REAL-TIME MONITORING OF CHLOROBENZENES
IN FLUE GAS

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Introduction
Continuous real-time monitoring of flue gas is needed for proper control of incinerator operation to reduce dioxin formation. However, the conventional dioxin analysis method may take several weeks due to the complicated cleanup and enrichment process. An alternative method for estimating the dioxin emission levels in a shorter time is to correlate them to measured dioxin precursor levels, such as chlorophenols[1] and chlorobenzenes[2]. In a previous paper, we reported development of a real-time chlorophenol monitor and preliminary results at a municipal waste incinerator[3].

In this paper, we report real-time monitoring of chlorobenzenes. The system uses positive atmospheric-pressure chemical-ionization (APCI) and ion-trap mass spectrometry (ITMS). Since various compounds are in incinerator flue gas, chemical noise interferes with chlorobenzenes in the mass spectrum. Multi-stage mass spectrometry (MS/MS) is thus used to isolate the chlorobenzene from chemical noise. This online monitor was used to measure dichlorobenzene at one-minute intervals at a stoker-type incinerator.

Methods and Materials
Figure 1 shows the schematic of the real-time chlorobenzene monitoring system. Incinerator flue gas is continuously introduced into the monitor at the flow rate of 2~3 lit/min. Ash and dust in the flue gas are removed with a 1μm mesh filter. The filter and piping temperature is set to the same temperature as the flue at sampling point, which is about 200 °C. Therefore, the chance of additional reaction such as de novo, or loss of dichlorobenzene will be small. Exceptionally, the flue gas is cooled to about 5 °C at the pre-treatment part to remove water vapor and other impurities. The remaining compounds, including chlorobenzenes, are ionized at an APCI ion source. Although negative APCI is used to monitor chlorophenols[3], the ionization of chlorobenzenes by using negative APCI is inefficient. Therefore, chlorobenzenes are measured using positive APCI. The process of ionization of dichlorobenzene by using positive APCI is described as follows. In the region of corona discharge, nitrogen is ionized[4] (reaction 1).
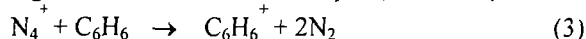
$$N_2 + e \rightarrow N_2^+ + 2e \qquad (1)$$

This nitrogen ion then reacts with other nitrogen and produces N_4^+ (reaction 2).

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \qquad (2)$$

The other traces of hydrocarbons in the flue gas are ionized by ion-molecule reaction. Horning[5] showed that benzene is ionized by a charge transfer reaction in nitrogen containing a trace amount of water vapor (reaction 3).

$$N_4^+ + C_6H_6 \rightarrow C_6H_6^+ + 2N_2 \qquad (3)$$

From reaction 3, we estimate that a similar reaction 4 should be also possible, which is probably the ionization process of dichlorobenzene in our case.
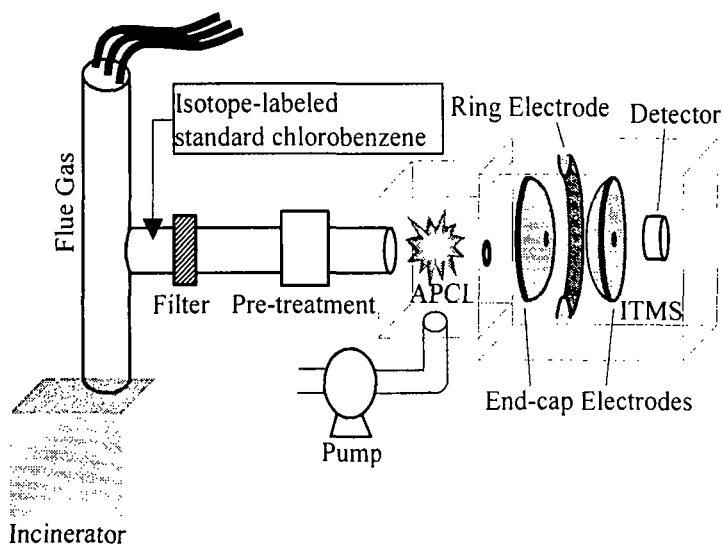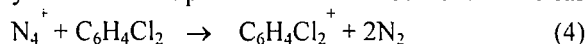
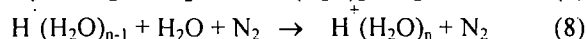$$N_4^+ + C_6H_4Cl_2 \rightarrow C_6H_4Cl_2^+ + 2N_2 \qquad (4)$$
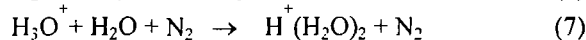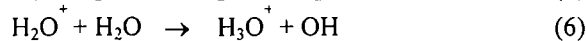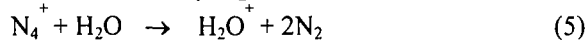

Fig. 1   Schematic of monitoring system

The presence of water vapor, however, reduces the ionization efficiency of reaction 4. Water vapor in flue gas is ionized by ion-molecule reaction (reactions 5,6,7,8). In the mass spectrum of flue gas, we found that the peaks of water-cluster ions, H_3O^+, $H^+(H_2O)_2$, and $H^+(H_2O)_3$ were relatively high.

$$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2 \qquad (5)$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \qquad (6)$$
$$H_3O^+ + H_2O + N_2 \rightarrow H^+(H_2O)_2 + N_2 \qquad (7)$$
$$H^+(H_2O)_{n-1} + H_2O + N_2 \rightarrow H^+(H_2O)_n + N_2 \qquad (8)$$

Reaction 5 probably interferes with reaction 4, and the ionization efficiency of dichlorobenzene is reduced. Therefore, water vapor should be removed as much as possible at the pretreatment part to obtain higher chlorobenzene ionization efficiency. In addition, the ionization source and the differential pumping region should be heated to 240 °C to avoid clustering of the water molecules. This step increases the ionization efficiency of chlorobenzene in flue gas by 10 to 100 times.

To calibrate the concentration of chlorobenzenes in flue gas, chlorobenzene labeled with deuterium ($C_6D_4Cl_2$) at a constant concentration is added to the flue gas to compensate for the varying ionization efficiency and for the loss at the pre-treatment part. The concentration ratio determined by GC/MS analysis of dichlorobenzene downstream the pre-treatment part is from 85 to 105% of the upstream concentration. In addition, there is no significant change of the ratio between the dichlorobenzene in the flue gas and the deuterated dichlorobenzene. These results show that the loss at pre-treatment part is in the range where the dichlorobenzene in flue gas can be calibrated by standard deuterated chlorobenzene.

Ions generated by APCI are sent through the differential pumping section to the ITMS. The ions are trapped in the space surrounded by the ring electrode and the end-cap electrodes, and analyzed. The chemical noise, which overlaps the mass spectrum peaks of dichlorobenzene, causes severe errors in the concentration data. Collisional-induced dissociation (CID) by MS/MS is used to remove the noise. The ions trapped in the ion trap collide with helium, and fragment ions are produced. The fragment ion $C_6H_4Cl^+$ (m/z = 111) is produced from the parent ion $C_6H_4Cl_2^+$ (m/z = 146) when the Cl molecule is extracted. Figure 2 shows the schematic mass spectrum of chlorobenzenes in flue gas before and after the use of MS/MS. The fragment ion $C_6H_4Cl^+$ is continuously monitored and the calibrated results yield the concentration data. CID by MS/MS is also used to analyze this standard chlorobenzene labeled with deuterium. The fragment ion $C_6D_4Cl^+$ (m/z = 115) is produced from the parent ion $C_6D_4Cl_2^+$ (m/z = 150). The calibration is done by comparing the signal intensities of chlorobenzenes in flue gas and the standard chlorobenzenes labeled with deuterium.
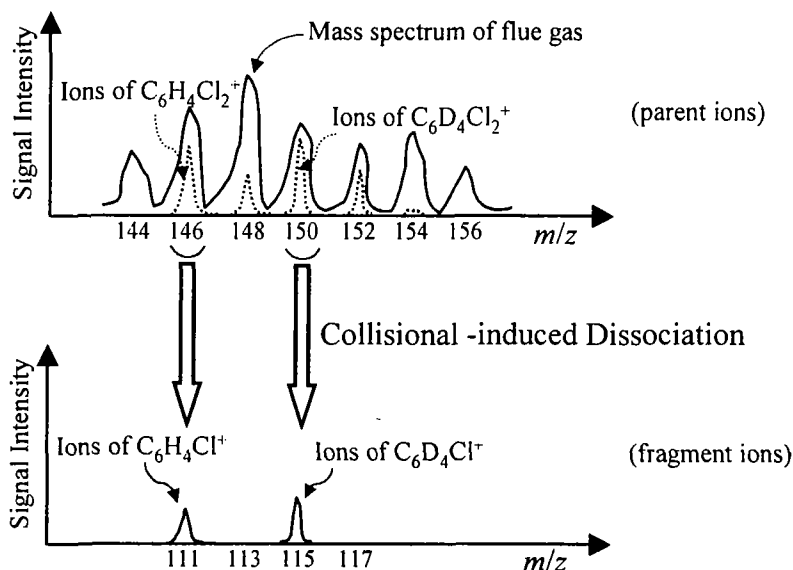

Fig. 2.　Mass spectrum schematic before and after MS/MS

Results and Discussion
Figure 3 shows the measured change of dichlorobenzene emission levels during incinerator startup. When an IDF (induced draft fan) started, the dichlorobenzene signal increased, even though the temperature inside the furnace was too low for combustion. This was probably because the flue gas in the furnace was stirred so that the residue dichlorobenzene inside the furnace was detected. When the incinerator started up, the temperature inside the furnace increased from 200 °C to 900 °C, during which the dichlorobenzene signal significantly increased until the combustion inside the furnace stabilized.

The emission data obtained by this online monitor were checked with the data obtained by offline GC/MS. The flue gas sample (200ml) was absorbed in a TENAX TA column and analyzed by a Hitachi GC/MS (G-7000M / M-7200). The circle marks in Fig. 2 show the concentration data obtained by GC/MS, which agreed well with the data obtained by the online monitor.

This online monitor can also measure chlorophenols in the flue gas if negative APCI is used. Further investigation using this monitor could reveal temporal correlation of chlorophenol and chlorobenzene emissions when incinerator combustion conditions change.
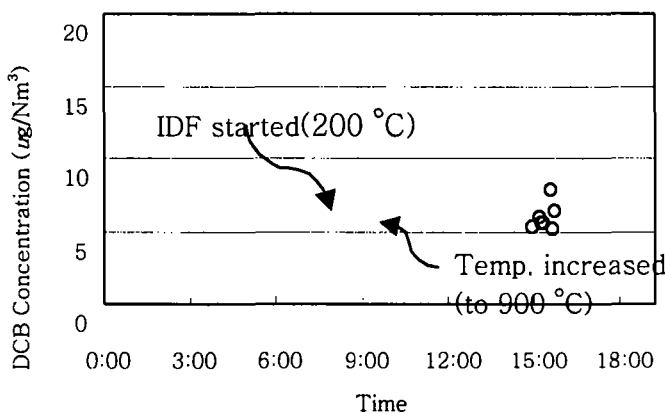

Fig.3.   Change of dichlorobenzene emission levels during incinerator startup

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