

COMPARISON OF THE EXTRACTION EFFICIENCY OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM SOILS USING ASE & SOXHLET

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INTRODUCTION

The most common extraction method in analysis of Polychlorinated-dibenzo-para-dioxins(PCDDs) and Polychlorinated dibenzofurans(PCDFs) in soil is the Soxhlet extraction. However, its extraction method generally requires a long hours or days and a large amount of hazardous organic solvents. Therefore, new extraction techniques have been developed in order to reduce the volume of solvents required for extraction, to reduce the time and cost of extraction and to improve the recovery of analyte. Accelerated Solvent Extraction (ASE) is a relatively new technique that utilizes elevated temperatures and pressures to achieve fast and efficient extraction of target analytes in solid matrix. In this study, ASE and Soxhlet extractor were used to determine PCDDs and PCDFs in soil samples. The efficiency and concentration of ASE extraction were compared with those of soxhlet extraction.

MATERIAL AND METHOD

Pre-extraction preparation: Soil samples were taken from the Seoul area consisting of at four sites, each with a different origin and degrees of contamination. Soil samples were taken within a depth of 15cm at a municipal solid waste incinerators(MSWIs) area, a heavy traffic jam area, a fresh background area, etc. Each sample was air-dried for approximately 5 days at the shade and then was strained into small pieces using 2mm strainer^{1,2}. They were kept cool in glass bowls until extraction

Soxhlet Extraction: All soxhlet extractor equipment was pre-rinsed with Toluene for three hours. Samples(20g d.m) were mixed with approximately 20g of pre-extracted sodium sulfate and then were transferred to a soxhlet in pre-extracted cellulose thimble. An internal standard solution of the fifteen 2,3,7,8-substituted ¹³C₁₂-labeled isomers(100-200pg/ml) was added to the soil sample prior to extraction. The soxhlet extraction was carried out with 350ml of toluene(pesticide grade) at the rate of 4 times/hr during 18hrs.

ASE Extraction : All cells were rinsed with n-Hexane and Acetone through sonication. The dried soil sample(20g d.m) in 33 cell was filled with pre-extracted sodium sulfate anhydrous(20g)². An internal standard solution of the fifteen 2,3,7,8-substituted ¹³C₁₂-labeled isomers(100-200pg/ml) was added to the soil sample prior to extraction. The sample was extracted with 30ml of toluene(pesticide grade) per sample. The ASE extraction was carried out with a Accelerated Solvent Extractor (Dionex ASE 200). The conditions of ASE extraction were at a temperature of 200°C, 1500psi. pressure, 5 minutes static time for three static cycles, an 80% flush volume, and 60 seconds purge time^{3,4}.

Cleanup procedures: Silicagel columns were packed by acid/base silicagel. All samples were cleaned by acid/base partitioning silica column and then put through a series of silica with 150ml of n-hexane as a mobile phase. Alumina columns were packed by neutral alumina and then eluted with 100ml of methylene chloride(5:95v/v) and then with 150ml of methylene chloride(50:50v/v). The final extract volume were concentrated to 20ml using Rotary evaporator. The recovery standard, $^{13}\text{C}_{12}$ -labeled 1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD, were added to the final extract before the analysis.

Analysis: The samples were analysed with a high resolution gas chromatograph series (Pisons GC8000 series, column SP-2331 : 60mx0.32mm i.d 0.25 film thickness) which was coupled to high resolution mass spectrometer (VG Autospec Ultima, UK) in SIM mode operating at a resolving power of 12,000. The injector and detector temperature are at 260°C and at 280°C, respectively. The temperature program was 100°C (held for 1min), increased at 20°C/min (held for 5mins) and increased at 4°C/min to 265°C (held for 22mins). The Helium at a flow rate of 1ml/min was used as a carrier gas.

RESULTS AND DISCUSSION

In this study, several soils from the Seoul area were analyzed for PCDDs/Fs after extraction with ASE and Soxhlet. The ASE extraction was compared with Soxhlet about recovery(%), concentration(pg/g), solvent volume and time of extraction. The results of the recovery(%) and concentration are shown in Table1 and Table2. The percent recovery of labeled analytes of ASE and Soxhlet methods range from 61.2% to 119.4%(ASE) and 61.7% to 118.1%(soxhlet). In the concentration, the results obtained are mainly considered as TCDD equivalents(TEQ), which are derived using international toxic equivalent factors(I-TEFs). The result of concentration using soxhlet was shown to be higher than ASE. These methods differed from each other when the labor hours and the volume of solvent required per sample were considered. After setup, the ASE extraction taken approximately 30mins while the soxhlet runs at least for 18hours per sample. The ASE required only 30ml and the soxhlet required 350ml per sample. The soxhlet method, which involved large volumes of hazardous chemical, took long time to evaporate, and created excessive waste. Based on these considerations, the ASE extraction were performed in less time and solvent than the Soxhlet extraction technique did. The ASE method showed equal or better recovery efficiency(%) of extraction than the Soxhlet extraction did. Therefore, the ASE method was capable to replace soxhlet method to analyze dioxins from soil sample.

REFERENCES

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Table 1. Comparison of ASE and Soxhlet for extraction from soil

Dioxins	Labeled fifteen isomers	Recovery efficiency(%)							
		Sample-1		Sample-2		Sample-3		Sample-4	
		ASE	Soxhlet	ASE	Soxhlet	ASE	Soxhlet	ASE	Soxhlet
PCDDs	¹³ C ₁₂ -2,3,7,8-TCDD	96.6	61.7	97.1	86.9	82.5	96.3	109.7	73.9
	¹³ C ₁₂ -1,2,3,7,8-PeCDD	81.9	81.5	83.2	76.5	73.4	98.3	103.7	81.7
	¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	96.3	90.3	91.7	83.6	88.3	95.6	107.5	68.4
	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100.3	88.3	88.4	84.0	87.7	99.6	106.7	73.7
	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	88.4	87.0	89.4	90.0	81.0	115.9	103.0	72.5
	¹³ C ₁₂ -OCDD	90.7	83.7	97.1	94.5	84.2	105.5	118.8	90.3
PCDFs	¹³ C ₁₂ -2,3,7,8-TCDF	94.1	88.2	94.1	81.5	81.5	94.4	117.0	79.8
	¹³ C ₁₂ -1,2,3,7,8-PeCDF	90.9	91.4	90.7	82.1	68.1	114.4	112.4	89.8
	¹³ C ₁₂ -1,2,3,7,8-PeCDF	89.4	85.6	88.8	82.2	61.2	111.9	112.9	91.3
	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	102.4	85.8	88.7	86.3	85.7	95.0	102.6	66.3
	¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	101.1	86.7	89.8	85.5	88.7	78.0	80.4	68.8
	¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	101.7	88.3	91.0	85.0	90.0	95.6	109.3	69.0
	¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	107.4	94.5	95.7	89.2	94.0	106.1	107.8	80.7
	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	99.3	90.9	93.4	89.4	81.1	116.2	119.4	66.7
	¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100.7	96.0	103.9	98.3	95.2	113.5	115.2	92.1
Average recovery(%)		96.1	86.6	92.2	86.3	82.8	102.4	108.4	77.7

Table 2. Concentration of PCDDs/Fs used with ASE and Soxhlet Extractor from soil

Dioxins	Native seventeen isomers	Concentration(pg-TEQ/g d.m)							
		Sample-1		Sample-2		Sample-3		Sample-4	
		ASE	Soxhlet	ASE	Soxhlet	ASE	Soxhlet	ASE	Soxhlet
PCDDs	C ₁₂ -2,3,7,8-TCDD	0.84	0.50	0.13	0.18	0.34	0.30	0.61	0.71
	C ₁₂ -1,2,3,7,8-PeCDD	0.77	0.80	0.14	0.18	0.19	0.29	0.44	0.48
	C ₁₂ -1,2,3,4,7,8-HxCDD	0.05	0.05	0.01	0.02	0.03	0.02	0.02	0.03
	C ₁₂ -1,2,3,6,7,8-HxCDD	0.12	0.13	0.03	0.05	0.08	0.05	0.07	0.07
	C ₁₂ -1,2,3,7,8,9-HxCDD	0.08	0.07	0.02	0.03	0.04	0.03	0.03	0.04
	C ₁₂ -1,2,3,4,6,7,8-HpCDD	0.07	0.07	0.04	0.05	0.07	0.05	0.05	0.05
	C ₁₂ -OCDD	0.07	0.04	0.03	0.03	0.06	0.04	0.04	0.03
PCDFs	C ₁₂ -2,3,7,8-TCDF	0.55	0.51	0.04	0.06	0.06	0.06	0.15	0.18
	C ₁₂ -1,2,3,7,8-PeCDF	0.33	0.26	0.02	0.02	0.04	0.04	0.08	0.09
	C ₁₂ -1,2,3,7,8-PeCDF	2.13	2.59	0.24	0.34	0.44	0.46	0.82	0.93
	C ₁₂ -1,2,3,4,7,8-HxCDF	0.53	0.41	0.06	0.06	0.11	0.10	0.15	0.17
	C ₁₂ -1,2,3,6,7,8-HxCDF	0.48	0.38	0.04	0.06	0.10	0.11	0.14	0.15
	C ₁₂ -2,3,4,6,7,8-HxCDF	0.35	0.28	0.06	0.08	0.12	0.11	0.13	0.14
	C ₁₂ -1,2,3,7,8,9-HxCDF	0.05	0.04	0.01	0.01	0.01	0.01	0.01	0.01
	C ₁₂ -1,2,3,4,6,7,8-HpCDF	0.11	0.09	0.00	0.03	0.04	0.05	0.06	0.06
	C ₁₂ -1,2,3,4,7,8,9-HpCDF	0.02	0.01	0.00	0.00	0.00	0.01	0.00	0.00
C ₁₂ -OCDF	0.04	0.01	0.00	0.00	0.00	0.01	0.01	0.01	
Total concentration(pg-TEQ/g d.m)		6.59	6.24	0.87	1.20	1.73	1.74	2.81	3.15

