

### ANALYSIS OF CHLOROPHENOL MONITORED BY AN ON-LINE MONITORING SYSTEM FOR DIOXIN PRECURSOR IN FLUE GAS

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#### Introduction

It is important to analyze the generation process and behavior of dioxins in various operations of municipal waste incinerators in order to reduce their emission. However quantitative measurements of dioxins by GC/MS take more than one week due to their complicated sampling and extracting process. Therefore some on-line systems for monitoring surrogates of dioxins are being developed<sup>1,2</sup>. We chose chlorophenol as a surrogate for dioxins and developed an on-line system for monitoring it in flue gas<sup>3</sup>.

The purpose of this study is to analyze the behavior of trichlorophenol (T<sub>3</sub>CP) monitored with the on-line system in various operations of a stoker furnace.

#### Method

**An On-line monitoring System:** Figure 1 shows a schematic drawing of the chlorophenol on-line monitoring system. The incinerator flue gas is carried to the monitor through a filter to remove ash or dust. The filter and piping are heated at 200°C to avoid trace gas adsorption. As an ionization method, the negative atmospheric-pressure chemical-ionization (APCI) method is used. Ions generated by APCI are sent to the ion-trap mass spectrometer (ITMS) and analyzed. To calibrate concentration of T<sub>3</sub>CP in flue gas, T<sub>3</sub>CP labeled with <sup>13</sup>C at a constant concentration is added to the flue gas to compensate for the varying ionization efficiency (Fig. 1).

**Operations of a Stoker Furnace:** We analyze the behavior of  $T_3CP$  in two stoker furnaces (furnace A and furnace B). We also analyze the behavior of carbon monoxide (CO) to compare their difference. The stoker furnaces have an electrostatic precipitator (EP) in the post-furnace region. The on-line system for  $T_3CP$  and CO is installed after the EP. In furnace A,  $T_3CP$  is monitored under normal operational conditions for about 1 month. In furnace B,  $T_3CP$  is monitored under the operational conditions which vary flue gas temperature in the post-furnace region.

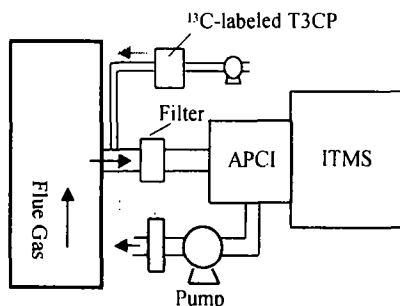


Fig. 1 Schematic drawing of monitoring system

## Results and Discussion

**Furnace A:** Figure 2 shows typical trend data of  $T_3CP$  and CO on a weekend in furnace A. Figure 3 shows those data on a weekday. These figures tell us the behavior of CO is similar on a weekend and a weekday, but the behavior of  $T_3CP$  on the two is different. The concentration of  $T_3CP$  from 9:00 to 12:00 is higher than that in other periods. Figure 4 shows the average of  $T_3CP$  concentration in two periods in one month. The feature noted above is clarified by the figure.

It is quite likely that the difference in  $T_3CP$  concentration in these periods is because of the difference of refuse burning in the period. That is to say, much refuse is collected in the morning on weekdays. So the refuse is put into the furnace as soon as it is collected without mixing in a refuse pit. It seems that this is the reason why the concentration of  $T_3CP$  from

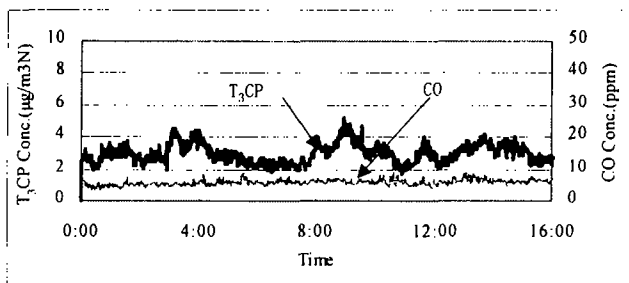


Fig.2 Trend data on a weekend

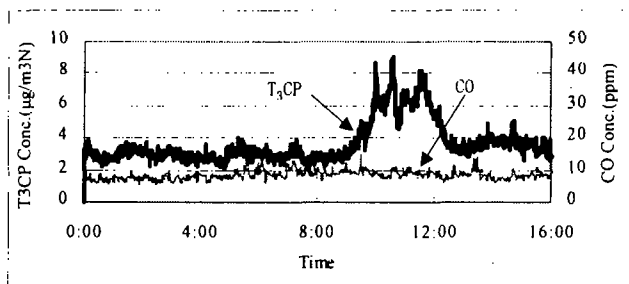


Fig.3 Trend data on a weekday

9:00 to 12:00 is higher compared with other times.

Much experience has shown that mixing refuse well in a refuse pit is effective to reduce emission of dioxins. It is likely that we can recognize the effect by monitoring T<sub>3</sub>CP.

**Furnace B:** Furnace B has no boiler system, so high temperature gas from the furnace is cooled by gas cooling equipment. The gas temperature at the exit of the gas cooling equipment is usually about 280 °C. After that, gas flows through a reaction tower to reduce the hydrogen chloride concentration in the flue gas and then it flows into the EP. The gas temperature at the entrance of the EP is usually about 190 °C. Figure 5 shows trend data for T<sub>3</sub>CP and CO in furnace B under operational conditions which vary flue gas temperature in the post-furnace

region. In this test, the set point of the flue gas temperature in the post-furnace region is increased in 10 °C intervals from 270 °C to 300 °C. As shown in Figure 5, the average concentration of CO is about 15 ppm and the burning condition of furnace seems to be stable. The behavior of T<sub>3</sub>CP has the following two features.

- (1) The average T<sub>3</sub>CP concentration is high when the gas temperature at the EP entrance rises.
- (2) T<sub>3</sub>CP concentration increases abruptly and decreases abruptly (spike pattern) just after the set point of the gas temperature at the EP entrance is made high.

The reason for phenomenon (1) seems to be that phenols are easily chlorinated because of rising gas temperature, so the concentration of T<sub>3</sub>CP increases. The reason for phenomenon (2) seems to be desorption of T<sub>3</sub>CP which is absorbed on the flue or ash on the EP because of rising gas

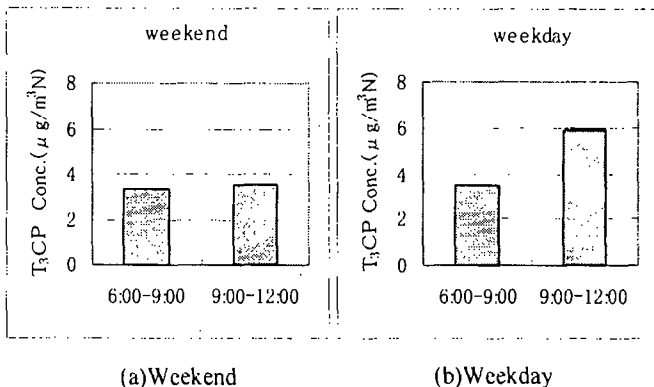


Fig.4 Average of T<sub>3</sub>CP concentration (1 month)

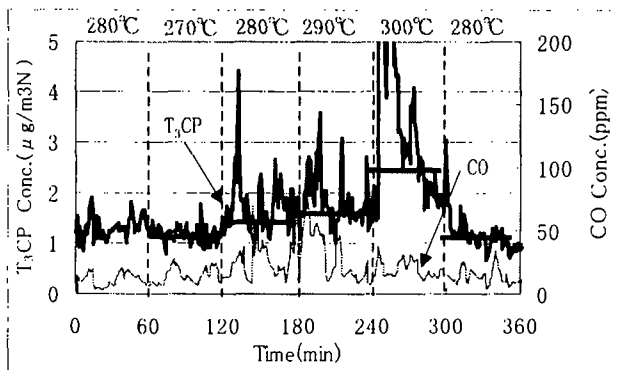


Fig.5 Behavior when varying flue gas temperature

temperature. The latter phenomenon is considered to be the same phenomenon as the memory effect of dioxins.

We found using the on-line-monitoring system was useful to analyze T<sub>3</sub>CP behavior, which differed from that of CO, in some operational conditions of a stoker furnace. By combining various technology to reduce dioxins, the on-line monitoring system will be applicable to operation management in the furnace.

### Acknowledgements

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