(5.3)	(7.1)	(2.4)	(2.8)			(3.0)	(2.2)	(0.9)	(11)	(3.0)	(6.7)
7D	-	10.3	9.7	10.0	39.0	49.9	36.1	42.0	45.5	64.5	48.8	49.8	-	-	-	-	38.1	38.7	35.4	35.1
		(2.8)	(0.4)	(1.0)	(2.0)	(6.8)	(2.4)	(2.4)	(6.2)	(6.2)	(3.3)	(5.2)					(4.0)	(11)	(2.2)	(5.0)
8D	-	12.2	12.0	12.5	38.1	53.6	38.6	35.7	47.9	69.7	53.1	49.4	-	-	-	-	39.4	36.3	37.1	37.4
		(2.1)	(1.5)	(1.7)	(1.2)	(7.4)	(0.9)	(1.9)	(4.2)	(4.3)	(2.9)	(3.7)					(3.8)	(12)	(2.5)	(4.6)

*Condition: Pressure 30.4MPa, Temperature 100°C, Flow rate 1.0mL/min, Dy time 15min.

cations of 2.0 and 4.0 mL, optimum static time was 5 min and the recoveries slightly decreased with time (to 15 min). Ling et. al.[19] and Lin et. al.[20] also found the decrease of recovery at longer static time than an optimal one. However, in dynamic modifications of 1.5 and 7.5 mL, static time had little effect on the extraction of analytes.

From the comparison of average recoveries, the static modification of 2.0 mL at 0 min was similar to the dynamic one of 7.5mL at 5 min and, especially, 4B–5D gave more recoveries in the dynamic modification of 7.5 mL, while 6D–8D did so in the static modification of 2.0 mL.

Table 4 and Table 5 represent the effect of a total modification through a combination of static and dynamic, and recovery ratio by the comparison of methods in Table 4, respectively. From I, II, III, IV, and V in Table 5, the recoveries naturally increased with both static and dynamic modifications because all the values were more than one (≥1.0). In addition, the values of 6D–8D were always higher than 4B–5D, indicating that 6D–8D have a stronger interaction with a matrix than 4B–5D. From a comparison between I and III, although the increased rate (three times) of the dynamic modification was higher than the static one (two times), the higher increased rate of recovery was shown inversely in the static ($1.3<1.4$, $1.9<2.1$). Therefore, static modification rather than dynamic affected the extraction of PCBs and PCDDs, especially in 6D–8D.

In V, in Table 5, 4B–5D did not show the remarkable increased rates of recovery—the ratio of recovery is 1.0—because the initial static modification

Table 4. Recovery [Mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by the Different Total Volumes of Modifier in a Combination of Static and Dynamic Modification*

Combination	A	B	C	D	E
St/Dy Md (mL/mL)	1.0/1.5	1.0/4.5	2.0/1.5	2.0/4.5	4.0/1.5
Total Md (mL)	2.5	5.5	3.5	6.5	5.5
4B	84.1(6.3)	88.0(4.8)	92.6(9.8)	96.6(7.6)	92.0(6.3)
5B	66.4(4.7)	77.1(0.1)	82.7(4.2)	82.8(7.6)	76.7(5.3)
4D	58.2(0.9)	80.4(5.8)	93.2(2.2)	95.8(3.9)	82.1(2.1)
5D	41.5(2.0)	66.0(1.0)	71.3(0.4)	79.6(7.7)	76.5(3.4)
6D	37.5(2.9)	75.5(3.7)	78.1(2.1)	90.3(3.9)	76.2(6.8)
7D	30.1(4.0)	58.9(6.6)	66.4(1.4)	77.6(2.5)	73.3(5.0)
8D	32.5(5.1)	58.4(8.8)	63.6(1.5)	80.7(0.4)	81.1(1.8)

*Condition: Pressure 30.4MPa, Temperature 100°C, Flow rate 1.0mL/min, St/Dy time 5/15min.

Table 5. Recovery Ratio Through a Comparison of Methods in Table 4

	I	II	III	IV	V	VI	VII
Comparison Variance	A vs. B St: 1.0 Dy: 1.5→4.5 (3 times)	C vs. D St: 2.0 Dy: 1.5→4.5 (3 times)	A vs. C Dy: 1.5 St: 1.0→2.0 (2 times)	B vs. D Dy: 4.5 St: 1.0→2.0 (2 times)	C vs. E Dy: 1.5 St: 2.0→4.0 (2 times)	B vs. E Const total Md : 5.5 St/Dy: 1.0/4.5 vs. 4.0/1.5	B vs. C St/Dy: 1.0/4.5 vs. 2.0/1.5
4B, 5B, 4D, 5D (4B-5D)	1.3 [a]	1.1	1.4	1.2	1.0	1.1	1.1
6D, 7D, 8D (6D-8D)	1.9	1.2	2.1	1.3	1.2	1.2	1.1

[a] The value was calculated by dividing the mean recovery of method B into that of method A of Table 4.
Condition: Pressure 30.4MPa, Temperature 100°C, Flow rate 1.0mL/min, St/Dy time 5/15min.

was 2.0 mL of efficient volume, although the increased rate of the modification is double. When considering the values of VI, in Table 5, static modification, rather than dynamic, elevated recoveries of analytes under constant total modification. In spite of lower total modification, the static modification of 2.0 mL, rather than of 1.0 mL yielded increasing recoveries (see VII of Table 5). These indicate that static modification rather than dynamic mainly contributes to extraction efficiency.

The comparative effect of static and dynamic modification on EFLE of PCBs and PCDDs under total modification of 5 mL, is shown in Table 6. Higher static modification from combination A to C gave an increase in recoveries. This trend was also shown in Table 4 or 5. From combination A to E, an optimal combination (that is, combination D, 3.0/2.0 mL) of static and dynamic modifications existed. From a comparison between the static/dynamic modifications of C (2.0/3.0 mL) and D (3.0/2.0 mL), the advantage of 3.0 mL of dynamic modification is apparent by noting that the recoveries were consistently better than those obtained by 2. 0mL for 4B – 5D. However, higher recoveries were obtained for 6D – 8D using a static modification of 3.0 mL over 2.0 mL.

In a comparison between B and E, the same trend was also found. From these results, it is concluded that dynamic modification relatively contributes to the extraction of 4B – 5D while static does so to the extraction of 6D – 8D. The reason why static modification elevated the recovery of analytes is that its effect allows a diffusion of modifier inside the matrix on which analytes adsorb strongly.[19,20]

Table 6. Recovery [Mean±S.D. (%) (n=3)] of PCBs and PCDDs from Fly Ash by the Constant Volume (5.0mL) of Modifier Under a Combination of Static and Dynamic Modification*

Combination	A	B	C	D	E
St/Dy Md (mL/mL)	0.5/4.5	1.0/4.0	2.0/3.0	3.0/2.0	4.0/1.0
4B	87.6(2.4)	90.3(5.2)	100.2(14)	92.3(5.3)	90.5(6.4)
5B	83.5(4.6)	66.0(3.8)	81.1(5.1)	65.0(4.8)	52.8(3.3)
4D	75.4(4.8)	65.6(3.3)	81.2(5.2)	71.0(0.8)	59.5(4.7)
5D	61.0(5.3)	59.8(2.7)	74.3(0.6)	69.5(4.6)	55.6(4.6)
6D	64.3(6.0)	60.9(4.3)	79.1(3.8)	84.8(9.6)	67.0(6.0)
7D	50.6(4.4)	46.7(3.3)	63.3(4.2)	69.8(3.7)	60.7(5.4)
8D	53.6(3.8)	46.0(3.8)	63.8(4.3)	72.8(3.0)	66.7(5.7)

*Condition: Pressure 30.4MPa, Temperature 100°C, Flow rate 1.0mL/min, St/Dy time 5/15min.

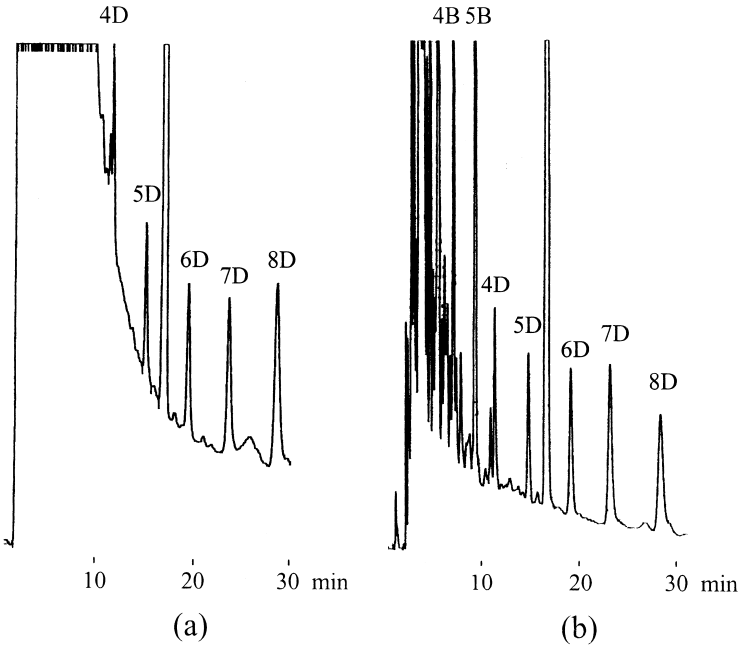

Figure 1. Chromatograms of fly ash extract. (a) No multilayer silica gel column clean-up. (b) Multilayer silica gel column clean-up. Peaks: 4B = 2,2,4,5-tetra chlorinated biphenyl, 5B = 2,3,4,5,6-penta chlorinated biphenyl, 4D = 1,2,3,4-tetra chlorinated dibenzodioxin, 5D = 1,2,3,4,7-penta chlorinated 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.

As shown in Figure 1, throughout the multilayer silica gel column clean-up, chromatographic interferences were removed, making the quantification of PCBs and PCDDs extracted possible.

CONCLUSION

The goal of this study was to evaluate the use of enhanced-fluidity liquids for the efficient extraction of PCBs and PCDDs. EFLE achieved a more efficient extraction by using a modifier at a higher concentration than modified SFE does. The rate of modification was the important variable while the effect of modifier volume controlled by flow rate was minimal. Static modification, rather than dynamic mainly contributed to the extraction of PCBs and PCDDs. The optimal

condition (3.0/2.0 mL) of a combination of static and dynamic modifications existed in a constant total modification (5.0 mL).

This work represents an important evaluation of enhanced-fluidity liquid for the extraction of adsorptive analytes from a strong interaction with a matrix.

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