

## Analytical Method for Dioxin and Organo-Chlorinated Compounds: (II) Comparison of Extraction Methods of Dioxins from XAD-2 Adsorbent

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Supercritical fluid extraction (SFE), ultrasonic extraction (USE), and accelerated solvent extraction (ASE) were compared with the well known Soxhlet extraction for the extraction of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs) from the XAD-2 resin which was used to adsorb PCDDs in the atmosphere. XAD-2 resin spiked with five PCDDs was chosen as a sample. The optimum conditions for the extraction of PCDDs by SFE were turned out to be the use of CO<sub>2</sub> modified with 10% toluene at 100 °C and 350 atm, with 5 min static extraction followed by 20 min dynamic extraction. SFE gave a good extraction rate with good reproducibility for PCDDs ranging from 68 to 98%. The ultrasonic extraction of PCDDs from XAD-2 was investigated and compared with other extractions. A probe type method was compared with a bath type. Two extraction solvents, toluene and acetone were compared with their mixture. The use of their mixture in probe type, with 9 minutes of extraction time, was found to be the optimum condition. The average recovery of the five PCDDs for USE was 82-93%. Accelerated solvent extraction (ASE) with a liquid solvent, a new technique for sample preparation, was performed under elevated temperatures and pressures. The effect of temperature on the efficiency of ASE was investigated. The extraction time for a 10 g sample was less than 15 min, when the organic solvent was *n*-hexaneacetone mixture (1 : 1, v/v). Using ASE, the average recoveries of five PCDDs ranged from 90 to 103%. SFE, USE, and ASE were faster and less laborious than Soxhlet extraction. The former three methods required less solvent than Soxhlet extraction. SFE required no concentration of the solvent extracts. SFE and ASE failed to perform simultaneous parallel extractions because of instrumental limitations.

### Introduction

The quantitative determination of polychlorinated dibenzo-p-dioxins (PCDDs) has always been a challenging analytical task. Largely because of their adsorptivity and very small amounts, PCDDs are hard to separate chromatographically and to extract from certain types of samples.<sup>1,2</sup> Among them, 2,3,7,8-substituted dioxins are of particular environmental concern because of their toxicities and accumulation in the environmental samples.<sup>3,4</sup>

Soxhlet extraction is the EPA method used commonly for the extraction of organic pollutants from solid matrices.<sup>5,6</sup> Some significant problems in the application of Soxhlet extraction to the determination of PCDDs in solid samples are well known.<sup>7</sup> Soxhlet extraction achieves good extraction rates, but requires large amounts of extraction time and large volumes of solvent. Often, more than 150 mL of toluene is required for each sample. After the extraction, this solution must be concentrated to a small volume, resulting in either contaminated air emission or costly solvent disposal.

Supercritical fluid extraction (SFE) is an attractive alternative to Soxhlet extraction.<sup>8,9</sup> SFE has been demonstrated as an effective method for the extraction of analytes from environmental samples. Applications include extraction of polynuclear aromatic hydrocarbons (PAHs),<sup>10,11</sup> organophosphorous and organochlorine pesticides,<sup>12</sup> and various priority pollutants in soil.<sup>13,14</sup> Ultrasonic extraction is also a useful alternative to classical Soxhlet extraction, owing to its

speed and simple operation.<sup>6,15,16</sup>

Accelerated solvent extraction (ASE) is another new extraction technique which allows faster extraction.<sup>17,18</sup> ASE requires small volumes of solvents. Extractions are performed at temperatures in the range of 50-200 °C to enhance the speed of elution. A pressure in the range of 5-200 atm is chosen to keep the solvent in the liquid state. Extraction time ranges from 5 to 15 min. It is generally known that the accelerated solvent extraction of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), basic, neutral, and acidic pollutants, pesticides, and herbicides achieve the similar results as the above-mentioned methods.<sup>19</sup> Similar to SFE, the automation of ASE allows a sequential extraction of samples.<sup>20</sup> Because of these advantages in speed, cost, and solvent quantities, SFE and ASE appear to be promising alternatives to other extraction methods.

The primary purpose of this study was to compare sample extraction methods for the HPLC determination of PCDDs adsorbed in XAD-2 resins. The extraction methods considered here are Soxhlet extraction, supercritical fluid extraction (SFE), ultrasonic extraction (USE), and accelerated solvent extraction (ASE). This study evaluated influences of factors such as solvents and instrumental types on the ultrasonic extraction of PCDDs. The influences of temperature on extraction efficiencies in SFE and ASE were examined. In addition to temperature, pressure and modifiers were considered to access the effect of experimental conditions on the

extraction rate of SFE. Conditions for the determination of PCBs and PCDDs in the XAD-2 resin using SFE and ASE were investigated and optimized. The results of these extractions were compared with the results of ultrasonic and Soxhlet extractions.

### Experimental Section

**Reagents.** We obtained reagent-grade standards of 2,2', 4,5'-tetrachlorinated biphenyl (TCB), 2,3,4,5,6-pentachlorinated biphenyl (PeCB), 2,2',3,3',6,6'-hexachlorinated biphenyl (HxCB), 1,2,3,4-tetrachlorinated dibenzo-p-dioxin (TCDD), 1,2,3,4,7-pentachlorinated dibenzo-p-dioxin (PeCDD), 1,2,3,4,7,8-hexachlorinated dibenzo-p-dioxin (HxCDD), 1,2,3,4,6,7,8-heptachlorinated dibenzo-p-dioxin (HpCDD), and octachlorinated dibenzo-p-dioxin (OCDD) from *Ultra Scientific* (250 Smith Street, North Kingstown). Stock solutions (PCBs: 5.0, PCDDs: 0.45 ppm) were prepared in toluene for each compound. XAD-2 resin was obtained from *Rohm and Haas* (Philadelphia, PA.). The XAD-2 resin, which had been washed and dried, was spiked with PCB and PCDDs at a few ng ( $10^{-9}$  g) levels. All solvents were HPLC grade from *Burdick & Jackson* (Muskegon, USA).

**Supercritical Fluid Extraction Procedure.** Supercritical fluid extraction (SFE) was carried out using a *Suprex Model SFE/50* extractor (Pittsburgh, PA). The  $\text{CO}_2$  was pressurized to 100–350 atm and passed through the extraction vessel at a flow rate of 1 mL/min. The extraction vessel was loaded with a 500 mg XAD-2 sample and was maintained at 35–120 °C throughout the experiment. Samples were subjected to static SFE for 5 min, followed by dynamic SFE during the extraction process. In a dynamic extraction lasting 20 min, the leached analytes were driven to a C18 column trap and then collected at -10 °C. The trap was rinsed with a liquid solvent (4.0 mL of dichloromethane) that was pumped through it at a flow rate of 0.5 mL/min and a temperature of 30 °C. The analyte solution was collected in a 7 mL vial.

**Ultrasonic Extraction Procedure.** The ultrasound-assisted extraction (USE) procedure used was based on a report by *Okamura et al.*,<sup>21</sup> with some modification. It was performed using a *Fisher Scientific* (Pittsburgh, PA, USA) *Solid State/Ultrasonic FS-28* (bath type) and *60 Sonic Dismembrator* (50W, probe type). Thus, 50 mL of a liquid solvent (acetone, toluene, or their mixture) was added to the sample (10 g of XAD-2 spiked with PCDDs). The mixture was sonicated in an ultrasonic bath for 30 min. The solvent supernatant was transferred to a round flask and the residue was subjected to the same procedure twice. The amount of solvent used was 30 and 20 mL, successively. The collected supernatant was concentrated to about 3 mL. The sonication of the probe type was performed in the same procedure as the above, except for an extraction time of 3 min. Therefore, a 10 g sample was extracted three times with acetone, toluene, or a 1 : 1 mixture of the two for 30 min for the bath type, and 3 min for the probe type at about 3 °C.

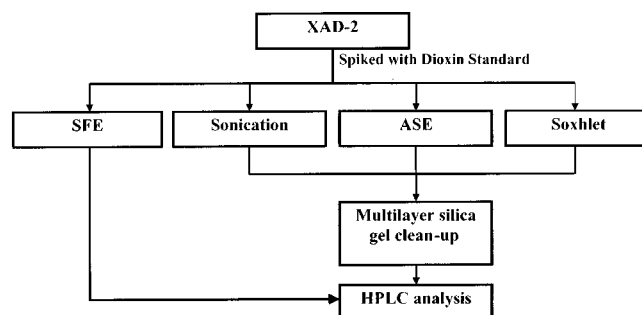
**Accelerated Solvent Extraction Procedure.** Extractions were carried out using a *Dionex ASE 200* (Dionex GmbH, Idstein, Germany) and a *Suprex SFE 50* (Suprex GmbH, Duisburg, Germany) at the temperatures of 70, 100, 130, and 160 °C, and a pressure of 2000 psi. A mixture of acetone/n-hexane (1 : 1, v/v) was used as the extraction solvent in all cases. On the *Dionex ASE 200*, a 0.5 g sample was extracted with stainless steel vessels of 11 mL volume. The time for static extraction was 5 min after a 5-min equilibration. After the static extraction, the vessel was rinsed with the same volume of solvent. Finally, the vessel was purged with gaseous nitrogen. The total amount of extraction solvent was about 20 mL.

**Soxhlet Extraction Procedure.** 5.0 g of XAD-2 was extracted with 200 mL of methylene chloride or toluene for 12 hr. The extracts were concentrated to about 3 mL, each using a rotary evaporator.

**Multilayer Silica Gel Column Clean-up.** After concentration of the extracts, the clean-up of samples was accomplished using a multilayer silica gel column,<sup>2</sup> which was packed in the order of neutral 2 g, acidic 6 g, and neutral 4 g. Eluate concentration was accomplished using a rotary evaporator. Final concentration was accomplished using the nitrogen evaporation technique. Extract clean-up, using a multilayer silica gel column, was performed after sonication, ASE, and Soxhlet extraction. This was not performed for SFE.

**HPLC-UV Detection Procedure.** The amount of PCBs and PCDDs in the liquid extracts was determined on a *Shodex C18-5B* (250×4.6 mm, 5  $\mu\text{m}$ ; Shoko, Kyoto, Japan) column with a 100  $\mu\text{L}$  sample loop. The HPLC system used in this work was a *Shimadzu Liquid Chromatograph* equipped with an SPD-10A UV-visible detector and a C-R6A integrator. The injected volume was 20  $\mu\text{L}$ , 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 in less than 30 min. Chromatograms were recorded at 240 nm (A.U.F.S. = 0.005).

**Sample Treatment.** As mentioned above, four different extractions were tested, and their respective extraction efficiencies were compared. The schematic diagram for the processes is shown in Figure 1.



**Figure 1.** Schematic diagram of the steps involving the four extraction methods proposed for the determination of PCBs and PCDDs in XAD-2 resin by HPLC.

**Table 1.** Comparison of extraction rates of PCB and PCDDs from spiked XAD-2 when using supercritical fluid CO<sub>2</sub> under 150 and 300 atm

	150 atm	300 atm
2,2',3,3',6,6'-HxCB	13.9	97.4
1,2,3,4-TCDD	6.0	62.1
1,2,3,4,7,8-HxCDD	DNQ <sup>a</sup>	30.3
OCDD	DNQ	20.8

<sup>a</sup>DNQ represents "Detect Not Quantified". HxCB, TCDD, HxCDD, and OCDD represent hexachlorinated biphenyl, tetrachlorinated dibenzodioxin, hexachlorinated dibenzodioxin, and octachlorinated dibenzodioxin, respectively.

## Results and Discussion

### Supercritical Fluid Extraction.

*The effect of pressure.* The effect of pressure on the extraction rate was studied at a constant temperature of 60 °C. The results are shown in Table 1. The solvent power of supercritical CO<sub>2</sub> below 150 atm (density: 0.6 g/mL) was too low to dissolve PCB and PCDDs (extraction rate: 0-13.9%). However, as expected, increased amounts of these compounds were extracted as the pressure was increased (extraction rate: 20.8-97.4%). This effect was observed for all the PCDDs used, which were extracted at a higher pressure.

*The effect of temperature.* The influences of extraction temperature on the extraction rate of SFE for PCDDs from the spiked XAD-2 resin were studied at a constant pressure of 350 atm. The results are shown in Table 2. Although the supercritical CO<sub>2</sub> solvent power decreased with increasing temperatures (CO<sub>2</sub> densities decreased from 0.93 to 0.65 g/mL for temperatures between 40 and 120 °C), the extracted amount of PCBs and PCDDs increased consistently (Table 2). This behavior revealed that the extraction rate was primarily controlled by analyte/matrix interaction rather than by CO<sub>2</sub> solubility. Therefore, increased temperatures accelerated diffusion and/or desorption.<sup>22</sup> The highest extractions of PCDDs were obtained at 100 and 120 °C. An extraction temperature of 100 °C was selected on account of the thimble cap lifetime, and no PCDD degradation was observed.

**Table 2.** The effect of temperature on the extraction rate for PCBs and PCDDs SFE conditions: 1 mL/min, 10% methanol modified CO<sub>2</sub> at 350 atm

	40 °C	60 °C	80 °C	100 °C	120 °C
TCB <sup>a</sup>	96.5	101.4	103.4	104.0	95.6
PeCB <sup>b</sup>	84.3	87.9	94.4	94.4	95.0
TCDD <sup>c</sup>	70.5	72.1	80.7	82.7	82.2
PeCDD <sup>d</sup>	60.6	51.8	69.6	73.1	74.8
HxCDD <sup>e</sup>	48.4	49.3	53.6	59.9	58.3
HpCDD <sup>f</sup>	40.7	39.9	42.2	49.0	46.5
OCDD <sup>g</sup>	28.6	28.5	28.9	38.0	32.9

<sup>a</sup>2,2',4,5'-tetrachlorinated biphenyl, <sup>b</sup>2,3,4,5,6-pentachlorinated biphenyl, <sup>c</sup>1,2,3,4-tetrachlorinated dibenzodioxin, <sup>d</sup>1,2,3,4,7-pentachlorinated dibenzodioxin, <sup>e</sup>1,2,3,4,7,8-hexachlorinated dibenzodioxin, <sup>f</sup>1,2,3,4,6,7,8-heptachlorinated dibenzodioxin, <sup>g</sup>octachlorinated dibenzodioxin.

At the higher temperature (120 °C), the extraction rate was found to decrease a little. This behavior may be attributed to the effect of temperature on CO<sub>2</sub> solubility parameters for both PCDDs and the extracting fluid, which are both functions of pressure and temperature.<sup>23</sup>

*The effect of CO<sub>2</sub> densities.* The extractions of PCDDs were performed with pure CO<sub>2</sub> at 0.148 (T=150 °C, P=100 atm), 0.266 (T=130 °C, P=150 atm), 0.489 (T=100 °C, P=200 atm), 0.741 (T=70 °C, P=250 atm), and 0.913 g/mL (T=40 °C, P=300 atm), with 5/95 mol % methylene chloride/CO<sub>2</sub> at 0.266, 0.489, 0.741, and 0.913 g/mL, and with 5/

**Table 3.** Effect of CO<sub>2</sub> densities on the extraction rate when using various modifiers

	CO <sub>2</sub> Density (g/mL)				
	0.266	0.489	0.741	0.913	0.955
No modifier					
HxCB <sup>a</sup>	2.1	14.1	83.1	74.7	- <sup>c</sup>
TCDD	DNQ <sup>b</sup>	7.1	50.5	42.0	-
PeCDD	DNQ	14.2	27.4	99.0	-
HxCDD	DNQ	DNQ	25.7	19.3	-
HpCDD	0	DNQ	10.1	5.5	-
OCDD	0	0	7.2	2.3	-
Dichloromethane 5%					
HxCB	20.9	33.1	81.3	88.6	-
TCDD	16.2	24.7	66.9	76.7	-
PeCDD	12.7	21.9	63.4	73.8	-
HxCDD	7.3	13.3	45.0	54.2	-
HpCDD	4.5	10.6	32.8	40.7	-
OCDD	2.2	7.8	30.8	38.1	-
Dichloromethane 10%					
HxCB	88.4	94.9	100.3	106.7	101.7
TCDD	67.4	77.8	87.1	89.1	87.6
PeCDD	101.7	98.1	102.1	102.9	100.7
HxCDD	87.8	85.0	97.7	99.7	93.2
HpCDD	76.6	75.4	85.8	92.2	84.2
OCDD	79.8	76.2	91.9	91.6	82.4
Toluene 5%					
HxCB	-	52.8	99.6	105.5	74.5
TCDD	-	42.4	82.5	96.9	65.2
PeCDD	-	41.6	78.2	97.3	63.3
HxCDD	-	33.4	63.6	88.7	52.7
HpCDD	-	31.4	52	79.2	43.5
OCDD	-	22.5	41.8	67.1	39.5
Toluene 10%					
HxCB	-	100.6	100.3	102.6	100.9
TCDD	-	92.1	92.8	98.2	95.6
PeCDD	-	100.9	97.1	100.1	96.3
HxCDD	-	87.1	92.6	92.8	87.5
HpCDD	-	82.8	86.5	84.9	81.6
OCDD	-	65.6	76.3	73.9	74.3

<sup>a</sup>2,2',3,3',6,6'-hexachlorinated biphenyl, <sup>b</sup>Detect Not Quantified, <sup>c</sup>Not Performed. TCDD, PeCDD, HxCDD, HpCDD, HpCDD, and OCDD was described in Table 2.

**Table 4.** Extraction rates and relative standard deviations for the addition of 10% modifiers to supercritical CO<sub>2</sub> at temperature of 40 °C and pressure of 350 atm

	No Modifier	Methanol	Acetone	Dichloromethane	Toluene
PeCB	54.3±3.3	80.2±2.6	76.7±6.4	89.8±2.9	93.5±6.3
TCDD	41.0±4.0	59.7±3.1	57.8±6.5	73.2±4.8	78.7±9.1
PeCDD	31.5±3.9	48.6±3.9	45.9±5.8	65.2±6.5	72.3±10.7
HxCDD	24.6±7.9	38.6±4.4	36.1±8.3	52.8±7.7	58.9±12.4
HpCDD	14.1±31.5	40.0±5.5	30.4±10.8	39.4±10.0	45.7±14.6
OCDD	DNQ <sup>a</sup>	21.3±7.9	19.9±17.6	36.2±10.7	42.5±17.5

<sup>a</sup>Detect Not Quantified. PeCDD, TCDD, PeCDD, HxCDD, HpCDD, HpCDD and OCDD were described in Table 2.

95 mol % and 10/90 mol % toluene/CO<sub>2</sub> at 0.489, 0.741, 0.913, and 0.955 g/mL. Table 3 shows the percent recoveries of SFE described above. The rate of extraction with CO<sub>2</sub> was enhanced with CO<sub>2</sub> densities, but did not reach a maximum at 0.955 g/mL. OCDD was recovered with a 92% yield at 0.913 g/mL of 10/90 mol % dichloromethane/CO<sub>2</sub>, while an 80% yield at 0.266 g/mL and an 82% yield at 0.955 g/mL, respectively.

*The effect of modifiers.* This study investigated the effect of modifiers on the extraction rate at an extraction time of 20 min, a pressure of 350 atm, and a temperature of 40 °C. Table 4 shows the influence of modifiers on the extraction rate. A modification of 10% toluene resulted in increased recoveries of PCB and PCDDs. Toluene, showing a larger solubility with PCDDs, could better substitute PCDDs from XAD-2 adsorptive sites of their aromatic structures than other solvents. On the other hand, decreased extraction rates from PCB to OCDD in Table 4 reveal that two oxygen- and planar structure-containing PCDDs interacted more strongly with XAD-2 adsorptive sites than PCB. More chlorine-containing PCDDs such as OCDD interacted more strongly with XAD-2 than those containing less chlorine such as TCDD. This seemed to be due to the  $\pi$ - $\pi$  interaction between the matrix and the analytes.

*The effect of static time.* In the static extraction stage, the sample matrix was in equilibrium with the supercritical fluid for a given period of time under the supercritical pressure and temperature. Static extraction of 10 min prior to 20 min dynamic SFE did not improve recoveries, compared with 5 min. Therefore, a 5-min equilibration time was selected for

**Table 5.** The ranges of variables studied and their optimum values in SFE

	Pressure (atm)	Temperature (°C)	Modifiers	Static time (min)
Studied range	100-350	35-150	None, methanol, acetone, dichloromethane, toluene	5-10
Optimum variables	350	100	Toluene	5

further experiments.

The effects of experimental variables were evaluated in order to develop a rapid, quantitative SFE method. The ranges of variables studied and the optimum values found within given ranges are shown in Table 5.

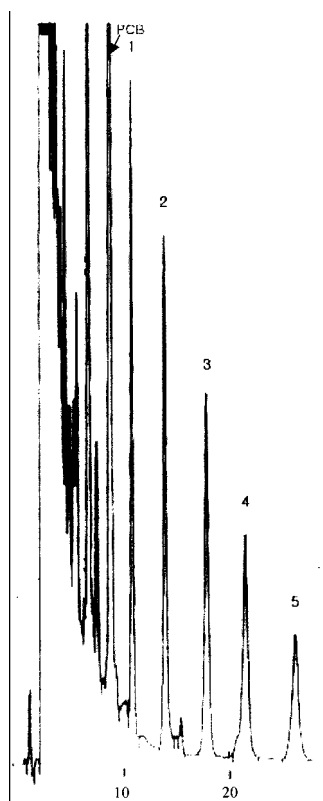
Table 6 represents the effect of the modifiers on the extraction rates and relative standard deviations at 100 °C under 350 atm. The precision of the SFE method for PCB and PCDDs, expressed as percent relative standard deviation, was from 1.0 to 7.6%. The chromatogram for spiked XAD-2 that was extracted with 10/90 mol % toluene/CO<sub>2</sub> at 350 atm and 100 °C is shown in Figure 2.

**Ultrasound-Assisted Solvent Extraction.** Three methods (A, B, and C) were compared using two different liquid solvents. The results, shown in Table 7, revealed that this method is as efficient as other methods. The mean recovery of PCDDs with acetone-toluene extraction was 106% relative to supercritical CO<sub>2</sub> extraction. The liquid extracts were heavily contaminated, so a clean-up step using a multilayer silica gel column was needed before injection into the HPLC column (Figure 3). The acetone-toluene mixture was the most efficient solvent among those studied (Table 7). Both higher polarity and the solubility properties of the mixed solvents are likely to lessen the interaction between XAD-2 and PCDDs. The polarity of acetone might swell XAD-2 resin particles, facilitating the penetration of toluene into XAD-2 adsorptive sites with PCDDs. A less polar and more soluble solvent such as toluene, which has been postulated to be better than the mixed solvent, was less suitable for extracting PCDDs. The polarity of acetone in toluene seemed to be crucial in assisting the extraction of PCDDs from XAD-2. The recovery of OCDD in method B (Table 7) was larger than that in method C. The recovery of TCDD in method B was between those of methods A and C. This suggests that

**Table 6.** Extraction rates and relative standard deviations for the addition of modifiers to supercritical CO<sub>2</sub> at temperature of 100 °C and pressure of 350 atm

	No Modifier	MeOH 5%	MeOH 10%	Acetone 5%	Acetone 10%	Dichloromethane 5%	Dichloromethane 10%	Toluene 5%	Toluene 10%
PeCB	71.4±7.6	81.2±0.6	93.8±0.6	85.6±2.8	94.5±0.7	92.9±0.9	84.3±0.4	101.5±2.5	107.8±1.7
TCDD	59.8±7.1	67.3±1.7	79.0±2.5	74.5±3.8	85.1±1.6	80.6±1.3	73.2±0.5	89.9±1.7	97.9±1.0
PeCDD	54.1±6.2	60.1±1.6	72.0±1.0	66.6±3.9	77.6±2.3	75.3±1.2	69.1±1.2	84.2±3.2	95.6±1.7
HxCDD	45.3±4.2	47.7±2.1	57.9±1.7	51.2±3.2	62.3±3.2	62.9±1.4	57.6±2.0	70.8±2.8	84.6±2.9
HpCDD	41.6±4.3	39.4±1.6	48.0±1.1	39.1±2.9	47.6±4.0	50.2±0.8	46.3±3.2	54.5±1.4	78.4±4.3
OCDD	27.9±4.0	29.0±3.7	37.8±1.0	30.0±2.1	39.6±5.2	42.4±3.1	37.5±4.2	49.4±2.8	68.5±4.5

\*TCDD, PeCDD, HxCDD, HpCDD, and OCDD were described in Table 2.



**Figure 2.** HPLC chromatogram of PCB and PCDDs that were extracted from XAD-2 with 10/90 mol % toluene/CO<sub>2</sub> at 350 atm and 100 °C. (PCB: 2,3,4,5,6-pentachlorinated biphenyl, 1: 1,2,3,4-tetrachlorinated dibenzodioxin, 2: 1,2,3,4,7-pentachlorinated dibenzodioxin, 3: 1,2,3,4,7,8-hexachlorinated dibenzodioxin, 4: 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin, 5: octachlorinated dibenzodioxin)

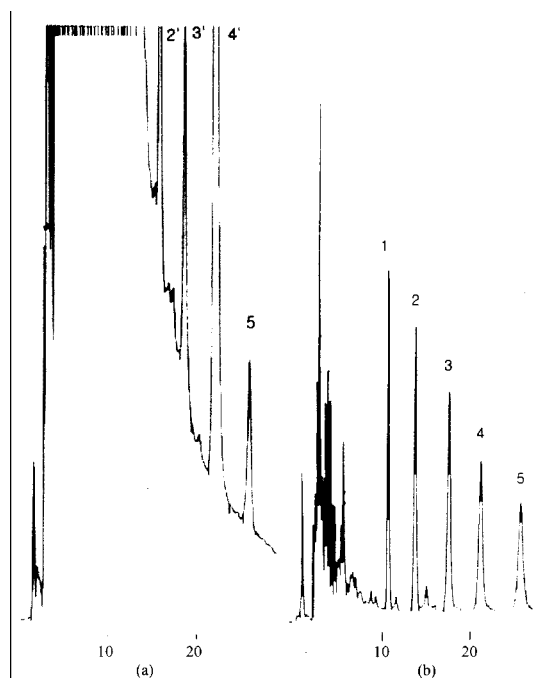
**Table 7.** Extraction rates and relative standard deviations of PCDDs when using three types of solvent and two types of extractor. Method A, B, and C represent the extraction methods using acetone, toluene, and acetone-toluene mixtures (1 : 1, v/v) respectively

	Method A		Method B		Method C	
	Probe Type	Bath Type	Probe Type	Bath Type	Probe Type	Bath Type
TCDD	76.6±5.6	63.9±5.3	78.3±8.0	80.9±4.8	93.1±1.5	87.3±2.9
PeCDD	79.9±3.3	76.0±6.3	88.5±4.0	70.4±6.3	95.5±2.8	89.7±4.9
HxCDD	73.8±2.4	73.2±7.4	80.1±4.0	81.7±3.6	92.1±3.3	84.1±5.9
HpCDD	68.7±1.9	56.9±7.2	77.4±5.7	60.6±5.2	88.0±4.9	60.5±7.1
OCDD	61.9±4.5	43.9±1.1	86.0±7.4	49.6±7.4	82.4±7.2	47.0±9.4

\*TCDD, PeCDD, HxCDD, HpCDD, and OCDD were described in Table 2.

OCDD has the less polar nature than TCDD. A probe type sonication for 9 min showed a larger extraction rate than a bath type sonication for 90 min. Thus, the parameters affecting extraction efficiencies of the ultrasonic method were found to be extraction type and solvent.

**Accelerated Solvent Extraction.** In ASE, the extraction temperature was above the normal boiling point of the solvent, while that of Soxhlet extraction was limited by the



**Figure 3.** HPLC chromatograms without(a) and with(b) multilayer silica gel column clean-up after ultrasonic extraction. The numbers of 2', 3', and 4' represent the overlapping peaks of dioxins and interferences. The numbers of 1,2,3,4, and 5 represent 1,2,3,4-tetrachlorinated dibenzodioxin, 1,2,3,4,7-penta chlorinated dibenzodioxin, 1,2,3,4,7,8-hexachlorinated dibenzodioxin, 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin, and octachlorinated dibenzodioxin, respectively.

boiling point of the solvent used. At increased temperatures, the diffusion of the components from the XAD-2 particles to their surface was enhanced,<sup>24</sup> and the transfer from the surface of the particles into the extraction solvent was accelerated.<sup>24</sup> Also, the solubility of the components in the extraction solvent was improved at increased temperatures.<sup>24</sup> Therefore, the extraction rate at increased extraction temperature was increased. In order to investigate the effects of temperature on the extraction rates from XAD-2 under ASE conditions, the extraction of PCB and PCDDs was performed with hexane-acetone (1 : 1, v/v) at various temperatures and at a pressure of 2000 psi. A static time of 5 min

**Table 8.** Temperature effect on extraction rate of PCBs and PCDDs from XAD-2 with accelerated solvent extraction

	Extraction Rate and Relative Standard Deviation			
	70 °C	100 °C	130 °C	160 °C
TCB	81.4±5.9	90.6±7.5	81.8±1.1	88.2±5.0
PeCB	87.5±0.5	93.2±1.6	84.6±0.7	90.5±3.4
TCDD	90.1±1.3	95.0±1.3	98.2±9.0	91.5±2.8
PeCDD	89.6±1.7	97.1±1.2	93.8±3.8	94.2±3.7
HxCDD	86.1±1.3	91.6±0.2	85.7±1.5	87.4±3.3
HpCDD	86.7±2.6	90.0±2.1	87.9±5.3	88.2±5.5
OCDD	101.9±4.4	102.7±6.9	95.3±8.2	88.8±5.2

\*TCB, PeCB, TCDD, PeCDD, HxCDD, HpCDD and OCDD were described in Table 2.

**Table 9.** Extraction of PCBs and PCDDs from XAD-2 using dichloromethane and toluene in Soxhlet extraction

	Extraction Rate and Relative Standard Deviation	
	Methylene chloride	Toluene
TCB	81.4±5.5	91.4±5.7
PeCB	103.0±3.4	111.0±13.2
TCDD	96.2±4.9	96.7±0.6
PeCDD	96.3±5.5	95.9±0.5
HxCDD	96.6±3.9	94.5±3.4
HpCDD	96.1±1.7	91.2±2.2
OCDD	96.6±2.2	98.9±1.7

\*TCB, PeCB, TCDD, PeCDD, HxCDD, HpCDD and OCDD were described in Table 2.

was used. The results are illustrated in Table 8. The extraction rates for XAD-2 increased consistently as the extraction temperature was raised from 70 to 100 °C. As discussed above, temperature was the most important factor affecting the kinetics of mass transfer in ASE. The extraction temperature, however, should not be above the melting point of the polymer, that is, the XAD-2 resin. Unfortunately, information on the melting point of XAD-2 resin was not available under ASE conditions. XAD-2 and dioxins had good thermal stability and were useful at temperatures as high as 200 °C. The temperature conditions in this study did not exceed the value of degradation of XAD-2 and PCDDs. Nevertheless, the optimal extraction solvent and temperature could only be determined experimentally because information on the acceptable temperature level was hardly available.

**Soxhlet Extraction.** Soxhlet extraction was performed three times. Table 9 shows the extraction rates and relative standard deviations (RSD). Toluene and dichloromethane gave similar extraction rates. The deviations were within an acceptable range. Only the RSD of the PeCB was higher than the other values, which seems to be due to overlapping with interference peaks in the HPLC chromatogram which was similar to that of Figure 2. The HPLC chromatographic interferences seems to come from the large amount of solvent that was used for a long time.

**Comparison of the Four Methods by General Criteria.** The extraction time of ASE was 15 min, SFE 40 min, ultrasonic extraction 1.5 hr, and Soxhlet extraction 12 hr per extraction. The solvent consumption in SFE was 15 mL including the modifier and trapping solvent; in ASE, 30 mL; in ultrasonic extraction, 100 mL; in Soxhlet extraction, 200 mL. The method development for SFE was laborious, while methods of Soxhlet and ultrasonic extraction were well established for a wide range of compounds. In ASE, only the extraction time and temperature had to be optimized. The solvents that gave good extraction rates in ASE performed poorly in Soxhlet and ultrasonic extraction. ASE at higher temperature was independent of the matrix.<sup>25</sup> In Soxhlet and ultrasonic extraction, simultaneous extraction could be performed. The costs of ASE and SFE equipment are higher than those of the other methods.

## Conclusion

This study showed that SFE and ASE were successful in extracting PCBs and PCDDs from XAD-2. The average recoveries of PCBs and PCDDs extracted by SFE and ASE were similar to the results obtained by Soxhlet and ultrasonic extraction. In SFE, recoveries were in the range of 68-108%, while those of ASE were 90-103%. The relative standard deviations of ASE and SFE were in the range of 0.2-9.0% and 0.6-7.6%, respectively.

Considering criteria such as solvent consumption, extraction time, and practical conditions among the different methods, SFE and ASE were the preferred methods. The principal advantage of ASE was its short extraction time (15 min). Solvent consumption in SFE was only 10 mL including the modifier and trapping solvent, compared to 20 mL in ASE. The use of a small amount of solvent in SFE and ASE made the concentration process much easier, reducing the possibility of analyte loss.

On the other hand, SFE was faster and simpler than the ultrasound-assisted extraction, and offered good efficiency and precision, with the merit of replacing toxic organic solvents with more environmentally preferred solvents such as supercritical CO<sub>2</sub>.

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