Analysis of Size Distribution of PCDD/PCDF in Wastewater with Ion Trap MS/MS Technique

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Introduction

Municipal solid waste incinerator (MSWI) has been considered as one of the major sources of polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzofuran (PCDD/PCDF) emissions into the environment[1]. Wet gas scrubbing device installed at MSWI removes PCDD/PCDF in the flue gas along with acidic gases such as HCl, SOx, and NOx[2]. During the removal process, PCDD/PCDF accumulates in the wet scrubbing systems[3].

Consequently, the water in the wet scrubber contains significant amount of PCDD/PCDF. Even if a water circulation device is equipped with, PCDD/PCDF in the overflow effluent is not negligible and needs to be treated before discharging. In addition, all of the circulated water has to be treated eventually at the time of the maintenance, reconstruction or closing of the incinerator.

The principal objectives of this study were to establish the analytical procedure in order to determine the size distribution of PCDD/PCDF in wastewater; and to investigate the relationship between particle size distribution and PCDD/PCDF concentration. Feasibility of PCDD/PCDF removal by coagulation-precipitation treatment was evaluated according to the distribution. The difference between "soluble" and "particle" PCDD/PCDF was also discussed.

Sampling was a crucial factor in the analysis due to uneven distribution of PCDD/PCDF in the scrubbing system. The only one solution was to multiply the number of the sampling. Ion trap MS/MS technique was the most appropriate analytical approach because of its relatively high productivity compared to HRMS. Immunoassay and bioassay could not be applied, as the information obtained from their results was not sufficient to determine the distribution.

Materials and Methods

Sampling Procedure: Residual wastewater in wet scrubber was taken from a closed incinerator. The scrubber was located downstream of fabric filter. Hence fly ash concentration in the water was expected to be considerably low. Schematic drawing of the incinerator is shown in Figure 1.

The $3m^3$ capacity tank was filled with wastewater at the time of the closing. The wastewater could be taken only from the bottom because of limited accessibility of this facility. First of all, 3L of the wastewater was taken for PCDD/PCDF analysis. This 3L sampling was repeated 10 times as total. Then, 200L was taken and mixed thoroughly before the analysis. The first 3L and the last 3L of the 10 times sampling, and the following 200L were analyzed. The sampling scheme was shown in Figure 2.

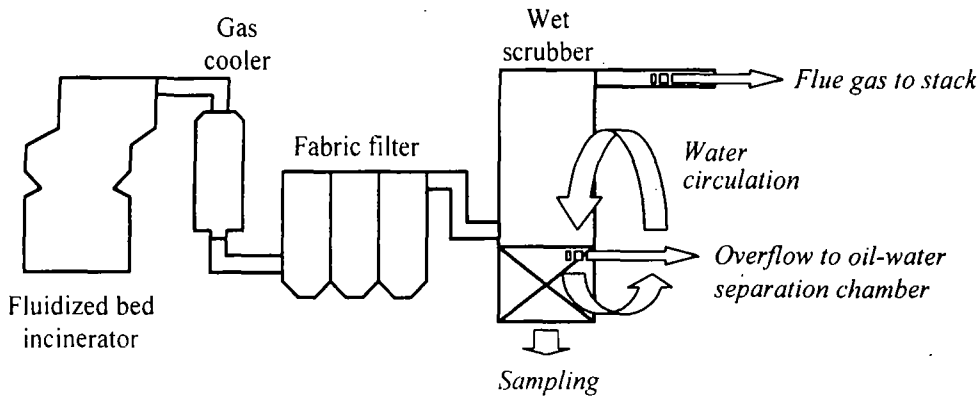

Figure 1. Schematic drawing of off-gas cleaning system

Particle separation: Particle separation flow is shown in Figure 3. Each sample was filtered with ADVANTEC (Tokyo, Japan) GS-25 glass filter (pore size 1μm) to separate the particle over 1μm. Then rest of the particles were separated using glass apparatus shown in Figure 4. ADVANTEC H-010A aquaphilic PTFE filter (pore size 0.1μm) was applied to trap the particle between 0.1μm and 1μm. "Soluble" PCDD/PCDF were absorbed on the 3M (St. Paul, MN) EMPORE™ C_{18} disk filter. Each filter was extracted with a DIONEX (Salt Lake City, UT) ASE200 extractor.

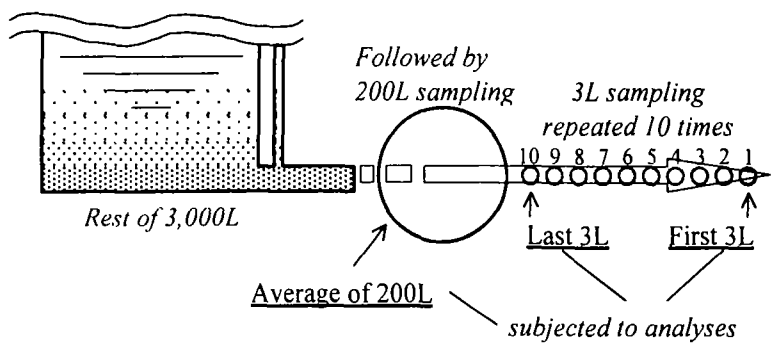

Figure 2. Sampling scheme

Analysis: Sample extracts were treated with sulfuric acid and put onto a silica-gel column. Then PCDD/PCDF were eluted with n-hexane, and concentrated to 200μL for the quantification. MS/MS analysis was performed on a THERMOQUEST (Austin, TX) POLARIS™ ion trap mass spectrometer. The MS/MS condition is described elsewhere[4].

Coagulation-precipitation: Batch scale jar tests were performed to evaluate the effectiveness of soluble PCDD/PCDF removal. Following two chemicals were tested as coagulants; 260mg/L of polyaluminium chloride (PAC), and 500mg/L of iron

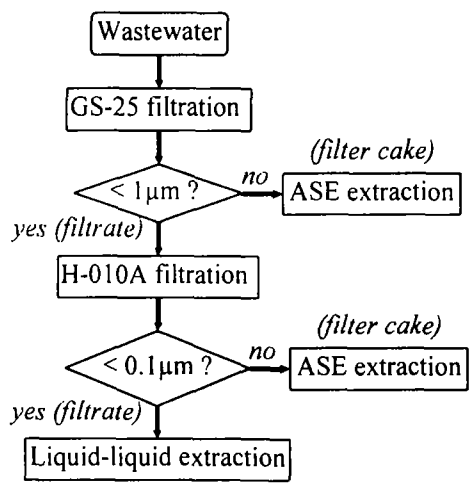

Figure 3. Filtration flow chart

(III) chloride. After flocculation, each sample was filtered with ADVANTEC No.5A cellulose filter (pore size 7μm) and the filtrate was subsequently subjected to analysis.

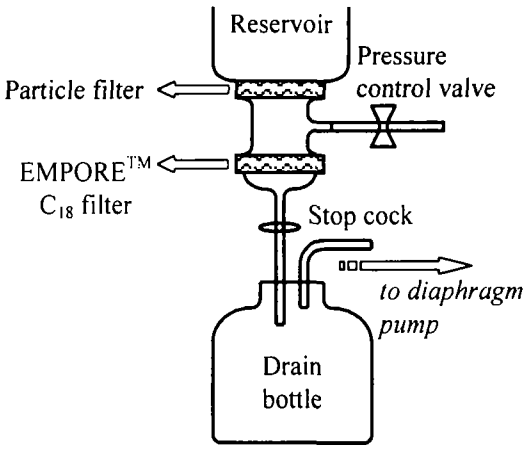

Figure 4. Glass Apparatus

Results and Discussion

PCDD/PCDF distribution: The relationship between PCDD/PCDF distribution and particle size is shown in Table 1. As total, PCDD/PCDF were unevenly distributed in the tank. However, there is noteworthy difference between particle fractions. PCDD/PCDF concentration in the over-1μm fractions varies a lot. On the other hand, the concentrations were almost the same in the under-0.1μm fractions as shown in Figure 5. The difference was due to PCDD/PCDF state. In the over-1μm fractions, PCDD/PCDF were "particle" state. These particles were unevenly dispersed by the turbulence cause by the sampling. On the contrary, PCDD/PCDF were "soluble" state in the under-0.1μm fraction and were evenly spread in the tank.

Table 1. Size distribution of PCDD/PCDF particle

Sampling	Concentration [pg-TEQ/L]			
	Total	< 0.1μm	0.1~1μm	> 1μm
First 3L	120,000	2,200	22,000	100,000
Last 3L	15,000	2,200	2,600	10,000
Average of 200L	7,900	2,400	4,300	1,300

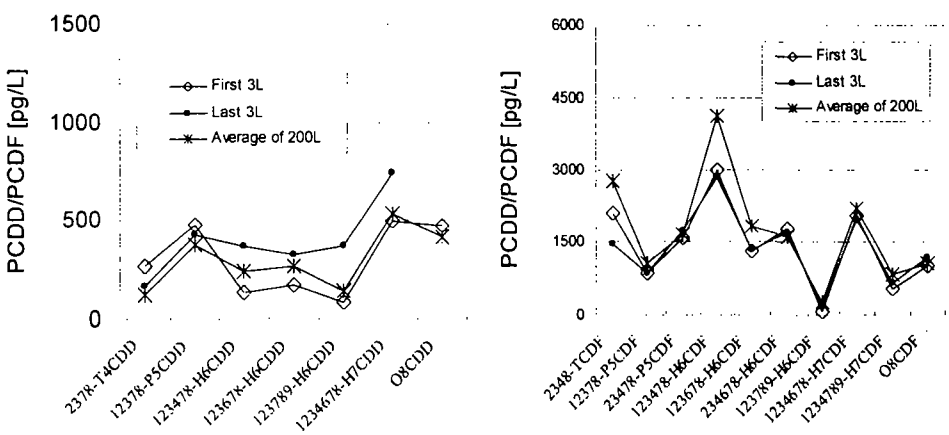

Figure 5. PCDD/PCDF concentration in under 0.1μm fraction

Removal efficacy by the coagulation-precipitation: PCDD/PCDF removal efficacy by the coagulation-precipitation treatment is shown in Table 2. Ion (III) chloride was added to raw wastewater and PAC was added to diluted wastewater. Not only the particle state, but the soluble state of PCDD/PCDF were also removed at high efficacy. The wastewater was taken downstream of the fabric filter so that particle over 7μm was negligible before the coagulation treatment. Along with the flocculation, soluble PCDD/PCDF were shifted to particle state and consequently trapped by No.5A cellulose filter.

Table 2. PCDD/PCDF removal efficacy by the coagulation-precipitation

	PCDD/PCDF in wastewater [pg/L]				PCDD/PCDF in treated water [pg/L]			
	Raw		Diluted		Ion (III) chloride		PAC	
	Total	(Soluble)	Total	(Soluble)	Conc.	Efficacy*(%)	Conc.	Efficacy*(%)
2378T4CDD	2,600	(190)	55	(11)	12	>99 (94)	2.3	>99 (79)
12378P5CDD	10,000	(430)	190	(25)	16	>99 (96)	< 3	>99 (>88)
123478H6CDD	4,600	(250)	94	(15)	6.3	>99 (98)	< 4	>99 (>73)
123678H6CDD	7,500	(260)	50	(15)	10	>99 (96)	< 4	>99 (>74)
123789H6CDD	4,900	(200)	94	(12)	10	>99 (95)	< 5	>99 (>58)
1234678H7CDD	15,500	(590)	350	(35)	47	>99 (92)	8.5	>99 (75)
O8CDD	10,000	(440)	250	(26)	72	>99 (84)	34	>99 (-30)
2348TCDF	7,900	(2,100)	180	(120)	38	>99 (98)	2.1	>99 (98)
12378P5CDF	31,000	(930)	650	(55)	49	>99 (95)	2.8	>99 (95)
23478P5CDF	29,000	(1,700)	590	(98)	51	>99 (97)	3.1	>99 (97)
123478H6CDF	29,000	(3,300)	590	(190)	42	>99 (99)	3.7	>99 (98)
123678H6CDF	31,000	(1,500)	650	(87)	45	>99 (97)	3.7	>99 (96)
234678H6CDF	25,000	(1,700)	650	(99)	43	>99 (97)	5.1	>99 (95)
123789H6CDF	1,400	(180)	34	(11)	< 8	>99 (>96)	< 5	>99 (>53)
1234678H7CDF	43,000	(2,100)	1,200	(120)	89	>99 (96)	18	>99 (85)
1234789H7CDF	5,900	(680)	190	(40)	29	>99 (96)	5.3	>99 (87)
O8CDF	26,000	(1,100)	590	(64)	100	>99 (91)	31	>99 (52)

*: The efficacy was shown based on both total PCDD/PCDF and soluble PCDD/PCDF (in parentheses)

Size distribution analysis provides additional information for the treatment of PCDD/PCDF in wastewater. On the other hand, large numbers of analyses were required to determine the distribution. Ion trap MS/MS technique was the most appropriate approach for the purpose of this study with relatively high throughput and adequate information.

References

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