On-line Monitoring Equipments of Dioxins and their Precursors for Incineration Plants

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It usually takes a few weeks to analyze dioxins concentration in flue gas from MSW incinerators by official method. In order to reduce the required time for analysis, we have developed an on-line measuring equipment for pentachloro-dibenzofuran (P5CDF) and a real-time measuring equipment for trichlorobenzene (T3CB). The following results were obtained from field tests carried out using these equipments. (1) The concentration of DXNs emitted can be estimated and monitored by measuring the concentration of P5CDF contained in flue gas using a vacuum ultraviolet ionization mass spectrometer (VUV analyzer) after automatic concentration of P5CDF. (2) Optimum operating conditions to reduce dioxins emission can be obtained by the T3CB measuring equipment which relates to dioxins' behavior inside furnaces real-timely, and (3) These equipments can be applied in adjusting operating conditions during the trial operation of an incineration plant by monitoring them and for basic research and development.

1. Introduction

Dioxin emissions (hereafter abbreviated as DXNs) emitted from incineration plants have become an issue of major social concern. As a manufacturer of incineration plants, MHI has developed various means for advancing the combustion control and flue gas treatment of incinerators, and has achieved fruitful results in order to reduce DXNs[(1),(2)].

On the other hand, it is necessary to verify the effectiveness of these measures by analyzing DXN levels based on official methods. However, a long time (several weeks) is needed to analyze DXNs because the concentration of DXNs is extremely small. Moreover, the DXNs must be separated into various isomers and each isomer must be quantitatively analyzed in order to assess the respective toxicities of each type of DXNs present. This problem has been a major barrier to verifying the effectiveness of the measurement of DXN levels. In addition, although DXN precursors have been suggested as being more effective in controlling DXNs than the CO conventionally used[(3)], they are said to be unsuitable as indices for controlling combustion because of the long time amount of time required to analyze them like DXNs.

Therefore, the rapid measurement of DXNs and their precursors is very useful for the operation of incinerator furnaces and flue gas treatment plants.

With the aim of finding suitable solutions to these problems, this paper introduces a monitoring system consisting of an on-line equipment for measuring pentachloro-dibenzofuran (P5CDF) and a real time equip-

ment for measuring trichlorobenzene (T3CB), which have been developed by MHI.

2. Configuration of system

The monitoring system is shown in **Fig. 1**. This system is basically composed of both equipments described above. **Table 1** shows the major specifications of this monitoring system. The following paragraphs describe the vacuum ultraviolet ionization mass spectrometer (hereafter abbreviated to VUV analyzer) used in common with both equipments, the on-line equipment for
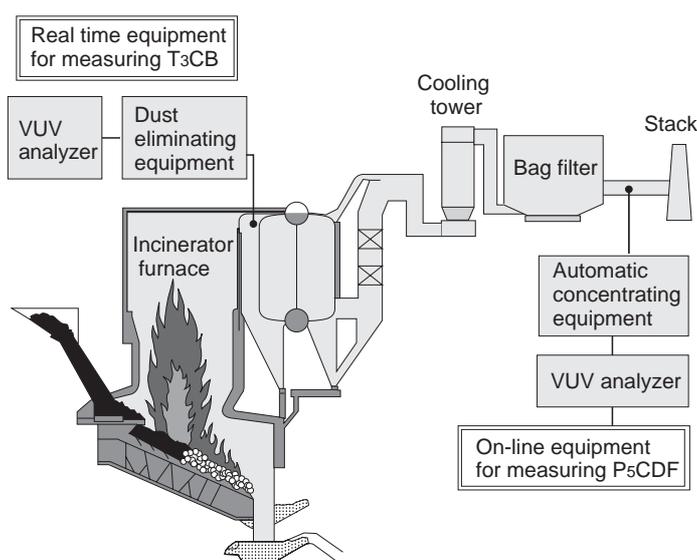

Fig. 1 Monitoring system
The system consists of an on-line equipment for measuring P5CDF and a real time equipment for measuring T3CB.

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Table 1 Specifications of system

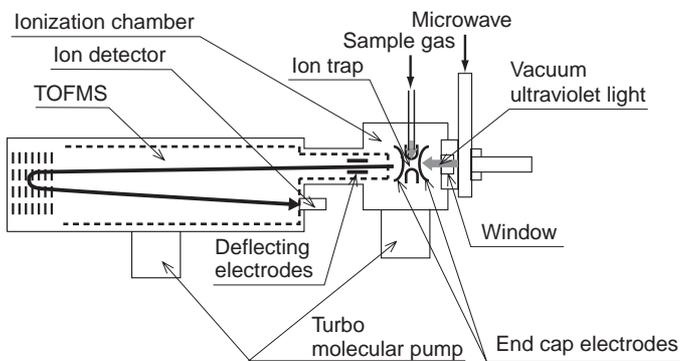| Items	Real time measuring equipment for T₃CB	On-line measuring equipment for P₅CDF
Substance measured	T$_3$CB (Trichlorobenzene)	P$_5$CDF (pentachloro- dibenzofuran)
Location where measured	Outlet of furnace (550 to 650°C)	Inlet of stack
Pre-treatment	Dust filtration	Concentrator
Lowest limit of measurement	80 to 240 ng/m³N (Depending on gas component)	0.05 ng/m³N (Depending on gas component)
Measurement interval	20 seconds	2 to 6 hours (depending on installation)
Feeding flow rate or amount	100 cc/min	50 to 1 000 L (depending on installation)
Outer dimensions (mm)	W1 400 X L3 000 X H1 900 (Measuring equipment) W400 X L400 X H900 (Dust filter)	W1 400 X L3 000 X H1 900 (Measuring equipment) W1 200 X L1 600 X H1 800 (Dust filter)
Mass (kg)	1 000 (VUV analyzer only)	1 300 (Including concentrator)

Fig. 2 Principle of VUV analyzer
After P$_5$CDF or T$_3$CB is selectively accumulated in an ion trap, either substance can be quantitatively determined by TOFMS.

Fig. 3 Correlation between P₅CDF and toxicity equivalency quantity (TEQ)
It can be seen from the graph that there is a strong correlation between DXNs and P$_5$CDF.

measuring P$_5$CDF, and the real time equipment for measuring T$_3$CB, respectively.

2.1 VUV analyzer

The principle of the VUV analyzer is shown in **Fig. 2**. A gas sample introduced into the ion trap in the VUV analyzer is irradiated with vacuum ultraviolet light through a window in order to ionize an target substance (P$_5$CDF or T$_3$CB in this case). When an electrical voltage with a specified frequency is applied between the end cap electrodes of the ion trap, only one kind of ion with a particular mass is selectively accumulated. After that, the target ions are dissociated into fragments by applying an electrical voltage with another specified frequency[4][5]. The target substance and any impurities can be separated using this procedure. Finally, the target substance can be quantitatively determined by supplying the ions dissociated into fragments to a time of flight mass spectrometer (TOFMS).

This VUV ionization method can measure a target substance stably and to a high degree of sensitivity without being influenced by coexisting components, even in systems in which various components are mixed together such as flue gas from an incinerator furnace.
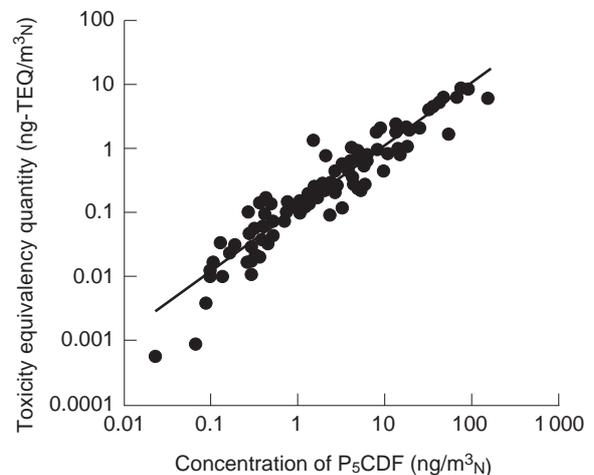
2.2 On-line equipment for measuring P₅CDF

This equipment is installed downstream from the bag filter (dust collector) in order to monitor the concentration of P$_5$CDF in gas emitted into the atmosphere, so as to contribute to the more effective operation of an incinerator or a flue gas treatment system. As shown in Fig. 1, this equipment consists of the automatic concentrator described later and a VUV analyzer.

It is very difficult to measure DXNs quickly, including various congeners and isomers in trace amounts. In fact, these components are analyzed in the present official method through GC/MS method. In the newly developed method described here, a particular congenrer that is closely correlated with toxicity equivalency quantity is chosen as an index, concentrated and then measured.

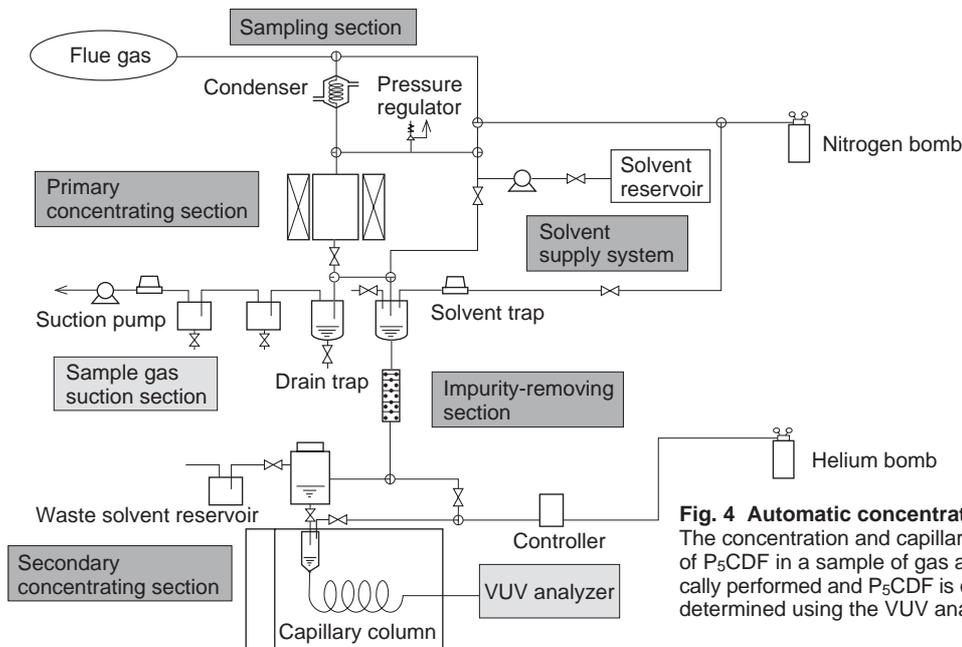**Fig. 3** shows relation between concentration of P$_5$CDF and the toxicity equivalency quantity of DXNs, which

Fig. 4 Automatic concentrator
The concentration and capillary-separation of P_5CDF in a sample of gas are automatically performed and P_5CDF is quantitatively determined using the VUV analyzer.

have been obtained by MHI. As can be seen in this figure, there is a strong correlation between the concentration of P_5CDF and the toxicity equivalency quantity of DXNs. As a result, it is concluded that P_5CDF can be effective as a monitoring index substance for DXNs.

Since the concentrations of DXNs to be monitored are as low as 0.01 to 0.1 ng-TEQ/m^3_N, they are difficult to measure even with a VUV analyzer. Therefore, in the newly developed on-line measuring equipment, the flue gas is concentrated before the P_5CDF concentrations are measured using the VUV analyzer. **Fig. 4** shows an overview of the automatic concentrating process.

The flue gas is cooled after all dust has been removed, and is then fed to the primary concentrating section of the equipment and P_5CDF is adsorbed with condensed water to be primarily concentrated. After drying the water adsorbed in the primary concentrating section, P_5CDF is then subjected to solvent-extraction under high temperature and high pressure. After impurities have been removed from the solvent-extracted P_5CDF solution, the solvent is evaporated in the secondary concentrating section. The concentrated P_5CDF sample (the entire amount) is separated in a capillary column in gas chromatography, and finally fed into the VUV analyzer to be quantitatively determined. In order to increase the accuracy of the analysis, an internal standard substance is added for each measurement.

2.3 Real time equipment for measuring T_3CB

It is known that incomplete combustion leading to formation of DXNs can be monitored by measuring the concentrations of CO. However, it is suggested that the concentration of DXN precursors has a better correlation with the combustion state than concentrations of CO in the low concentration region[3]. Basic data obtained by MHI also supports this suggestion. Hence, the present
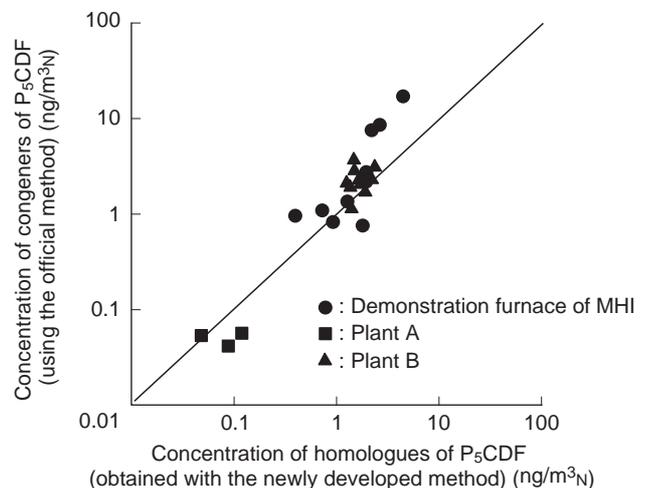

Fig. 5 Comparison of VUV measurement and official method
There is a good correlation between measurements obtained with the VUV analyzer and the official method, thus confirming the practical applicability of the VUV approach.

equipment can be used to monitor the DXNs formation in the furnace and to determine the operating condition by measuring T_3CB levels real-timely at the outlet of furnace, because T_3CB is a good index of DXNs among DXNs precursors.

The analysis procedure is as follows. The dust in the flue gas from the outlet of a furnace is at first removed by filtration. The gas is then cooled to an appropriate temperature, after which the VUV analyzer is used to measure the amount of T_3CB present in real time for each approximately 20 second interval.

3. Field test results

3.1 Result of P_5CDF measurement

The results of measurements carried out in the field and results measured using the official method are shown in **Fig. 5**. The good correlation observed in the figure in the concentration range from 0.05 to 10 ng-TEQ/m^3_N con-
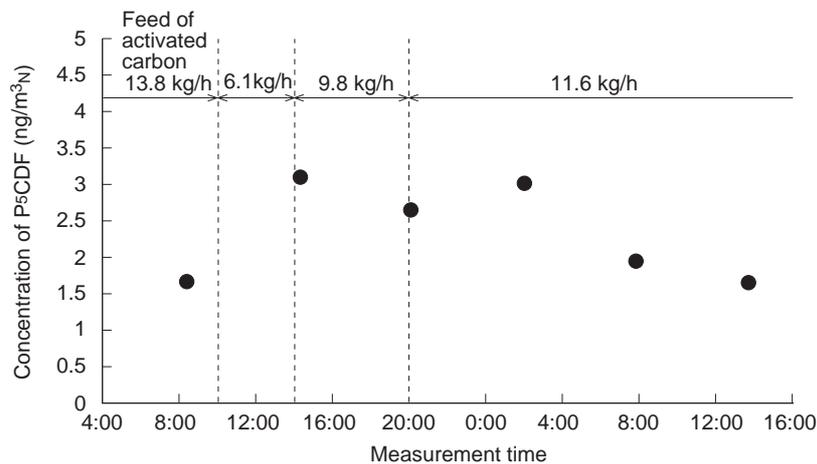
Fig. 6 P5CDF concentration profile
The tendencies in the concentration of P5CDF can be determined by on-line measurement.

firms that measurement with a VUV analyzer is practically applicable.

In order to confirm the applicability of this method, a plant equipped with an electrostatic precipitator and a unit for supplying activated carbon powder into the flue gas for reducing DXNs was adopted as an example in the field tests. **Fig. 6** shows the results obtained by measuring concentrations of P5CDF when the amount of activated carbon powder was varied at the plant.

The tendency that the concentration of P5CDF decreases with increasing the amount of activated carbon powder can be confirmed from Fig. 6. In addition, since the optimum amount of activated carbon powder in this plant can be determined with this equipment, the operating conditions of the flue gas treatment can also be controlled using this equipment. Accordingly, it has been proved that this equipment is also useful in reducing the running costs of the plant.
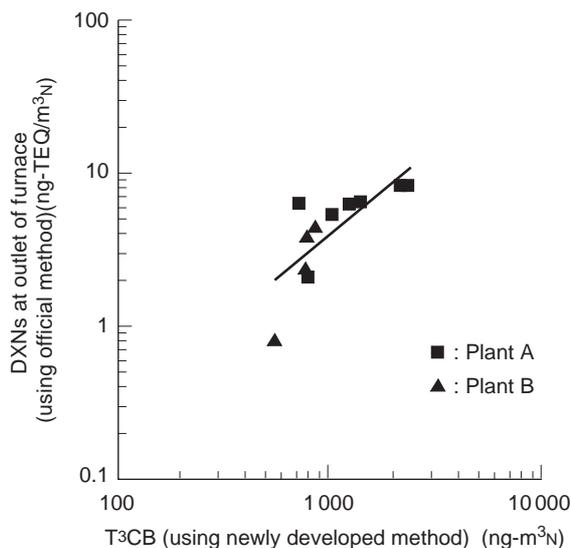

Fig. 7 Correlation between DXNs and T3CB
It can be seen that there is a good correlation between DXNs and T3CB.

The present frequency for taking measurements is once per each two to six hours, depending on the concentration of P5CDF. These timings are considered to be very effective for adjusting operating condition in an flue gas treatment plant, bearing in mind the time needed for the operation state to become stabilized after the condition has been changed. When the concentration of P5CDF needs to be measured more frequently, the measuring interval can be shortened by multiplying concentrator.

3.2 Result of T3CB measurement

The effectiveness of the T3CB-measuring equipment was also investigated by the field tests using flue gas in the same way as the measurement of P5CDF. **Fig. 7** shows the test results. It can be seen from this figure that there is a very good correlation between the T3CB concentrations and the values analyzed by the official method. Therefore, it was confirmed that the concentrations of DXNs at the outlet of an incinerator furnace can be estimated by measuring the concentration of T3CB.

Fig. 8 shows the concentrations of T3CB and CO obtained during continuous measurement with an interval of twenty seconds. From this figure, the amount of T3CB formed increases as the level of CO in the region where the concentration of CO is high increases. Thus, it is conceivable that the combustion state inside a furnace can be understood by this equipment and the optimum combustion condition can be found. The utilization of this concept is expected to be useful in ranges where concentrations of CO are low.

As described above, the ability to estimate the amount of DXN precursors continuously at the outlet of a furnace is very useful. This method is not only applicable for predicting and better understanding the mechanism of DXNs formation at the outlet of the furnace, but also possible to be utilized to a large extend in the research of combustion behavior varying according to the variation of the combustion condition in a furnace in the future.
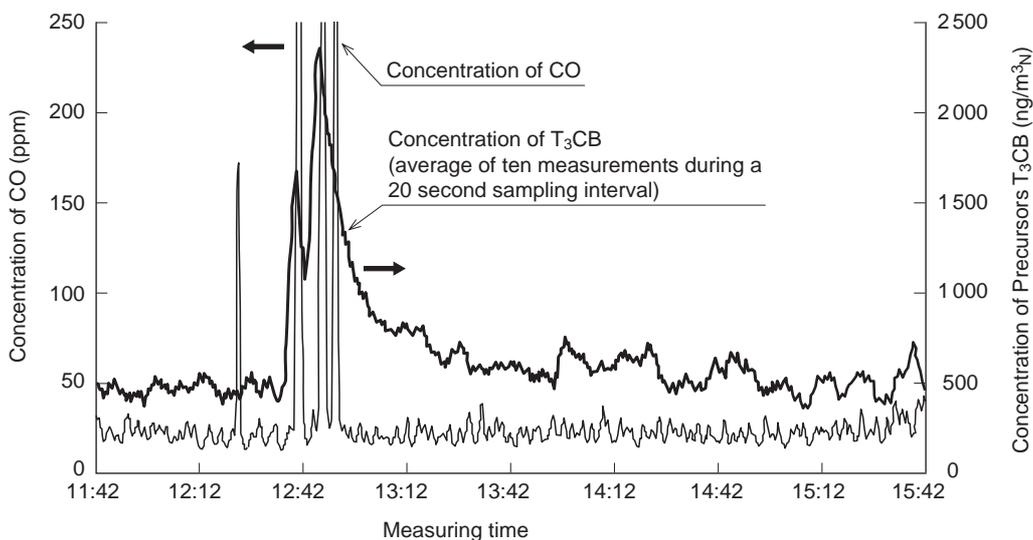
Fig. 8 Trend in concentration of T₃CB
It has been confirmed that the combustion state can be understood by measuring T₃CB.

Moreover, by assessing DXNs levels, the T$_3$CB-measuring equipment can also be applied to adjusting combustion conditions in the trial operation of a furnace.

4. Conclusion

The achievement described above can be summarized as follows:

(1) The concentration of DXNs emitted can be estimated and monitored by measuring the concentration of P$_5$CDF in flue gas using a VUV analyzer after automatically concentrating the flue gas.

(2) The conditions under which DXNs are formed inside a furnace can be grasped by measuring T$_3$CB levels, thereby making it possible to determine the optimum combustion conditions for controlling DXNs.

(3) During the trial operation of an incinerator furnace, the on-line monitoring system could be used to adjust operation by monitoring DXNs concentrations, so that it can be effective in reducing running costs.

(4) The technology described above can be applied to the basic research and development of incinerator furnaces.

At present, the measured values using the on-line monitoring system cannot replace the values analyzed by the official method. However, the fact that measurement of DXNs or their precursors, which requires several weeks to analyze, can be completed in several hours or even in several dozens of seconds means that the very effective information that had not been previously obtainable can be presented in a timely manner for the more effective operation of incinerators and flue gas treatment. It is certain that the technology introduced in this paper is also applicable to a wide range of fields such as basic research and development other than the applications reported here.

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