CHLOROBENZENES AND CHLOROPHENOLS AS ALTERNATIVE INDICES TO DIOXINS IN FLUE GASES UNDER STEADY STATE AND AT STARTUP

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Abstract

Chlorobenzenes (CBs) and chlorophenols (CPs) were measured along with dioxins (DXNs) and organic halogenated compounds (OHC) in flue gases at the inlet and outlet of the bag filters of two municipal solid waste incinerators in Japan to investigate alternative indices to DXNs. Data was taken not only during steady state operation but also under startup conditions. CB and CP concentrations were basically well correlated with DXN levels in the test runs. However, the degree of correlation tended to differ with the incineration plant and with the point of sampling point of the flue gases, probably because of the differences that occur in the types of waste incinerated and the operational parameters under field conditions. The concentrations of congeners with 3–6 (CBs) or 2–5 (CPs) chlorine atoms were well correlated with DXN levels. These compounds are easy and fast to measure, especially in the case of CBs. CB concentration is therefore expected to be a useful alternative index for the daily monitoring and quick feedback control of plant operation.

Introduction

Monitoring and control of dioxins (DXNs) in flue gas are becoming increasingly important because regulating DXNs now becomes general in Japan in the context that protection of safety and security has become a task in all fields. Therefore, monitoring techniques for DXNs are desired to have accuracy for estimation as alternative indices of DXNs along with a rapidity and simplicity to measure. Simple methods for sampling and pretreatment are necessary to establish such monitoring techniques. Present organic indices suggested according to these conditions are organic halogens, chlorobenzenes (CBs), and chlorophenols (CPs) which have specific monitoring techniques[1-4]. This report describes a study based on observed values in municipal solid waste incinerators as part of efforts to find indices for convenient and appropriate flue gas monitoring.

Experimentals

Flue gas sampling

Flue gases emitted from two solid waste incineration plants shown in Figure 1 were sampled. A-incineration plant has two stoker-type furnaces with a processing capacity of 150 tons of wastes and B-incineration plant has a 450-ton capacity for processing per day, respectively. Sampling was performed at two points which were the inlet and the outlet of the bag filter (SP1 and SP2) in Plant A, and at one point of the outlet of the bag filter (SP3) in Plant B. Two-hour sampling was performed four times during a steady-state operation immediately after the startup of the plant, followed by single four-hour sampling. Sampling and measurement according to official methods were conducted for DXNs. As for CBs, four methods for sampling and measurement were applied as shown in Table 1, including methods by thermal desorption after adsorption and method which the
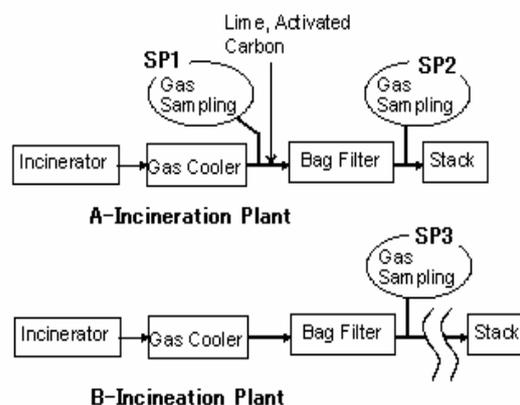

Fig. 1 Incineration plant flows and gas sampling points

Table 1   Methods of sampling and measurement of CBs

Method	Trapping temperature (ºC)	Trapping medium	Concentration of solution	Sampling point in facility
1	Room temp.	Tenax TA adsorbent	-	SP1, SP2
2			-	SP3
3	0 (in water with ice)	Dioxin sampling train including XAD II resin	Not performed	SP1, SP2
4			Flashing of nitrogen gas	SP3

extracted solvent was fractionated after trapping according to official methods for DXNs. The extract for measurement of DXNs was also used to analyze CPs.

Experiments

Aside from sampling for DXNs and CPs, flue gas sample was trapped in a solid cartridge for thermal desorption in order to analyze CBs in the flue gas. The gas sample trapped was analyzed by a quadrupole GC-MS (Method 1 and 2). This method has a merit that a loss of compounds by volatilization rarely occurs because the concentrating process at the intermediate stage can be cut out unlike a method which part of the extract during the sampling process for DXNs is used for analysis, and therefore, values are easy to obtain even on chloride and bichloride with a high volatility.

Analysis

The samples for analyzing CBs trapped in the solid adsorbent (Tenax TA) by Method 1 and 2 were analyzed by SIM method using a GC-MS instrument (HP6890-HP5973 produced by Agilent Technologies）equipped with a thermal desorption device (ATD400 produced by Perkin Elmer). DXNs were analyzed by using HRGC-HRMS after concentrating the extract by official methods. For CPs and CBs by Method 3 and 4, parts of the crude extract from the intermediate stage of concentration (after extraction with CS_2 medium) in the process of analyzing DXNs were used. The extract was concentrated if needed, and analyzed by GC-MS. However, a loss due to emission may occur in some of CBs and dichlorobenzenes at this stage.

Results and Discussion

Evaluation of the measurement method of chlorobenzenes

With respect to the concentration of CBs by each measurement method, results of the four-hour sampling after the eight-hour steady state operation are shown in Table 2. However, the results are less reliable because numbers in parenthesis were the values that were not good in the recovery ratio in the analysis procedure. This is because the best performance of the solid absorbent (Tenax TA) was not delivered because of influences of water and oil contents in the gases analyzed in Method 1 and some factors in the concentration process possibly influenced in Method 4.

Results obtained by Method 2 and 3 met requirements as a quantitative value, and in particular, clear

Table 2   Measurement of chlorobenzenes (ng/m^3$_N$) in flue gases in four cases

Compound	A-MWI (SP1)		A-MWI (SP3)	
	Method 1	Method 3	Method 2	Method 4
Chlorobenzene	-	-	1,200	(390)
1,2-Dichlorobenzene	(280)[a]	60	830	(13,000)
1,3-Dichlorobenzene	(330)	50	760	(230)
1,4-Dichlorobenzene	(2,020)	930	790	(740)
1,2,3-Trichlorobenzene	(100)	40	150	(360)
1,2,4- Trichlorobenzene	(440)	270	1,000	(2,200)
1,3,5- Trichlorobenzene	(520)	160	710	(1,400)
1,2,3,4-Tetrachlorobenzene	(150)	150	490	(1200)
1,2,3,5 & 1,2,4,5-Tetrachlorobenzene	(260)	310	800	(720)
Pentachlorobenzene	(290)	370	840	(3,200)
Hexachlorobenzene	-	80	430	(1500)
Total CBs	(4,070)	2,100	8,000	(25,000)

a   Numbers in parentheses are values that gave poor recovery ratios in the analytical procedure.

quantitative results were obtained even for monochlorobenzene by Method 2. The results from the analyses by Method 2 and 3 are used in the subsequent discussion.

Concentration of dioxins and chlorobenzenes

Table 3 shows the measurement data of CBs and DXNs in the flue gases at the outlet of the bag filter (SP2) in A-incineration plant. Although the concentrations of DXNs were approximately five to 20 ng/m^{3}N, the concentrations of CBs were demonstrated to be about several hundred-fold higher than those of DXNs, ranging from approximately 400 to 6000 ng/m^{3}N. In addition, values of p-dichlorobenzene and 1,3,5- or 1,2,4-trichlorobenzene were relatively high among CBs.

Table 3   Measurement of chlorobenzenes (ng/m^3_N) and dioxins in flue gases at the outlet of the bag filter (SP2) in plant A

Compound	Run 1	Run 2	Run 3	Run 4	Run 5
1,2-Dichlorobenzene	310	190	180	130	11
1,3-Dichlorobenzene	250	160	200	100	12
1,4-Dichlorobenzene	1,300	1,100	1,200	800	270
1,2,3-Trichlorobenzene	130	55	61	69	6
1,2,4- Trichlorobenzene	740	360	350	250	35
1,3,5- Trichlorobenzene	1,000	390	330	190	28
1,2,3,4-Tetrachlorobenzene	400	180	140	89	9
1,2,3,5 & 1,2,4,5-Tetrachlorobenzene	840	390	320	230	29
Pentachlorobenzene	530	270	210	160	21
Hexachlorobenzene	150	82	72	59	9
Total CBs	5,700	3,200	3,100	2,100	430
Dioxins (ng/m^3_N)	19	9.6	8.6	6.4	5.4
Dioxins (ng-TEQ/m^3_N)[a]	0.084	0.041	0.038	0.013	0.018

a Numbers below the detection limit were calculated as one-half of the limit.

Concentration of chlorophenols

Table 4 shows the measurement data of CPs in the flue gases at SP2 as well as the data of CBs mentioned above. The dioxin concentrations in individual runs were the same as those in Table 3. Total measurements of CPs in individual runs were further higher than those of CBs, ranging from 600 to 14000 ng/m^3_N.

Table 4   Measurement data of CPs (ng/m^3_N) in flue gases at the outlet of bag filter (SP2) in plant A

Compound	Run 1	Run 2	Run 3	Run 4	Run 5
Chlorophenol	3,800	550	870	450	140
Dichlorophenols	3,300	790	1,000	460	150
Trichlorophenols	6,500	2,300	2,600	1,100	240
Tetrachlorophenols	620	280	330	130	50
Pentachlorophenol	190	70	100	35	16
Total CPs	14,000	4,000	4,900	2,200	600

Relationship between Chlorobenzenes/Chlorophenols and Dioxins

The relationship between total CBs and DXNs concentrations is shown in Figure 2. Although it reveals a positive correlation between total CBs and DXNs concentrations as separately demonstrated in Figure 2 a), the relationship was apparently different by each incineration plant or sampling point such as the outlet or the inlet of the bag filter. When the relationship of hexachlorobenzene with DXNs was individually examined, a good correlation between the two compounds was observed as shown in Figure 2 b). Such a trend was observed at the inlet of the bag filter (SP1) in Plant A, and it was also pointed that isomeric form with chlorine atoms more than those in trichlorobenzene contributed good correlations with DXNs. Thus, there were better correlations between compounds with a greater number of chlorine atoms and DXNs when the measurement data was separately examined by each incineration plant.

It is unlikely that a universal relationship among incineration plants because of differences in combustion characteristics and individual variability. Therefore, it is expected to be useful to rapidly conduct the daily monitoring by using a simple procedure such as the measurement of CBs in each plant.

In addition a similar trend was observed in the relationship between CBs and toxic equivalents of DXNs which are directly related to laws and regulations in Japan.
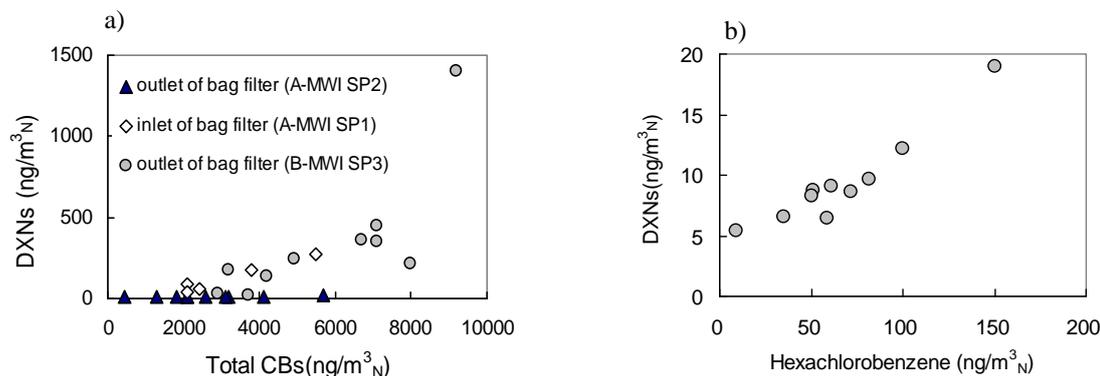
Fig.2   Relationship between total chlorobenzene and dioxin concentrations.
a) All the data, including those from the inlet of the bag filter, were plotted.
b) Only the hexachlorobenzene data at SP2 in plant A were plotted.

Next, the relationship between total CPs and DXNs concentrations is shown in Figure 3. There are no clear correlations between the concentrations of CPs and DXNs obtained from all the points measured (Figure 3 a). This is the same as the result in CBs. However, at SP2, there is a correlation between pentachlorophenol and DXNs (Figure 3 b) and a relatively good correlation between total concentrations of CPs and DXNs.
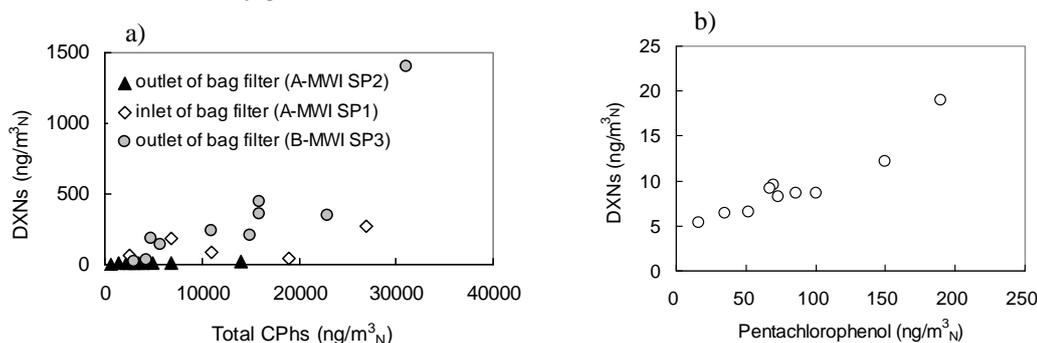

Fig.3   Relationship between total chlorophenol and dioxin concentrations.
a) All the data, including those from the inlet of the bag filter, were plotted.
b) Only the data on pentachlorophenol at SP2 in plant A were plotted.

CBs and CPs were confirmed to be constituents of organic halogen compounds (OHC) because the two compounds were detected in thermal desorption components trapped by the same adsorbent which trapped OHC in another report [5].

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