Checking Analytical Procedure of PCDDs and PCDFS for Incineration Samples

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ABSTRACT

Four flue gas sampling methods were compared with respect to the congeners of PCDDs and PCDFs. The gas temperature and dust concentration seem to affect the analytical results. Flyashes from four municipal refuse incinerators were distributed to four laboratories to examine the differences among the laboratories. Although four laboratories used their own laboratory procedure and their own reference standards, the results showed comparatively good agreement.

KEYWORDS

Sampling, flue gas, flyash, PCDDs, PCDFs, interlaboratory study

INTRODUCTION

The amount of municipal refuse are steadily increasing and the residents require more and more comfortable environment. There are many problems in municipal refuse treatment and disposal system. The Ministry of Health and Welfare of Japan has launched a new project, WI 21 C (Waste Innovation 21 Century) to facilitate the research and development in the field of municipal refuse incineration system.

As for air pollution problem from municipal refuse incineration plant, dioxins emission is one of the most serious problems. The emission must be minimized in a few years. Otherwise it will become very difficult to

construct new incineration plants.
The Ministry has investigated the concentration of PCDDs and PCDFs from municipal incineration plants for several years. However the sampling and analytical method have not yet been established in Japan. The authors conducted three analytical examinations; Comparison of Sampling Method, Interlaboratory Calibration and Comparison of Cleanup Procedure.
This paper presents the results of the former two examinations.

COMPARISON OF SAMPLING METHODS

Methods

Four sampling methods were compared at a municipal refuse incineration plant. The front-end system in the four sampling methods were shown in Figure 1. The first one (No. 1 Sampling Method) has a water cooled probe in the duct, and it has a dust tube and a cylindrical thimble filter before the sampling train. The second one (No. 2 Sampling Method) has only a dust tube and a cylindrical thimble filter. The third one (No. 3 Sampling Method) has only a cylindrical thimble filter outside the duct. This system is authorized as JIS (Japan Industrial Standard) II Type. The last one (No. 4 Sampling Method) has only a cylindrical thimble filter inside the duct. This system is authorized as JIS I Type.

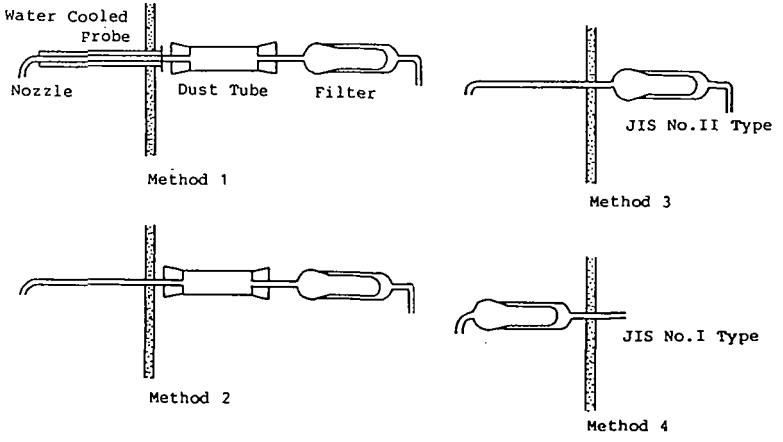

Figure 1 Gas Sampling Apparatus

Results

No. 1 Sampling Method and No. 2 Sampling Method were compared at the outlet of the incinerator, where both the gas temperature and dust concentration were high. The result is shown in Figure 2. The gas temperature at the sampling point was 770 deg. Celsius. The concentrations by No. 2 Method were 2.5 times to 25 times of those by No. 1 Method. The authors think that much amount of PCDDs and PCDFs were synthesized on the dust collected on the filter, in the case of No. 2 Method where the flue gas was not cooled down. So the data by No. 2 Method do not reflect the actual state of the outlet of the furnace.

No. 2 Sampling Method and No. 4 Sampling Method were compared at the inlet of the electrostatic precipitator, where the gas temperature was comparatively low and the dust concentration was high. The result is shown in Figure 3. The gas temperature at the sampling point was 300 deg. Celsius. The

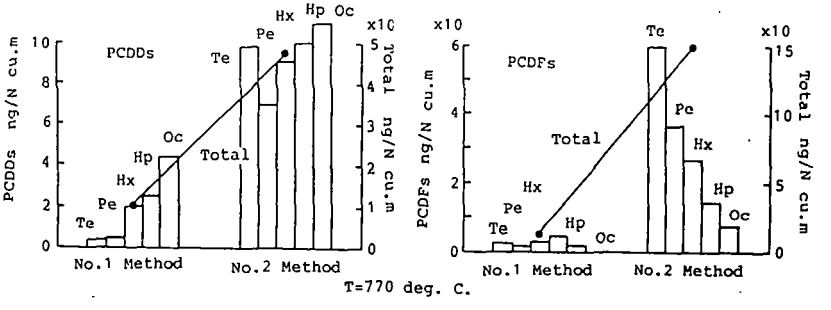

Figure 2 Comparison of No. 1 with No. 2 Sampling Method (Outlet of Furnace)

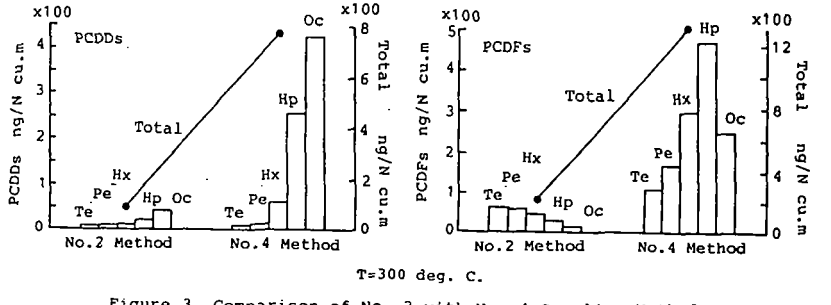

Figure 3 Comparison of No. 2 with No. 4 Sampling Method (Inlet of ESP)

concentrations by No. 4 Method were higher by 1.2 times to 16.7 times than those by No. 2 Method. At the place of high dust concentration, so much amount of dust is kept in the cylindrical thimble filter that PCDDs and PCDFs are synthesized on the dust within the long sampling period.

No. 3 Sampling Method and No. 4 Sampling Method were compared at the outlet of the electrostatic precipitator where the gas temperature was comparatively low and the dust concentration was low. The results are shown in Figure 4.

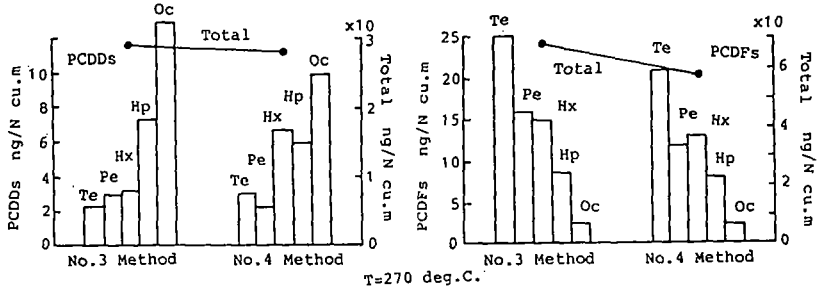

Figure 4 Comparison of No.3 and No.4 Sampling Method (Outlet of ESP)

The temperature of the gas was 270 deg. Celsius. The PCDDs and PCDFs concentrations by No. 4 Method were 0.75 times to 2.13 times of those by No.3 Method. So these two sampling methods are comparative when both the temperature and the dust concentration are low.

Table 1 shows the other analysis by an Institute, comparing No. 3 Method with No. 4 Method. Also in these data, the effect of dust at high temperature are

Table 1 Comparison of Method 3 with Method 4 (ng/N cu.m)

		Temperature deg.C.	TeCDD	PeCDD	HxCDD	HpCDD	OcCDD	Total
Outlet of ESP	Method 3	266	1,620	5,830	8,820	9,990	8,300	34,600
	Method 4	266	1,680	5,340	8,030	8,270	7,300	30,600
Inlet of FF	Method 3	138	0.2	0.5	2.4	2.2	2.8	8.1
	Method 4	138	0.2	0.3	2.3	1.7	4.8	9.3
Outlet of Furnace	Method 3	304	9.8	5.4	4.6	2.5	3.5	25.8
	Method 4	304	ND	3.5	12.4	22.8	34.6	73.3

		TeCDF	PeCDF	HxCDF	HpCDF	OcCDF	Total
Outlet of ESP	Method 3	12,900	17,800	2,000	17,800	9,060	77,600
	Method 4	12,800	15,400	22,100	20,200	10,200	80,700
Inlet of FF	Method 3	2.0	0.6	1.9	1.7	0.8	6.3
	Method 4	4.2	3.6	1.5	1.0	0.6	10.9

not seen at the outlet of electrostatic precipitator and fabric filter, but there are notable differences in the concentrations at the outlet of the furnace, where both the temperature and the dust concentration are comparatively high.

The authors conclude;

1.The temperature of dust collection portion should be below 200 deg. Celsius.

2.When the gas temperature in the duct is over 200 deg. Celsius, JIS II Type of sampling system should be used. Water cooled probe may be recommended.

3.When the flue gas temperature is over 500 deg. Celsius, water cooled probe should be used.

INTERLABORATORY CALIBRATION

Methods

Flyash samples from four incineration plants (A, B, C and D)were collected and well mixed after pulverization. Each sample was divided into four portions and provided to four Laboratories (R, S, T and U) in Japan. The laboratories have their own procedure to analyze PCDDs and PCDFs as shown in Figure 5.

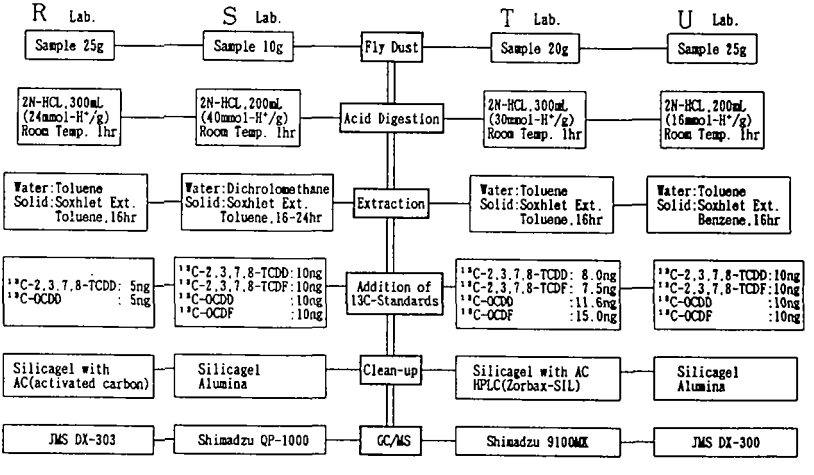

Figure 5 Analytical Procedure for Interlaboratory Calibration

Results

The concentrations of PCDDs and PCDFs in the flyashes A and D are shown in

Figure 6, and the variances are presented in Table 2. Although they used individual procedures, reference standards and instrumentation, their results show relatively good agreement. Only some uncertainties in the chromatogram charts gotten by several laboratories were pointed out.

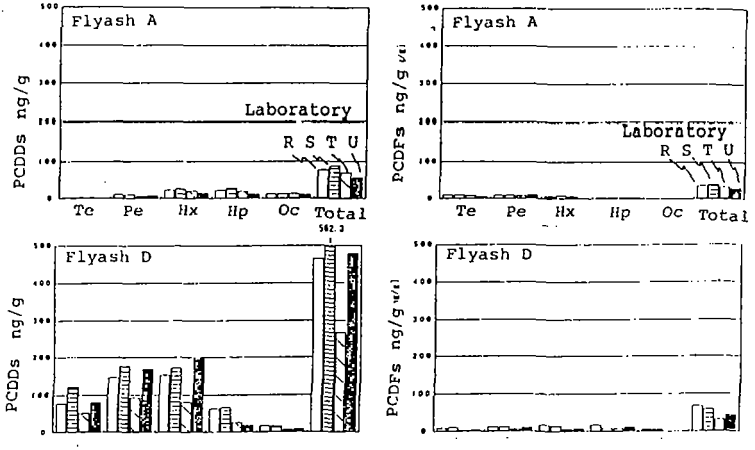

Figure 6 Results of Interlaboratory Calibration

Table 2 Variance amang Four Analyses (%)

	TeCDDs / TeCDFs	2,3,7,8-TeCDD / TeCDF	PeCDDs / PeCDFs	2,3,7,8-PeCDD / PeCDF	HxCDDs / HxCDFs	2,3,7,8-HxCDD / HxCDF	HpCDDs / HpCDFs	2,3,7,8-HpCDD / HpCDF	OcCDD / OcCDF	Total PCDDs / PCDFs	2,3,7,8-PCDDs / PCDFs
A	14.8	14.6	18.4	32.9	20.6	28.9	30.0	32.7	6.6	17.3	31.7
	15.5	49.6	13.0	10.2	36.4	46.3	6.3	9.7	33.5	12.2	22.8
B	28.0	38.1	31.2	47.8	29.5	40.9	53.9	55.5	28.2	33.7	52.9
	19.9	68.8	26.2	25.1	22.3	33.5	59.3	58.3	31.7	19.7	31.3
C	32.8	30.5	25.1	44.5	46.1	60.5	54.7	58.2	57.6	44.0	56.3
	19.5	43.5	10.6	24.4	38.0	52.6	11.4	37.8	56.5	20.1	34.7
D	34.2	66.5	25.7	53.0	32.8	40.4	53.8	54.6	37.1	28.2	49.8
	37.5	77.1	26.2	33.3	41.6	53.6	33.8	35.3	43.2	31.0	39.0

To complete the interlaboratory cross-check program, raw extracts, purified extracts and reference standards should be exchanged.

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