### MONITORING TECHNIQUE OF PCDDS/DFS FROM MSW INCINERATORS USING DIOXIN PRECURSOR ANALYZER

Masaru Tanaka<sup>1</sup>, Hideaki Fujiyoshi<sup>2</sup>, Satoshi Hatazawa<sup>3</sup>, Takashi Yokoyama<sup>4</sup>, <u>Hideki Nagano</u><sup>4</sup>, Toshihiko Iwasaki<sup>4</sup>

<sup>1</sup>Department of Environmental and Civil Engineering, Faculty of Environmental Science and Technology, Okayama University, 1-1 Tsushima-Naka, 3-chome, Okayama 700-8530, Japan

<sup>2</sup>Japan Environmental Sanitation Center, 11-15 Yotsuyakami-cho, Kawasaki-ku, Kawasaki 210-0828, Japan

<sup>3</sup>Environmental Services Bureau The City of Yokohama, 355 Kariba-cho, Hodogaya-ku, Yokohama 240-0025, Japan

<sup>4</sup>NKK Corporation, 1-1 Minamiwatarida-cho, Kawasaki-ku, Kawasaki 210-0855, Japan

#### Introduction

There is an urgent social need to control and reduce the amount of dioxin emissions from municipal solid waste (MSW) incinerators. However, it takes much manpower, cost and time to measure the amount of dioxins by the conventional dioxin analysis method. Although simple methods of analyzing dioxins have been investigated, they mainly focus on techniques for speeding up the official analysis method. It is ultimately effective to measure the amount of dioxins emission on site directly, but such technology has not yet been established.

One solution is to measure the dioxin precursors instead of dioxins directly, as it has been reported that there is a high correlation between dioxins and their precursors. Moreover, the concentration of dioxin precursors is about 1,000 to 10,000 times higher than that of dioxins.

Last year, we reported at DIOXIN 2001 that it was possible to monitor the amount of dioxins by measuring of chlorobenzenes concentration <sup>1), 2)</sup>.

In this paper, we report on a technique for monitoring dioxin emissions from MSW incinerators, and show the results of its application to an operating MSW incinerator to measure the dioxin precursors rapidly and continuously using a dioxin precursor analyzer.

#### **Methods and Materials**

### System configuration of dioxin precursor analyzer

Figure 1 shows the configuration of the dioxin precursor analyzer. This analyzer has a non-radioactive electron capture detector (ECD), which can detect chlorinated organic compounds such as chlorobenzenes and dioxins. Generally, ECDs that use a radioactive isotope such as <sup>63</sup>Ni and <sup>3</sup>H to detect compounds are used at the laboratory analyses, but permission would need to be obtained in order to use this type of ECD at incinerators. In contrast, the dioxin precursor analyzer adopts a non-radioactive ECD, so it is not necessary to obtain permission.

#### Outline of the analyzer operation

A filter installed in sampling probe tube rejected the dust in the sampled flue gas from the duct. The sampling probe and tube were heated to prevent condensation. The sampling gas passed through the sampling tube and was transported to the joint box, and almost of the sample gas was separated from mist and was exhausted after passing through an activated carbon filter. The measured sample was

### ORGANOHALOGEN COMPOUNDS Vol. 59 (2002)

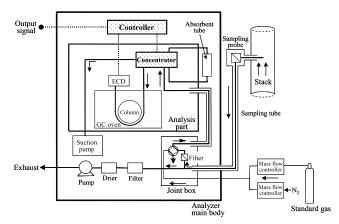


Fig.1 Configuration of dioxin precursor analyzer

introduced into the constant temperature bath through the heated tube and to the concentrator. Sample gas passed through the concentration tube and then was adsorbed and concentrated there.

The gas flowed out of the constant temperature bath through the concentrated tube and was sucked in by the absorption unit. The components of sample gas were heated in the concentration tube at sample collection time, fell away from concentration tube and were transported to the separation column in the temperature oven.

The components of the measured gas introduced into the separation column moved in the column in sequence and finally were separated in the capillary column. The separated components were detected by ECD.

#### Continuous monitoring at operating MSW incinerator

The dioxin precursor analyzer was applied to an operating MSW incinerator (capacity: 300 t/day, stoker type of full-continuous operation furnace) to measure the chlorobenzenes continuously. The flue gas was sampled from a duct downstream side of an electrostatic precipitator. Along with the operation of the dioxin precursor analyzer, sampling the flue gas was sampled in order to analyze the concentration of dioxins to investigate the correlation between dioxin precursors concentration and dioxins concentration.

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

#### **Results and Discussion**

#### Evaluation of chlorobenzenes concentration as substituted index of dioxins concentration

The concentration of chlorobenzenes measured by the dioxin precursor analyzer in this MSW incinerator was compared with the actual concentration of dioxins measured by the official method. The concentration of 1,2,4-trichlorobenzene showed the highest correlation with the concentration of dioxins among all the chlorobenzenes measured by the dioxin precursor analyzer, with a correlation factor of 0.95 (dioxin toxic equivalents). Thus, the concentration of dioxins could be accurately estimated from the measurement of 1,2,4-trichlorobenzene by the dioxin precursor analyzer.

The estimated equation of the dioxins concentration using the concentration of 1,2,4-trichlorobenzene was as follows,

$$[DXN] = a x [TrCB]^{b}$$
(1)

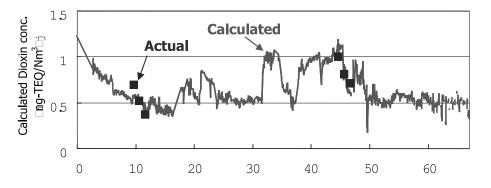


Figure 2. The trend of concentration of calculated dioxins

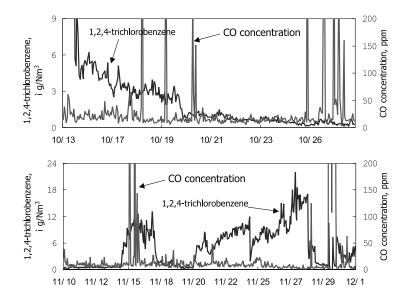


Figure 3. The trend of 1,2,4-trichlorobenzene concentrations and CO concentrations

[DXN] showed the concentration of dioxins (toxic equivalents), and [TrCB] showed the concentration of 1,2,4-trichlorobenzene. The coefficient a and b were 37and 0.23, respectively.

Figure 2 shows the trend of the concentration of dioxins calculated from equation (1) and actual dioxins concentrations measured by the official method. The actual measurements of the dioxins were identical to the calculated measurements of the dioxins. Thus, the dioxins concentration range in the flue gas from downstream side of an electrostatic precipitator could be estimated at 0.5 to 1.0 (ng-TEQ/Nm<sup>3</sup>) in this MSW incinerator.

#### Possibility of combustion control by measurement of chlorobenzenes

Figure 3 shows the trend of 1,2,4-trichlorobenzene concentrations and that of CO, which indicated the situation of incomplete combustion. The trend of 1,2,4-trichlorobenzene concentrations was different from that of CO concentration.

In a different MSW incinerator, the trend of chlorobenzenes concentrations was more sensitive than that of the CO concentration, which was stable at less than 10 ppm.

These results indicated that measurements of chlorobenzenes by the dioxin precursor analyzer could be used to control the combustion and reduce the amount of dioxins emissions from MSW incinerators.

This study was conducted with the financial assistance of the "Study on integration of technology to reduce generation of dioxins", which is a grant study of the Ministry of Health, Labor and Welfare that started in FY2000. We would like to express our appreciation to the related organizations and their staff for their cooperation.

### References

1. M. Tanaka et al., Organohalogen Compounds, Vol. 54, pp266-269 /2001

2. M. Tanaka et al., Organohalogen Compounds, Vol. 54, pp222-225 /2001