

Semi-automated disk type extraction method of dioxin analysis for ambient water

Jaewon Choi, Jaehee Lee¹, Bushik Moon, Kyungsim Kim¹, Sunheong Kim¹, Kyunghee Baek¹

¹Kowaco, Idwc

Introduction

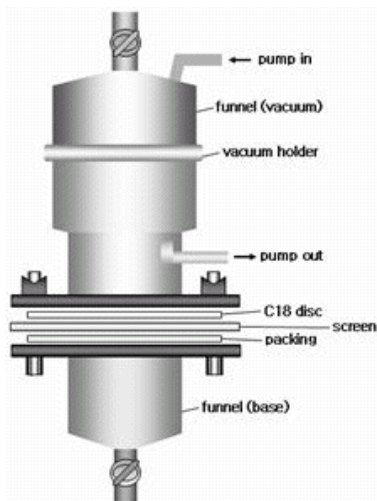
Dioxin formation needs thermal reactions such as in the incinerator, industrial thermal processes and chemical impurities. Lately, possibility of dioxin formation in the chlorination process of drinking water treatment was reported¹. Because the presence of dioxin in the finished water is extremely low compare to wastewater, the measurement needs large sample volume. As a minimum sample volume, 20L for raw and drinking water was estimated using sample volume calculation². Liquid-liquid extraction method (LLE) has limitations for the applications due to sample volume, extraction time, man power and solvent wastes. Disk type octadecyl (C18) solid phase extraction (SPE) is one of the alternative extraction methods when the concentration in aqueous sample is very low. Small size of disk (50 mm i.d.) was applied to the analysis of water³. At present study, we used semi-automated SPE system using C18 disk (90 mm i.d.) to extract 20L sample. Main objectives of the present study were to validate these extraction methods by comparing recoveries, method detection limits, noise level, preparation time, labors, and solvent needed etc. between LLE and SPE and to apply SPE to the finished water samples.

Material and Methods

Extraction system for solid phase extraction 3M Empore™ octadecyl (C18) disks (90mmID, 0.5mm thick, capacity 70mg) and glass fiber filter (90mmID, pore size 0.7µm) were purchased from GL science (Tokyo, Japan). Separating funnels (500mL) were obtained from Shibata (Tokyo, Japan). Nonane, dichloromethane and toluene were grade for dioxin analysis. HPLC grade acetone and hexane were supplied by J.T. Baker. PCDD/F standard solutions including labeled compounds were purchased from Wellington Laboratories (Toronto, Canada). Semi-automated SPE system was obtained from GL science (Tokyo, Japan). The conceptual structure of SPE system is illustrated in Figure 1. Glass fiber filter holds particles prior to C18 disk adsorption. This system can extract water sample continuously with a flow rate of 100-200 mL/min. Flow rate of this study was set at 150-180 mL/min.

Table 1. Extraction conditions for SPE and LLE

Extraction methods	SPE	LLE
Sample No	n=3	n=3
Internal Spike-1	Native dioxins from tetra to octa-CDD/F	
Adsorption	After conditioning disk, adsorption, drying and extraction	Native std. (MeOH) spikign to water Sampling std. (MeOH) spikign to solvent
Internal Spike-2	Sampling Standard : 37cl TCDD	
Extraction and Evaporation	Soxhlet (16hr) Rotary evaporator	Liquid-liquid extraction (20min/450mL, 2 times) Dehydration, Rotary evaporator
Internal Spike-3	Cleanup Standard (13C for 16 CDD/Fs)	
Clean up Evaporation	Multilayered silica gel, Activated carbon Rotary evaporator, N2 gas	
Internal Spike-4	Syringe Standard (13C-tetra and hexaCDD congeners)	
Measurement	GC/HRMS	



Experimental conditions from spiking to clean up are summarized in Table 1. Native PCDD/Fs including 1368-TCDD/F and OCDD/F were dissolved in the distilled water by MeOH to observe the reproducibility and to compare the recoveries of labeled compounds (clean up spike). As sampling spike, 37Cl 2,3,7,8-TCDD was added in the C18 disk for SPE and in the extraction solvents for LLE. After extraction and evaporation, fifteen 13C labeled internal standards to calculate clean up recovery were added. Two 13C labeled compounds for syringe calibration also added in the N2 purging step.

Figure. 1. Semi-automated solid phase extraction system using C-18 disk

Chemical analysis Analysis of PCDD/Fs was performed on a GC/HRMS (Trace2000- MAT95XP, Thermo-Finnigan) with multi ion detection (MID, same as SIM) mode. The HRMS was operated in electron impact ionisation (42eV) at a resolution $R > 10,000$ (10% valley). A gas chromatograph equipped with capillary column SP-2331 (60 m \times 0.32 mm i.d., 0.2 μ m) from Supelco was connected to the MS. GC ramping condition is as following ; injector at 255 $^{\circ}$ C,

initial oven temperature at 120 $^{\circ}$ C, held for 3.0 min, heated to 220 $^{\circ}$ C at 20 $^{\circ}$ C/min, held for 2.0 min, then to 265 $^{\circ}$ C at 25 $^{\circ}$ C/min, with 18 min hold. Helium was used as the carrier gas with the flow rate 1.2 ml/min.

QA/QC All solvents, reagents and internal standards were tested for the contamination by native PCDD/Fs. A method blank was performed from the extraction step. Calibration standards for EPA1613 ranged from 0.5 (5.0 for OCDD/F) – 200 (2000 for OCDD/F) ng/mL were run with samples. Ranges for limits of detection (LODs) of GC/HRMS were from 0.001 pg/L for TCDD to 0.005 pg/L for OCDD. After data acquisition, the selected ion chromatograms were integrated and calculated using software Quan Desk (ver 1.0). PCDD/F congeners were identified and quantified by the criteria of JIS K 0312⁴.

Results and Discussion

Recoveries and stabilities between two methods Individual, mean recoveries and %RSD are summarized in Table 2. Whole recoveries of SPE ranged 62-97%, higher than LLE ranged 58-81%. Particularly, for the low chlorinated congeners like tetra- and pentaCDD/Fs, SPE showed higher recoveries with low %RSD compared to LLE. For LLE, %RSD of TCDD/F and PeCDD/F is much higher than that of HpCDD/F and OCDD. We assumed that this is due to the differences of partition coefficients dependent with chlorination. For example, log Kow of TCDD and OCDD are 6.64 and 8.6 respectively. Therefore, relatively stable extractions might be obtained in the high chlorinated congeners. Unstable extraction of hepta- and OCDD were observed in SPE compared to low chlorinated congeners in SPE or hepta- and octaCDD in LLE (see %RSD in Table 2). This may indicate that strong adsorption of hydrophobic congeners like heptaCDD/F and octaCDD to the C18 disk cause low extractions in the Soxhlet extractor.

Recoveries and stabilities for natives spiked Individual, mean recoveries and %RSD for unlabelled 1368-TCDD/F and OCDD/F spiked are summarized in Table 3. Concentrations of 1368-TCDD and 1368-TCDF showed no significant differences between two methods with stable %RSD. However, lower concentrations than expected values for OCDD/F were obtained in SPE method with high %RSD. At present, we are assuming that longer extraction time for Soxhlet extraction should be performed from 16hr to 24hr.

Application to finished water Finished water samples from 5 treatment facilities for drinking water were tested. SPE method tested above was applied with flow rate of 140-160 mL/min. After chromatography including carbon column, instrumental analysis by GC/HRMS was performed based on the criteria JIS K 0312⁴. LOD for the water sample were ranged from 0.003 pg/L for TCDD to 0.02 pg/L for OCDD. No 2,3,7,8-PCDD/F congener was detected. These results indicating that large sample volume more than 20L should be taken for the monitoring of drinking water.

Table 2. Range, mean and %RSD of recoveries between SPE and LLE

	Solid Phase Extraction					Liquid-Liquid Extraction				
	SPE-1	SPE-2	SPE-3	MEAN	%RSD	LLE-1	LLE-2	LLE-3	MEAN	%RSD
2378-TCDF	98	88	88	91	6.3	65	92	78	79	14.2
2378-TCDD	99	96	95	97	1.9	62	89	81	77	14.8
12378-PeCDF	97	85	78	86	9.2	66	78	63	69	9.3
23478-PeCDF	85	73	72	77	8.0	56	74	64	65	11.1
12378-PeCDD	84	78	70	77	7.1	59	76	65	67	10.7
123478-HxCDF	94	83	75	84	8.9	68	81	83	77	8.8
123678-HxCDF	88	88	86	88	1.4	73	75	75	75	1.6
234678-HxCDF	83	91	86	87	3.7	83	83	75	81	4.6
123789-HxCDF	83	86	70	80	8.6	78	81	75	78	2.7
123478-HxCDD	91	81	75	82	7.9	70	75	70	72	3.4
123678-HxCDD	88	78	75	80	6.8	68	73	75	72	4.5
1234678-HpCDF	81	83	70	78	7.2	75	68	68	70	5.2
1234789-HpCDF	88	78	70	79	9.5	73	73	78	75	3.3
1234678-HpCDD	76	74	63	71	8.0	70	62	65	66	5.0
OCDD	69	57	59	62	8.4	60	53	62	58	6.1
MEAN	87	81	76	81	6.9	68	75	72	72	7.0

Table 3. Range, mean and %RSD of congeners spiked between SPE and LLE

	Solid Phase Extraction					Liquid-Liquid Extraction				
	SPE1	SPE2	SPE3	MEAN	%RSD	LLE1	LLE2	LLE3	MEAN	%RSD
1368-TCDD	4.6	5.2	5.0	4.9	3.3	5.2	4.9	4.9	5.0	2.9
1368-TCDF	5.0	4.9	4.4	4.8	6.8	5.9	5.1	5.5	5.5	7.7
OCDD	8.7	8.3	7.4	8.1	8.1	9.2	8.8	9.0	9.0	2.2
OCDF	6.2	7.2	6.0	6.5	10.2	7.7	7.2	7.7	7.5	3.8

Acknowledgement

This research was supported by KOWACO research fund.

References

1. Kim, H.K., Kazui, H., Matsumura, T., Ohno, K., Kamei, T., Magara, Y. (2001) *Organohalogen Compd.* 51: 135-138.
2. Choi, J.W., Lee, J.H., Kim, K.S., Kim, S.H., Baek K.H. (2005) *J. Kor. Soc. Water Quality.*, 21: 1-11.
3. Pujadas, E., Diaz-Ferrero, J., Marti, R., Broto-Puig, F., Comellas, L., Rodriguez-Larena, M.C. (2001) *Chemosphere*, 43: 449-454.
4. JIS K 0312 (1999) 1-61.