AN ONLINE SYSTEM FOR MONITORING DIOXIN PRECURSOR IN FLUE GAS

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Introduction

One of the most effective methods to reduce dioxin formation and concentration in incinerator flue gas is to control the operation of the incinerator. Continuous on-line monitoring of toxic trace gas is essential to enable feedback control of the incinerator. Quantitative analysis of dioxin by GC/MS takes more than one week due to the complicated sampling and extracting process. Therefore, this analysis can not detect rapid changes in incinerator combustion conditions. Instead of direct analysis of dioxin, surrogates of dioxin are attracting attention for use in short-time quantitative analysis, which is suitable for continuous online monitoring.[1]

In the present work, chlorophenol is chosen as a target trace gas for online monitoring. The correlation between chlorophenol and dioxin has been reported.[2] The authors developed an online system for monitoring chlorophenol in flue gas. This system uses atmospheric-pressure chemical-ionization (APCI) and ion-trap mass spectrometry (ITMS). This online monitoring can output one chlorophenol concentration data within 1 minute. The test is performed with a stoker-type industrial incinerator that has electrostatic precipitator, and trichlorophenol is monitored. The monitor can keep running for more than one month without maintenance.

Experiment

Figure 1 shows the schematic of the chlorophenol online -monitoring system. The incinerator flue gas is carried to the monitor through a 10μm mesh filter (to remove the ash or dust) and a 1/4" inner glass-coated stainless-steel piping. The filter and piping is heated at 200_ to avoid trace gas adsorption. As an ionization method, the negative atmospheric-pressure chemical-ionization (APCI) is used. And the process of chlorophenol ionization by negative APCI is given as follows.[3]
In the first chemical reaction, oxygen is ionized:

$$O_2 + e^- = O_2^-$$

This ionized oxygen becomes the reagent ion in the second chemical ionization:

$$CP + O_2^- = (CP\text{-}H)^- + HO_2$$

During the second chemical ionization, the ingredients with relatively high acidities are ionized. Trichlorophenol is ionized with high selectivity, since it has high acidity. The incinerator flue gas consists of many kinds of acid, such as hydrogen chloride, hydrogen bromide, NOx, and SOx with high concentration at about 1-1000 ppm. These ingredients also have high ionization efficiencies by APCI and reduce the ionization efficiency of the trichlorophenol. Naturally, the concentration of the above-mentioned impurities in flue gas is changed by the incinerator operation conditions. The ionization efficiency of trichlorophenol is thus changed by the incinerator operation conditions; that is, the sensitivity for the quantification of trichlorophenol is also changed. To calibrate this change in sensitivity, trichlorophenol labeled with ^{13}C at a constant concentration is added to the flue gas to compensate the varying ionization efficiency (Fig. 1). The influences on ionization efficiency of the ^{13}C-labeled trichlorophenol by the impurities are the same as those of the trichlorophenol in the flue gas; therefore, the ionization efficiency of trichlorophenol in the flue gas is known by observing the sensitivity of the added ^{13}C-labeled trichlorophenol. The concentration of added ^{13}C-labeled trichlorophenol is 12 $\mu g/Nm^3$.

Ions generated by APCI are sent to the ITMS through the differential pumping region. The ions are trapped in the space surrounded by the ring electrode and the end-cap electrodes, then they are analyzed. Helium gas is used as the buffer gas for collisional cooling in the ITMS. To remove interfered chemical noise, multi-stage mass spectrometry (MS/MS) is used. The principles of ITMS are described in detail in references of 4 and 5.

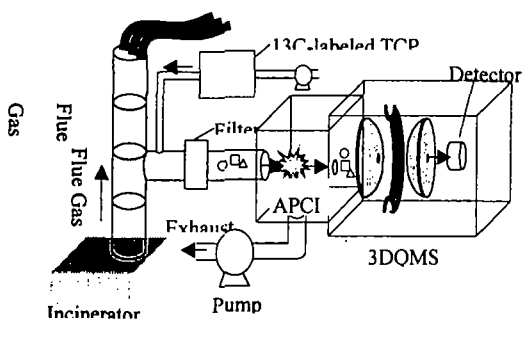

Fig. 1 Schematic drawing of monitoring system

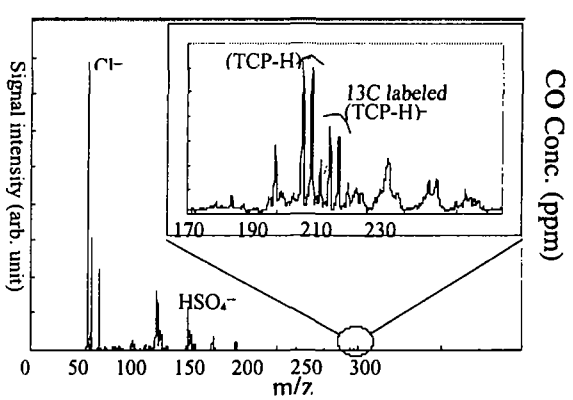

Fig. 2 Flue-gas mass spectrum

Results and Discussion

Figure 2 shows the typical mass spectrum of incinerator flue gas. As mentioned above, the impurities with high acidities, such as hydrogen chloride and sulfuric acid, can be observed as Cl^- (m/z=35,37) and HSO_4^-(m/z=98). Besides these impurities with high concentration, the ion peak of targeted trichlorophenol can be observed as $(M-H)^-$.

Figure 3 shows the measured chlorophenol concentration and carbon mono-oxide trend. During the test, the reaction tower operation to reduce the hydrogen chloride concentration in the flue gas was stopped between 220 and 380 min., and the air flow distribution in the incinerator was

modified between 450 and 500 min. As shown in Fig. 3, at about 10 and 470 min., the trend of trichlorophenol concentration is similar (rapidly increases and decreases) to that of carbon mono-oxide. However, only trichlorophenol concentration increases between 220 and 380 min. when the reaction tower was not operated. The conventional incinerator control for reducing the dioxin formation is by monitoring carbon mono-oxide concentration analyzed by an infrared sensor system.

Figure 3 reveals that, even though monitoring of carbon mono-oxide concentration could not detect the change in trace ingredient concentration in the flue gas, monitoring of chlorophenol concentration could detect it when the incinerator operation is changed. Using this online-monitoring system, adequate control of incinerator operation to reduce the dioxin precursor concentration and dioxin formation will be possible in the future.

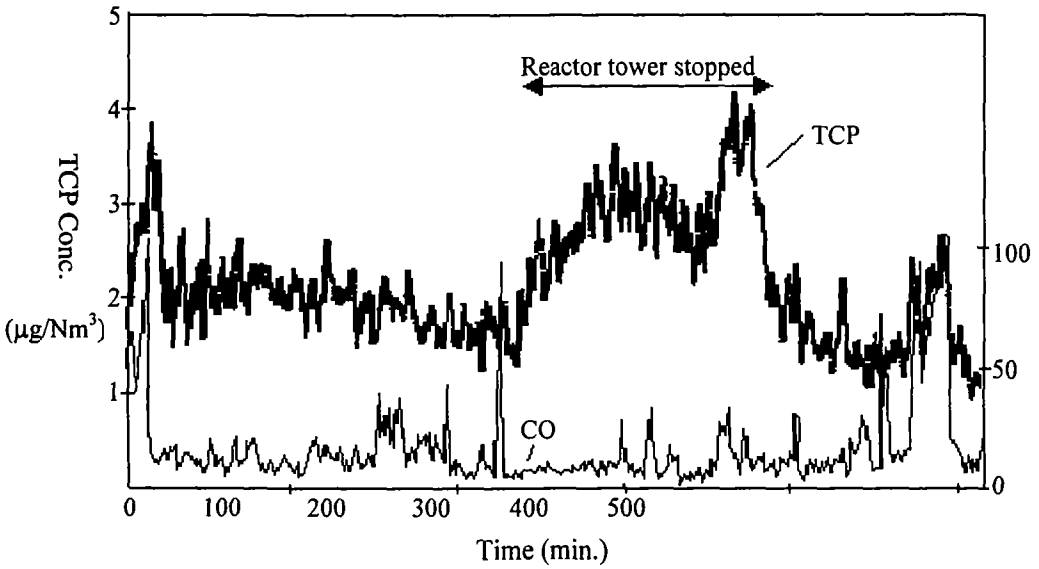

Fig.3 TCP and CO concentration in the flue gas

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