

DIOXINS AND THEIR PRECURSORS ON-LINE MONITORING METHOD FOR INCINERATION PLANTS

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1. Introduction

Dioxins (hereafter abbreviated as DXNs) emitted from incineration plants have become an issue of major social concern. As a manufacturer of incineration plants, we have developed various means such as advanced combustion control and flue gas treatment of incinerators, and have 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 because the concentration of DXNs is extremely low. 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 by the measurement of DXN levels. In addition, although DXNs precursors have been suggested as being more effective in controlling DXNs than the CO conventionally used³, they are said to be unsuitable as indices for controlling combustion because of the long time required to analyze them like DXNs. So we have developed a monitoring system using a Vacuum Ultra-violet light ionized Ion Trap Time of Flight Mass Spectrometry (VUV light ionized IT-TOFMS, hereafter abbreviated as VUV analyzer) in order to solve these problems. The principle of VUV light ionized IT-TOFMS and configuration of a monitoring system have been reported in detail^{4,5,6}. This paper reports results of field test carried out using a monitoring system consisting of an on-line equipment for measuring P₅CDF (pentachloro-dibenzofuran) and a real time equipment for measuring T₃CB (trichlorobenzene).

2. Methods

All field tests were carried out at two commercial incineration plants A and B and a demonstration furnace. Fig.1 shows a schematic diagram of these tests. Plant A and a demonstration furnace are equipped with bag filters, whereas Plant B is equipped with electrostatic precipitator (EP) as a dust collector.

2.1 On-line equipment for measuring P₅CDF

This equipment is installed in the downstream part of the dust collector(EP or Bag filter) in order to monitor the concentration of P₅CDF in the flue gas. As shown in Fig. 1, this equipment consists of the automatic concentrator⁵ and the VUV analyzer^{4,6}.

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. In the newly developed method described here, a particular congener that is closely correlated with toxicity equivalency quantity is chosen as an index, concentrated and then measured.

Fig. 2 shows relation between concentration of P₅CDF and the toxicity equivalency quantity (TEQ) of DXNs, which have been obtained by ourselves. As can be seen in this figure, there is a strong correlation between the concentration of P₅CDF and the toxicity equivalency quantity of DXNs. As a result, it is concluded that P₅CDF 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/m³_N, they are difficult to measure even with the VUV analyzer. Therefore, in the newly developed on-line measuring equipment, the flue gas is concentrated automatically before the P₅CDF concentrations are measured using the VUV analyzer. The automatic concentrator has steps as described below⁵.

- (1) The flue gas is cooled after all dust has been eliminated, and is then fed to the primary concentrating section of the equipment and P₅CDF is adsorbed with condensed water to be primarily concentrated.
- (2) After drying the water adsorbed in the primary concentrating section, P₅CDF is then subjected to solvent-extraction under high temperature and high pressure.
- (3) After impurities have been eliminated from the solvent-extracted P₅CDF solution, the solvent is evaporated in the secondary concentrating section.
- (4) The concentrated P₅CDF 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.

2.2 Real time equipment for measuring T₃CB

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 DXNs precursors has a better correlation with the combustion state than concentrations of CO in the low concentration zone of DXNs³. Basic data obtained by ourselves also supports this suggestion. Hence, the concept that formation of DXNs can be monitored by measuring T₃CB levels in real time at the outlet of an incinerator furnace and the measurements of T₃CB can be fed back to determine the operation condition of the furnace is useful.

The analysis procedure is as follows.

- (1) The dust in the flue gas from the outlet of a furnace is at first removed by filtration.
- (2) The gas is then cooled to an appropriate temperature.
- (3) Then the VUV analyzer is used to measure the amount of T₃CB present in real time for each approximately 20 second interval(see Fig.1).

3. Results and Discussion

3.1 Result of P₅CDF measurement

The results of measurements carried out in the field and results measured using the official method are shown in Fig.3. The good correlation observed in the figure in the concentration range from 0.05 to 10 ng/m³_N confirms that measurement with a VUV analyzer is practically applicable.

In order to confirm the applicability of this method, a plant equipped with an EP and a unit for supplying activated carbon powder into the flue gas for reducing DXNs was adopted as an example in the field tests (Plant B). Fig.4 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. 4. 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.

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 multiple concentrations of samples⁵.

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. 5 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.6 shows the concentrations of T₃CB and CO obtained during continuous measurement with an interval of 20 seconds. From this figure, the amount of T₃CB formed increases as the level of CO in the zone where the concentration of CO is high increases. Thus, it is conceivable that the combustion state inside a furnace can be estimated 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 extent in the research of combustion behaviour varying according to the variation of the combustion condition in a furnace in the future.

Moreover, by assessing DXNs levels, the T₃CB-measuring equipment can also be applied to adjusting combustion conditions in the trial operation of a furnace.

Figure1: Schematic diagram of the field tests

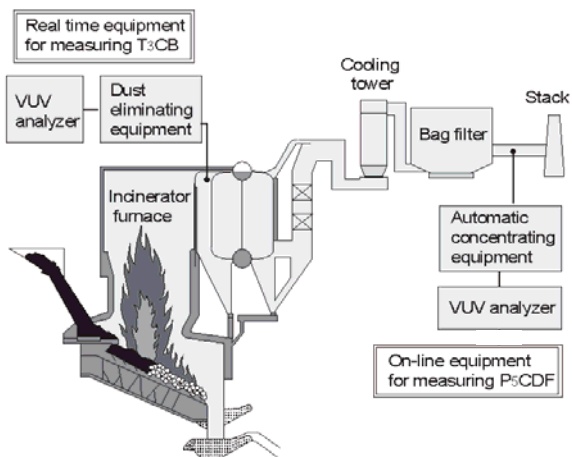


Figure 2: Correlation between P₅CDF and TEQ

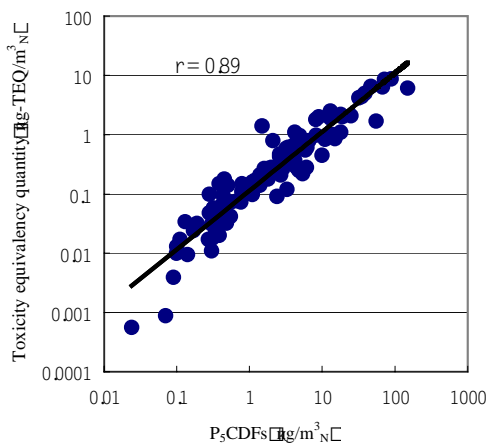


Figure 3: Comparison of VUV analyzer and the official method

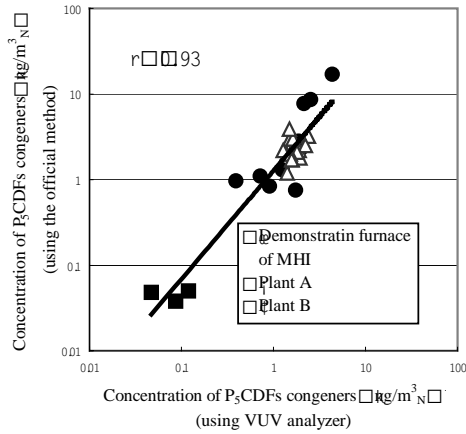


Figure4: Trend in concentration of P₅CDF

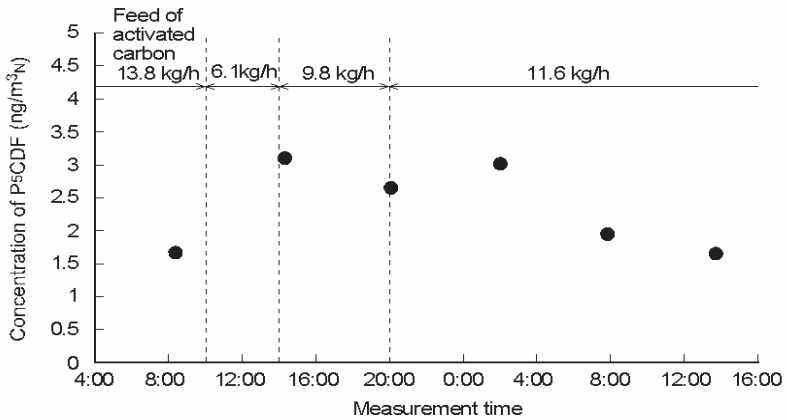


Figure 5: Correlation between DXNs and T₃CB

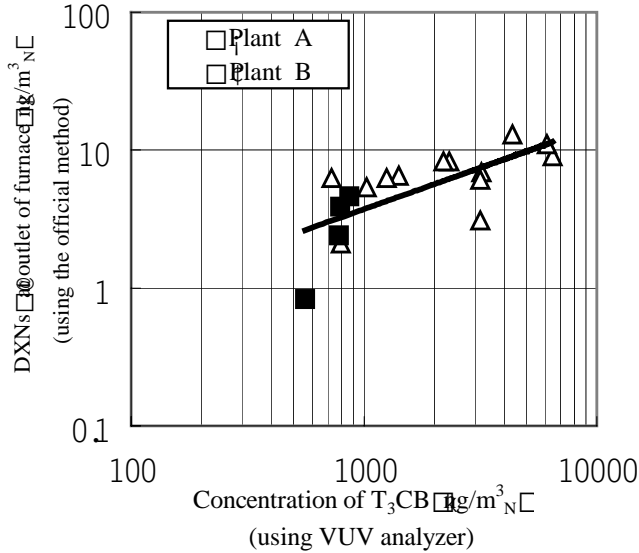
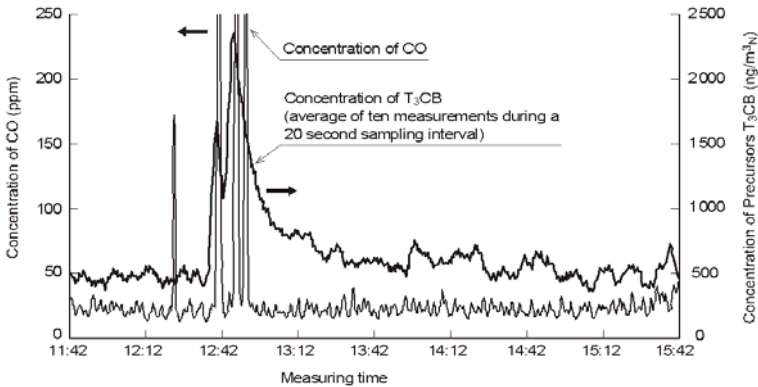


Figure 6: Trend in concentration of T₃CB



Acknowledgement

Part of this research was supported by the Ministry of the Environment through the scientific research grant for waste treatment “Integration of DXNs Reduction Technologies”. The authors are grateful to many related people.

References

1. Uoya, K., Shida, S., Mamiya, H., Matsuura, S., Okada, M.; (1992) Mitsubishi Juko Giho, "Reduction of Dioxins from Refuse Incinerator Plant", 29, No.4, 327, (in Japanese)
2. Uoya, K., Shida, S., Takei, A., Okada, M., Ose, K., Kobayasi, K.; (1992) Mitsubishi Heavy Industries Technical Review, "Technology on Flue Gas Treatment of Fine Harmful Compounds from Municipal Incinerators", 29, No.2, 131.
3. G. Sandstrom; (1990) 10th Int. Symp. on Dioxin, 3, 151.
4. Tsuruga, S., Futami, H., Sakai, S., Yamakoshi, H., Danno, M., Kuribayashi, S.;(2003) Organohalogen Compounds, 60, 432.
5. Okada, M., Yoneda, K., Morii, S., Suzuki, T., Seki, K.; (2003) Mitsubishi Juko Giho, "Dioxins and their Precursors On-line Monitoring Equipments for Incineration Plant", 40, No.5, 290, (in Japanese)
6. Kuribayashi, S., Danno, M., Yamakoshi, H., Sakai, S., Tsuruga, S.;(2004) Mitsubishi Heavy Industries, Ltd. Technical Review, "Ultra-sensitive High-speed Monitoring Technology for Trace-level Toxic Halogenated Hydrocarbon Compounds", 40, No.6, 1.