Technique of Monitoring Dioxins in Flue Gas from MSW Incinerators using Dioxin Precursor Analyzer

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The dioxin precursor analyzer developed by NKK was experimentally adopted at a running MSW (Municipal Solid Waste) incinerator to measure the concentrations of dioxin precursors continuously for a period of 70 days. It was verified that the concentration of a specific type of dioxin precursor and that of dioxins were closely correlated, hence it is possible to estimate the concentration of dioxins by measuring that of a dioxin precursor.

1. Introduction

There is an urgent need to reduce dioxins emitted from MSW (Municipal Solid Waste) incinerators and other sources. The Law Concerning Special Measures against Dioxins obligates the concentration of dioxins to be measured at least once a year, but to reduce the emissions of dioxins from waste incinerators and other sources, measurement only once a year is inadequate; more frequent measurement and comprehensive control of facility operations are required. For this purpose, a technology for quickly measuring the concentration of dioxins and monitoring it continuously is needed. In the past, the analysis of dioxins required much manpower, time, and cost. In order to link the measurement of dioxins with the operation control of a waste incinerating facility, directly monitoring the emissions of dioxins on site would be effective, but no technology has yet been established for analyzing dioxins directly and quickly.

In view of the close correlation found between the concentration of dioxins and those of dioxin precursors, particularly chlorobenzenes, a dioxin precursor analyzer that can measure the concentrations of dioxin precursors quickly, economically, and continuously was developed. This paper reports the results of applying the newly developed analyzer at a running MSW incinerator for measuring the concentrations of chlorobenzenes continuously for a period of 70 days.

2. Outline of the dioxin precursor analyzer

The concentrations of dioxin precursors in the flue gas were measured at a running MSW incinerator by the GDX-2000 dioxin precursor analyzer developed and commercialized jointly by NKK and Toa DKK.

This instrument is composed of the analyzing system and sampling system as shown in **Fig.1** and **Photo 1**[1),2)]. The analyzing system has a temperature programmed process gas chromatograph containing an ECD (Electron Capture Detector) and a sample concentration mechanism. The sampling system has a heated sampling probe and a sampling tube, which collect flue gas samples from the duct of an incinerator. The analyzing system is composed of the control section, concentration section, and analyzing section. The flue gas sample collected from the duct is concentrated in the concentration section, and separated, detected, and quantified in the analyzing section. The ECD employed for detection is characterized by high sensitivity for chemical compounds that have high electron affinity. Dioxin precursors and dioxins in the flue gas of incinerators contain chlorine that has high electron affinity, so this detector can detect these chemical compounds with high sensitivity. Therefore, the detector can perform the measurement using only a small amount of the flue gas sample, and one cycle of measurement can be completed within 60 minutes; or within 15 minutes if the chemical components to be measured are specified.

The performance of this analyzer has been verified at many running MSW incinerators. The following are the results of the performance verification by the long-term continuous measurement carried out for the first time at a running incinerator. In addition, the effectiveness of various substitutional indexes for dioxins in estimating the dioxin concentration was evaluated.

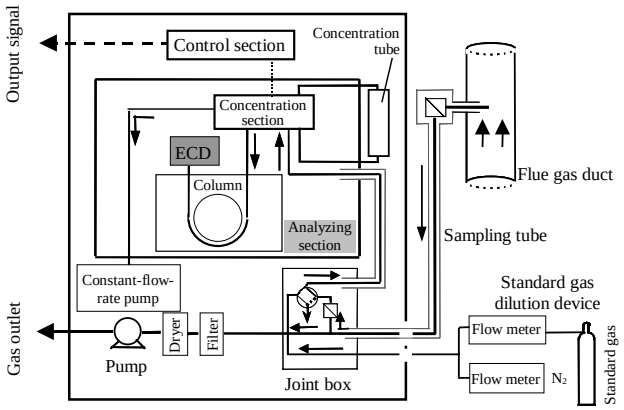

Fig.1 Outline of the dioxin precursor analyzer

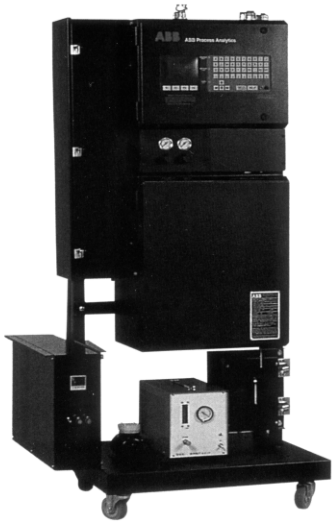

Photo 1 Appearance of the dioxin precursor analyzer

3. Experimental method

The running waste incinerating facility where the continuous flue gas measurement was carried out was a stoker-type facility with a 300 t/day capacity that can continuously operate 24 hours a day. Flue gas samples were collected from the duct downstream of the electrostatic precipitator of one of the lines in the facility through the sampling tube heated to 150°C (**Fig.2**). The flue gas sample of 900 mL was collected at one time, and continuous measurement was performed using the dioxin precursor analyzer at intervals of 60 minutes. Dioxin precursors in the flue gas were separated, detected, and quantified in the analyzer. The calibration curve applied to quantification was prepared by using standard gas that contained dioxin precursors at known concentrations. **Table 1** shows the measurement conditions for the dioxin precursor analyzer.

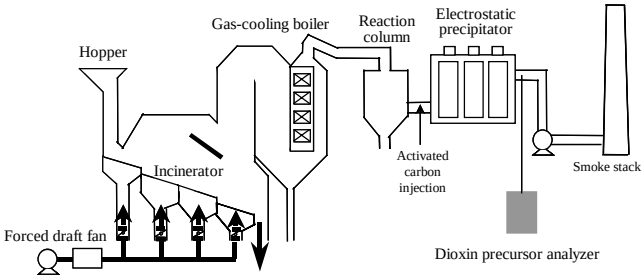

Fig.2 Outline of the incinerating facility and location of the analyzer

Table 1 Measurement conditions for the dioxin precursor analyzer

Item	Condition	
Concentration	Concentration tube material	TENAX TA
	Concentration temperature	100℃
	Concentrated gas flow rate	30 ml/min
	Heating recovery temperature	270℃
	Recovered gas flow rate	1.5 ml/min
Gas chromatography	Column temperature	50℃, 10℃/min, 200℃, 16℃/min, 270℃
	Column type	UA5-60M-0.25F 60m×0.25mmID×0.25 μm
	Carrier gas	He
	Carrier gas flow rate	1.5 ml/min
ECD	Discharge gas	He 30 ml/min
	Dopant gas	Xe 3% / He balance
	Cell temperature	330℃

Along with the continuous measurement by the dioxin precursor analyzer, the concentration of dioxins in the flue gas was also measured in order to investigate its correlation with the concentrations of dioxin precursors measured by the dioxin precursor analyzer. During the measurement, the operating conditions of the waste incinerating facility were varied as needed. Generally, an incinerator operating under a stable condition continues to emit an almost constant amount of dioxins, which makes it difficult to evaluate the correlation with dioxin precursors. Therefore, the operating conditions were varied to cause variations in the emissions of dioxins.

For investigating the correlation, the concentration of dioxins in the flue gas samples was analyzed in accordance with the official analysis method defined by JIS (JIS K 0311).

4. Experimental results and discussions

4.1 Measurement results of dioxin precursors

Dioxin precursors in the flue gas were measured at the downstream side of the electrostatic precipitator by the dioxin precursor analyzer for a period of 70 days. In this experiment, the focus was on detecting chlorobenzenes. **Fig.3** shows a chromatogram of the actual flue gas components.

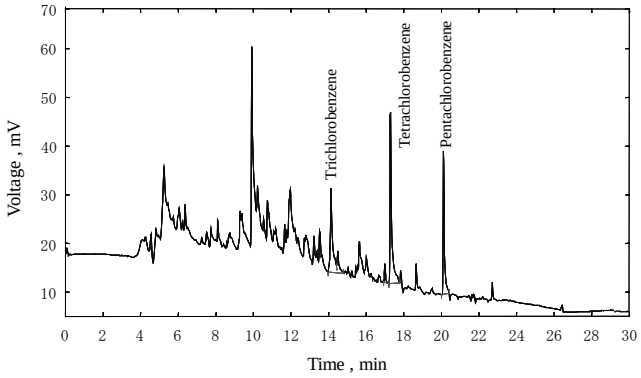

Fig.3 Chromatogram of the actual flue gas components

As an example of the measurement, the variation in the emissions of 1,2,4-trichlorobenzene continuously measured during the operating period is shown in **Fig.4**. The concentration of the dioxin precursor varied according to the operating conditions of the incinerator. The variations in the concentration of CO and that of 1,2,4-trichlorobenzene were compared as these data are considered to represent the operating conditions of the waste incinerating facility during this experiment (**Fig.5**). Even during the period when the concentration of CO was low and the combustion in the incinerator was believed to be stable, sometimes 1,2,4-trichlorobenzene was emitted at high concentration levels. Conversely, even during the period when the concentration of CO fluctuated widely, that of 1,2,4-trichlorobenzene stayed relatively stable.

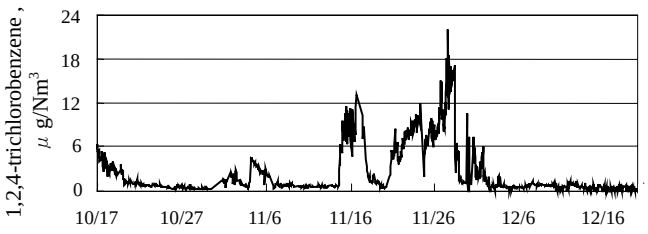

Fig.4 Variation in the emissions of dioxin precursor

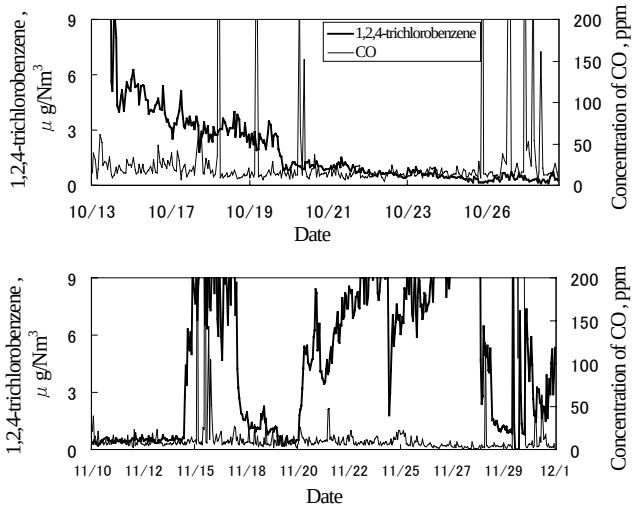

Fig.5 Relation between the emissions of CO and those of dioxin precursor

The measurement performance of the analyzer was excellent throughout the experiment, and showed no problem even when applied to the long-term continuous measurement of the flue gas from an actual running waste incinerating facility that contains large quantities of impurities. During the 70 day continuous measurement, the analyzer measurement performance was kept stable by carrying out maintenance such as (1) calibration by standard gas once a week, (2) change of carrier gas (high-purity He) once every three weeks, and (3) change of the filter in the sampling probe once every 30 days. It was also found that the dopant gas (Xe/He) for the ECD needed to be changed only once every three months.

Thus, the analyzer, which can measure the concentrations of dioxin precursors quickly and continuously, makes it possible to closely monitor the emission levels of dioxin precursors at waste incinerating facilities.

4.2 Correlation between the concentration of dioxins and those of dioxin precursors

The correlation between the concentration of dioxins measured by the JIS method and the concentrations of dioxin precursors measured by the dioxin precursor analyzer was investigated. With regard to the concentrations of dioxin precursors, three types of chlorobenzenes were investigated this time, and their measured concentrations were averaged over the period corresponding to the sampling interval for dioxins (four hours). **Table 2** shows the resultant correlation between the concentration of dioxins and those of dioxin precursors. The concentration of each type of chlorobenzene investigated this time had a different degree of correlation with the concentration of dioxins. The highest correlation was with 1,2,4-trichlorobenzene with

an R^2 value of 0.97 in oxygen 12% equivalent and 0.91 in TEQ (Toxicity Equivalent). These strong correlations suggest that the concentration of dioxins can be estimated based on the concentrations of dioxin precursors. The correlation diagrams with 1,2,4-trichlorobenzene that indicated the highest correlation are shown in **Fig.6** (in oxygen equivalent) and **Fig.7** (in toxicity equivalent).

Table 2 R^2 values between the concentration of dioxins and those of dioxin precursors

Concentration of dioxin precursor, μ g/Nm^3	Concentration of dioxin precursor, in oxygen 12% equivalent, ng/Nm^3	Concentration of dioxin precursor, in toxicity equivalent, ng-TEQ/Nm^3
1,2,4-trichlorobenzene	0.97	0.91
1,2,4,5-tetrachlorobenzene	0.76	0.66
Pentachlorobenzene	0.88	0.80

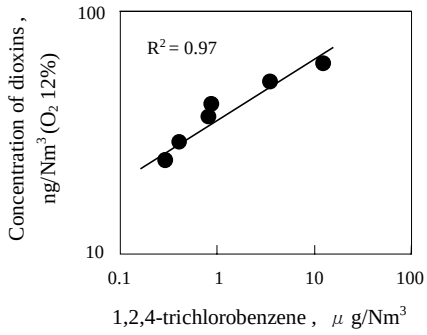

Fig.6 Correlation diagram between the concentration of dioxins (in oxygen equivalent) and that of 1,2,4-trichlorobenzene

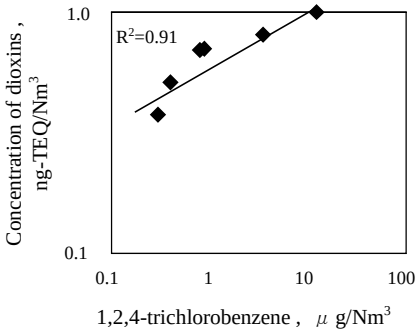

Fig.7 Correlation diagram between the concentration of dioxins (in toxicity equivalent) and that of 1,2,4-trichlorobenzene

4.3 Estimation of the concentration of dioxins

Based on the correlation between the concentration of dioxins and those of dioxin precursors obtained in the previous section, emissions of dioxins were estimated. The following equation was used for estimating the concentration of dioxins.

$$[DXN] = 37 \times [TrCB]^{0.23} \quad \cdots\cdots(1)$$

where, [DXN] is the concentration of dioxins (in toxicity equivalent), and [TrCB] is the concentration of 1,2,4-trichlorobenzene that showed the highest correlation.

Using Equation (1), the variation in the concentration of 1,2,4-trichlorobenzene shown in **Fig.4** was converted into the variation in the concentration of dioxins (**Fig.8**). From this diagram, it is possible to estimate that the concentration of dioxins varied in the range of 0.5 to 1.0 ng-TEQ/Nm^3 at this facility.

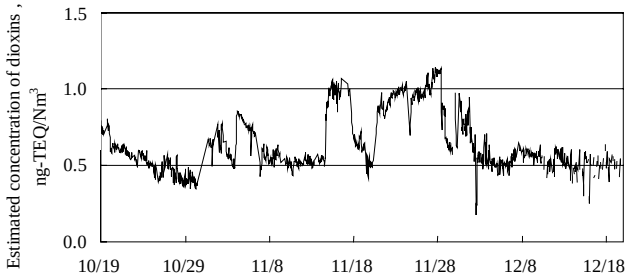

Fig.8 Variation in the estimated concentration of dioxins

As stated above, it is possible to convert the concentration of a dioxin precursor measured by the dioxin precursor analyzer to the variation in the estimated concentration of dioxins.

A similar investigation of the correlation carried out at a different facility showed that the concentration of dioxins was closely correlated with the concentration of a different type of dioxin precursor[3]. In view of this result and our investigation, the following is presumed. Each of the waste incinerating facilities has different operating parameters such as the waste quality processed, temperature of each step of the waste incinerating process, and the amount of air injected. These differences in operating parameters result in differences in the process of generating dioxin precursors, and therefore lead to the difference in their correlation with the concentration of dioxins. Hence, in order to accurately estimate the concentration of dioxins, it is important to select the type of dioxin precursor that has the highest correlation with the concentration of dioxins. In this analyzer, the collected flue gas sample is first separated by the gas chromatograph, and each component is subjected to detection by the ECD. Therefore, it is possible to quantify multiple components at the same time, and hence to select the substance that has the highest correlation among various dioxin precursors each having a different correlation with the concentration of dioxins.

5. Conclusions

Using the newly developed dioxin precursor analyzer, continuous measurement was carried out at a running waste incinerating facility. The following findings were obtained.

(1) The investigation revealed a high correlation between the concentration of dioxins and those of dioxin precursors, indicating that the concentration of dioxins can be accurately estimated.

(2) The concentration of each type of dioxin precursor has a different degree of correlation with the concentration of dioxins. Therefore, for an accurate estimation, the type of dioxin precursor that has the highest correlation must be selected.

(3) The dioxin precursor analyzer functioned smoothly throughout the long-term continuous measurement that lasted 70 days, and was confirmed to be applicable to practical purposes such as monitoring running facilities.

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