EVALUATION OF SUBSTITUTED INDEXES FOR CHLOROBENZENES USING DIOXIN PRECURSOR ANALYZER

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Introduction

Control and reduction of amount of Dioxin emitted from municipal solid waste (MSW) incinerator have become an urgent social need. In Japan, a modified law enforces the analysis of dioxin emissions every year. To reduce the amount of Dioxin emitted from MSW incinerator, it is necessary not only to measure the emitting Dioxin every year but also to positively grasp the amount of emitting Dioxin, thus to connect the grasped amount to operation control. In this regard, rapid determination and monitoring of Dioxin have been emphasized. On the other hand, the analysis of Dioxin is understood to consume large quantity of human resources, time, and cost. At least at present, there required to sample stack gas or other exhaust gas, to bring the sample back to a laboratory, to give complex preliminary treatment, and to conduct analysis with high-resolution GC-MS apparatuses. Although the direct monitoring of the amount of Dioxin emissions at an operating MSW incinerator is effective to positively connect the analyzed result with operation control of MSW incinerator. But there is no established technology of direct rapid analysis of Dioxin, unfortunately.

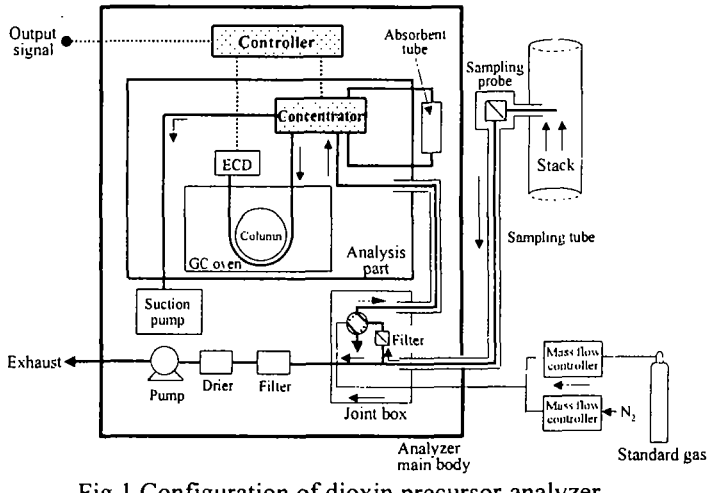

Fig.1 Configuration of dioxin precursor analyzer

To this point, this study focused on chlorobenzenes that are reported to have very close correlation with Dioxin. An operating MSW incinerator was adopted to install a dioxin precursor analyzer that can analyze dioxin precursors rapidly at a low cost, and continuously. Thus, chlorobenzenes were measured for a period of total 70 days to give evaluation on applicability of the analyzed result as substituted indexes. The evaluation proved efficacy of the indexes.

Methods and Materials

Brief description of the dioxin precursor analyzer

To determine chlorobenzenes in a stack gas, a dioxin precursor analyzer (GDX-2000, made by NKK-Toa DKK) was applied.

The analyzer comprises: an analyzer body which contains a heating type process gas chromatograph, an ECD detector (Electron Capture Detector), and a sample concentration mechanism; and a heating and sampling tube that samples stack gas from a gas duct of incinerator, (Fig. 1).[1),2)] The analyzer is separated to a control section, a concentration section, and an analysis section. The stack gas sample that was collected from gas duct through a sampling tube is concentrated in the concentration section, then it is separated and determined in the analysis section.

Method for determining chlorobenzenes in stack gas

The dioxin precursor analyzer collected 900 ml of the stack gas (at 30 ml/min of flow rate for 30 minutes), and conducted the continuous measurement at a 60 minutes cycle. Table 1 shows the operating conditions of the dioxin precursor analyzer.

The applied operating MSW incinerator was a full-continuous operation furnace of stoker type having a capacity of 300 t/day. The stack gas was sampled from a duct downstream side of an electrostatic precipitator.

Along with the operation of the dioxin precursor analyzer, sampling of Dioxin was carried out to investigate the correlation between the precursors and the Dioxin.

Table 1 Condition for determining dioxin precursors

Concentration condition	
Material of concentration tube	TENAX TA
Concentration temperature	100 ℃
Concentrated gas flow rate	30 ml/min
Heating and recovery temperature	270 ℃
Recovered gas flow rate	1.5 ml/min
GC condition	
Column temperature	50 ℃, 10 ℃/min, 200 ℃, 16 ℃/min, 270 ℃
Kind of column	CA5-60M-0.25F 60m □0.25mmID □0.25μm
Carrier gas	He
Carrier gas flow rate	1.5 ml/min
ECD condition	
Discharged gas	He 30 ml/min
Dopant gas	Xe 3% / He balance
Cell temperature	330 ℃

The analysis of Dioxin conformed to an official method for analysis in Japan (JIS K 0311).

Results and Discussion

(1) Result of continuous analysis of chlorobenzenes

The determination of chlorobenzenes in stack gas was given using the dioxin precursor analyzer for a period of total 70 days. The operating status of the analyzer was favorable, and the analyzer was concluded to give no practical problem for a long period of operation even in operating MSW incinerator that are exposed to lots of inclusions.

Fig. 2 shows an example of variations in concentration of 1,2,4-trichlorobenzene, observed continuously during the operation days. The observation revealed that totally the variation behavior of each of chlorobenzene homologues is similar to each other, but that the change of concentration differs from each other. The phenomenon is presumably caused from the difference in chemical properties such as boiling point between homologues that have different number of chlorines.

(2) Relationship between concentration of chlorobenzenes and concentration of Dioxin

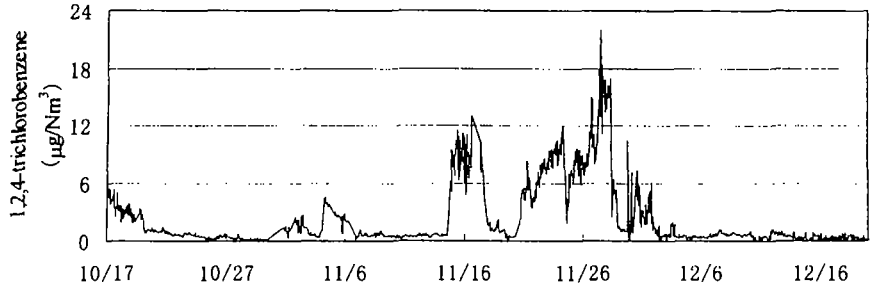

Fig. 2 Variations of concentration of 1,2,4-trichlorobenzene

Table 2 Correlation factor between the concentration of chlorobenzenes and the concentration of Dioxin

Chlorobenzenes	Converted to O2 12%	TEQ
1,2,4-trichlorobenzene	0.97	0.91
1,2,4,5-tetrachlorobenze	0.76	0.66
Pentachlorobenzene	0.88	0.80

An investigation was given on the relationship between the observed values of concentration of chlorobenzenes and the dioxin concentration determined by the official analysis method. Table 2 shows the correlation factor between them. Since the relation between the three kinds of chlorobenzenes analyzed in the study and the Dioxin concentration showed a difference, it is important to select a dioxin precursor that has highest correlation for estimating the concentration of Dioxin at high accuracy.

Fig. 3 shows the relation with 1,2,4-trichlorobenzene that gave the largest correlation factor. The correlation factor with 1,2,4-trichlorobenzene that gave largest correlation factor was 0.97 (converted to oxygen 12% state). Thus, the concentration of Dioxin was confirmed to be determined at high accuracy. Fig. 4 shows the relation between the concentration of 1,2,4-trichlorobenzene and the concentration of Dioxin, in gas phase and in particle phase. Since the dioxin precursor analyzer determines the gas phase chlorobenzenes, the analyzer should give a high correlation with the gas phase Dioxin.

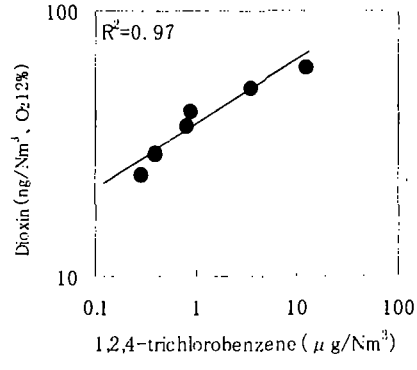

Fig. 3 Correlation between 1,2,4-trichlorobenzene and Dioxin

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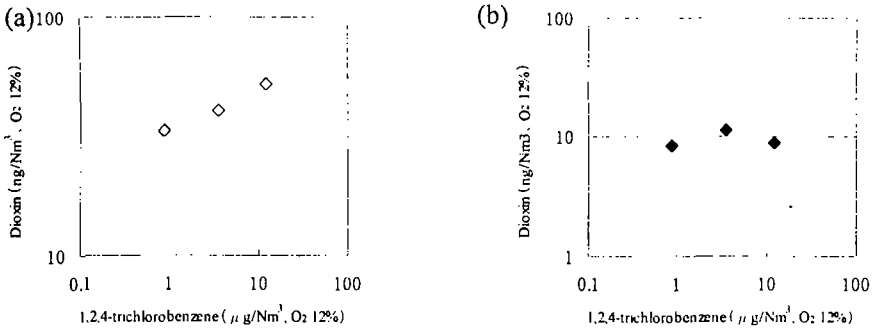

Fig. 4 Relationship between 1,2,4-trichlorobenzene and Dioxin
(a):Gas phase, (b):Particle phase

References

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